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DISSERTATION

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for the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Gary Donald Richmond, B.A.

****

The Ohio State University
1968

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PART ONE
ADDITION OF ELECTRON-DEFICIENT CARBON-CARBON MULTIPLE
BONDS TO STRAINED POLYCYCLIC HYDROCARBONS

I. Introduction and Historical Review

The unique chemical and physical properties of cyclopropane, the simplest cyclic hydrocarbon, are well documented. As discussed in most elementary organic textbooks, ring cleavage resulting from the addition of hydrogen or electrophilic reagents is typical of cyclopropanes. This chemical reactivity has been attributed to an inherent strain of 27.15 kcal/mole in cyclopropane, and to the structural requirements of bond deviations from normal sp<sup>3</sup> orbital hybridization.

This initial interest in cyclopropane has led to a study of strain energy and bonding characteristics as a basis for chemical reactivity in a variety of small polycyclic hydrocarbons. Two such ring systems are bicyclo[1.1.0]butane (1) and bicyclo[2.1.0]pentane (2).

---

The most recent determination of strain energy from heats of hydrogenation assigned a total strain of 68.2 kcal/mole (17 kcal per carbon) to 1,3-dimethylbicyclo[1.1.0]butane. This high degree of strain energy is probably not localized in the ring fusion bond, but is distributed over several bonds. The hydrogenation of the 1,3-bond produces a cyclobutane derivative and releases 43.6 kcal/mole. The cleavage of a 1,2-bond relieves 42.2 kcal/mole of the total strain energy. The measured strain energy of 1 itself is 63.9 kcal/mole. A previous value of 67.4 kcal/mole was calculated from heats of formation obtained from an SCF MO theoretical treatment.

From a consideration of heats of hydrogenation and heats of formation, the total strain energy of 2 was found to be 54.1 kcal/mole. Since hydrogenation of the 1,4-bond forms cyclopentane with a strain energy of 6.0 kcal/mole, the strain energy of this ring fusion bond must be 48.1 kcal/mole. This value is greater than that for 1,3-bond cleavage of 1, by approximately 10 kcal/mole, con-


sidering the strain energy of cyclobutane to be 25.8 kcal/mole. 6
The 1,4-bond dissociation energy is 30.7 kcal/mole compared with 54.4 kcal/mole for cyclopropane. 7 The strain energy of a related structure, quadracyclane, was found to be 95.1 kcal/mole (13.6 kcal per carbon). 8

It will become apparent that much of the chemistry of these small ring hydrocarbons is explicable on the basis of bonding characteristics in addition to strain energy. For example, the chemical reactivity of cyclopropane is indicative of considerably more $p$ character in the carbon-carbon bonds than that provided by normal $sp^3$ hybridization. The shortened distance between the carbon atoms, 9 the nmr ring current, 10 and the ability of cyclopropanes to stabilize $\pi$-electron systems, 11 all indicate increased $p$ character. In fact, the hybridization of the carbon-hydrogen bonds has been calculated to be close to $sp^2$. 12

In 1949, Walsh\textsuperscript{13} described the carbon-carbon bonding in cyclopropane as the overlap of three pure $\mathbf{p}$ orbitals plus the overlap of three pure $\text{sp}^2$-hybridized orbitals which were directed toward the center of the ring. The remaining $\text{sp}^2$ orbitals formed carbon-hydrogen bonds. Coulson and Moffitt\textsuperscript{14,15} published another bonding description in which the carbon-carbon bonds were considered to be $\text{sp}^2$ hybridized. Later $\text{C}_3\text{H}_2$ spin coupling constants showed $\text{sp}^2$ hybridization for the carbon-hydrogen bonds.\textsuperscript{16,17} This description results in an angle of about $104^\circ$ between the two overlapping orbitals of the carbon-carbon bond. Thus, this bond is "bent" from the intercarbon angle of $60^\circ$ and the normal $\text{sp}^3$ tetrahedral angle of $109.5^\circ$. Electron diffraction data on cyclopropane show a HCH angle of $118.2 \pm 2^\circ$, a CCH angle of $116.4 \pm 2^\circ$, and an intercarbon distance of $1.54$ Å.\textsuperscript{18}

As discussed earlier, bicyclo[1.1.0]butane is much more highly strained than cyclopropane. Consequently, its structure has re-

\textsuperscript{14} C. A. Coulson and W. E. Moffitt, Phil. Mag., \textbf{40}, 1 (1959).
\textsuperscript{18} O. Bastiansen and O. Hassel, Chem. Abstr., \textbf{40}, 6059 (1946).
ceived increasing theoretical and experimental attention. Consideration of the infrared and Raman spectra indicated that the molecule consists of two triangles fused together at an angle of $126 \pm 3^\circ$ with a bridgehead hydrogen forming an angle of $163 \pm 3^\circ$ with the ring fusion C-C bond.\(^{19}\) On the basis of the microwave spectrum and several unproven assumptions, Cox\(^{20}\) produced a tentative structure. All carbon-hydrogen distances equal 1.08\(\text{Å}\) and $\angle\text{HCH} = 116^\circ$, $\angle\text{HCC}$ (bridgehead) = $130^\circ$. The bridge C-C distance is 1.49\(\text{Å}\), the ring C-C distance equals 1.51\(\text{Å}\), and interplanar angle = $121^\circ$. His conclusion was that since the bridge C-C distance is less than the ring C-C distance, the bridgehead bond should be stronger and have a higher electron density than the 1,2-bonds in agreement with the calculated dipole moment of $0.675 \pm 0.01\text{D}$ along the C\(_2\) axis. This was also implicated by the breaking of the 1,2-bonds and not the 1,3-bond of bicyclo[1.1.0]butane in thermal decomposition at $200^\circ$.\(^{21,22}\) This contrasts with the thermal reaction\(^{23}\) of bicyclo[2.1.0]pentane in which the 1,4-bond is broken.

Based on the Walsh model for cyclopropane, two models for the electronic structure of bicyclo[1.1.0]butane have been postula-

\begin{itemize}
  \item \textbf{23.} J. P. Chesick, ibid., \textbf{84}, 3250 (1962).
\end{itemize}
In one model $sp^2$ orbitals, two from each bridgehead carbon, and one from each of the other carbons, overlap in the center of each of the three membered rings. The remaining $p$ orbitals on each carbon can then form $\pi$-like orbitals. The second model consists of overlap, in the center of the molecule, of one $sp^2$ orbital from each methylene carbon and an $sp$ orbital from the bridgehead carbons. The $\pi$-like orbitals are then formed from a remaining $p$ orbital on the methylene carbons and the two $p$ orbitals on each bridgehead carbon. Thus, more $'\pi$-character' $'$ is attributed to the 1,3-bond than to the 1,2-bonds.

This high degree of $\pi$-character ascribed to the 1,3-bond in the bicyclo[1.1.0]butane system is in agreement with the high $s$-orbital character of the bridgehead C-H bond. The $C_{13}$-H spin coupling constants range from 200 to 212 cps indicating $40-42\%$ $s$-character. The acidic nature of the bridgehead hydrogens has been demonstrated by their removal with alkyllithium reagents.

Similar results are indicated by the lowering of the pKa value for cyclopropane carboxylic acid (4.82) to 4.53 for 3-methylbicyclo-

butane-l-carboxylic acid and 4.6 for tricyclo[4.1.0.0^2,7]-heptane-l-carboxylic acid. Also, the UV spectrum of methyl 3-methylbicyclo[1.1.0]butane-l-carboxylate shows conjugative interaction with $\lambda_{\text{max}}$ 208 and $\epsilon$ 7000.

Chemical reactivity of the strained 1,3-bond of these bicyclo[1.1.0]butane systems has received much publicity. The addition of methylene formed 1,4-pentadiene as the major product. Reaction with halogens resulted mainly in 1,3 addition, and addition of acids proceeded with initial attack of the proton on a bridgehead carbon and breakage of both the 1,3- and 1,2-bonds.

Catalytic hydrogenation proceeded under mild conditions. Nucleophilic additions to 3-methylbicyclo[1.1.0]butanecarbonitrile took place across the 1,3-bond to form 3-substituted 3-methylcyclobutanecarbonitrile.

One of the more remarkable reactions brought into focus has been the addition of electron deficient carbon-carbon multiple bonds to the strained bent bonds of the bicyclo[1.1.0]butane and the bicyclo[2.1.0]pentane systems. The initial observation of such reactions was made by Gassman and Mansfield in their study of bicyclo-


When this hydrocarbon and dicarbomethoxyacetylene were heated to 100° for seven days, a high yield of a two component mixture was obtained. This was found to consist of a cycloaddition product, \( \text{Reaction of } \) with the powerful dienophile, dicyanoacetylene (6) at room temperature for 7.5 days formed analogous products. Compound (8), which was isolated from the reaction mixture was shown to have arisen from isomerization of initially formed 2 on alumina. The inertness of bicyclo[2.1.0]pentane to diphenylacetylene and to perfluoro-2-butyne indicated that both strongly electron-withdrawing substituents in the

dienophile and resonance stabilization of the transition state are requisite for reaction to occur. The less highly strained bicyclo[3.1.0]hexane failed to react with \( \mathcal{Z} \) at 100° for nine days.

Kinetic studies, including observation of a negligible solvent effect on rate and product ratios, supported the proposed formation of a diradical intermediate in the formation of cycloaddition and ene-type products. This two-step mechanism was further substantiated by the conclusion that in the reaction of \( \mathcal{Z} \) with maleonitrile and fumaronitrile, rotation about a central bond in these reagents must have occurred at an intermediate diradical stage in order to account for the observed products. Furthermore, addition of maleic anhydride to exo-2,3-dideuteriobicyclo[2.1.0]pentane to give the endo adduct showed that addition was occurring from below the flap of the strained bicyclic system.

As a logical extension of this work, Smith found that the highly strained quadricyclane system (10) reacted stereospecifically with \( \mathcal{Z} \) to form 11.

\[
\begin{align*}
10 & + \text{CH}_3\text{O}_2\text{C} &= & \text{C} &= \text{C} &= \text{O}_2 \text{CH}_3 \\
\rightarrow & & & & & \\
11 & & & & & \\
\end{align*}
\]


Blanchard and Cairncross have studied the reactions of 3-methylbicyclo[1.1.0]butanecarbonitrile (12) with acids, nucleophiles, halogens, and reagents containing multiple bonds such as 1,1-bis-(trifluoromethyl)-2,2-dicyanoethylene, butadiene, maleo- and fumaronitrile, ethylene and styrene. Some of the more pertinent reactions are summarized by the following equations. The loss of 26-27% stereopurity in the maleo- and fumaronitrile reactions gave support to the proposed formation of a 1,5-diradical intermediate.

Evidence was presented to eliminate the possibility of thermal activation of the 1,3-bond of the bicyclobutane system to form a 1,3-diradical prior to addition.

Gassman found that the addition of dicyanoacetylene to 12 gave 13 (7.6%) as the only isolable product obtained from stirring the reactants for five days at room temperature in chloroform.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CN} + \text{NCC}=\text{CCN} \quad \rightarrow \quad \text{H}_3\text{C} \quad \begin{array}{c}
\text{CN} \\
\text{C}=\text{C} \\
\text{H} \\
\text{CN}
\end{array} \\
12 & \quad 13
\end{align*}
\]

The reaction of 1,3-dimethylbicyclo[1.1.0]butane (14) with maleic anhydride was reported to proceed rapidly to give an 85% yield of ene-type product (15).

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 + \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \quad \rightarrow \quad \text{H}_3\text{C} \quad \begin{array}{c}
\text{O} \\
\text{O} \\
\text{CH}_3
\end{array}
\end{align*}
\]

Bicyclo[1.1.0]butane has been found to react with benzyne (16) to give a 6:7:1 ratio of 3-phenylcyclobutane (17) and benzobicyclo-[2.1.1]hex-2-one (18). When 1,3-dimethylbicyclo[1.1.0]butane

41. M. Pomerantz, G. W. Gruber, R. N. Wilke, ibid., 90, 5040 (1968).
was reacted with benzyne, the only product isolated was 1,3-dimethyl-

\[
\begin{array}{ccc}
1 & + & 16 \\
\rightarrow & & 17 \\
& + & 18
\end{array}
\]

3-phenylcyclobutane.

As this survey of chemical literature has shown, the only reports dealing with the stereochemical features of the addition of electron-deficient carbon-carbon multiple bonds to highly strained small ring systems have been those of Gassman and of Cairncross. Although much attention has been directed to additions to bicyclo[1.1.0]butane systems, little information has been available concerning the stereochemistry of such reactions. Also, little specific information is known about the relative reactivities of small ring systems undergoing attack by electron-deficient olefins and acetylenes, although predictions based on strain energies and hybridization effects could be made. Several questions remain. How general are the stereochemical features of attack on 'bent' bonds? What is the influence of the steric environment of the ring system? How do the reactivities of various polycyclic hydrocarbons toward addition compare? To answer these questions, an investigation was ex-

42. For a report of research concurrent with this investigation see: M. Pomerantz, G. W. Gruber, R. N. Wilke, J. Am. Chem. Soc., 90, 5040 (1968).
tended to addition reactions of tricyclo[4.1.0.0^{2,7}]heptane (19, a bridged bicyclo[1.1.0]butane derivative) and tricyclo[4.1.0.0^{3,7}]heptane (20, a bridged bicyclo[2.1.0]pentane derivative).

II. Results

A. Tricyclo[4.1.0.0^{2,7}]heptane

1. Preparation

Tricyclo[4.1.0.0^{2,7}]heptane (19) was obtained by treating 7,7-dibromonorcarane (21) with methylithium in ether at 0° according to a procedure of Moore and Ward. 44

\[
\begin{align*}
\text{Br} & \quad \text{CH}_3\text{Li} & \quad \text{Br} \\
(21) & \\
+ & \\
(19) &
\end{align*}
\]

2. Reactions

a. Dimethyl Acetylenedicarboxylate

Dimethyl acetylenedicarboxylate is a well known dienophile. In view of its facile reaction with bicyclo[2.1.0]pentane to give easily characterizable products, it drew our initial attention. When a mixture of equimolar amounts of 19 and 2 was sealed in a glass ampoule under nitrogen and heated to 96° in the absence of light for 9 hours,


it was found that 80% of 19 was consumed. Thin layer chromatography of the crude heavy oil obtained indicated one major and four minor products plus polymeric materials. The products were completely resistant to vacuum distillation. Decomposition was also apparent during attempted v.p.c. analysis, in contrast to the stability of addition products from bicyclo[2.1.0]pentane.

Column chromatography produced two main fractions, each of which, however, were contaminated with small amounts of polymeric material. Crystallization attempts were unsuccessful. Spectra data (IR, UV, nmr) indicated highly conjugated ester functions and olefinic protons. Variation of reaction and work-up procedures including the use of hexane as a reaction solvent brought about no improvement.

b. Dicyanoacetylene

Dicyanoacetylene is an extremely powerful acetylenic dienophile as evidenced by its addition to substituted benzenes. It can be stored for only short periods of time at dry ice temperatures and was thus freshly prepared before use by the dehydration of acetylene-dicarboxamide with phosphorus pentoxide at 200°. Due to the greatly increased reactivity of dicyanoacetylene over that of di-


methyl acetylenedicarboxylate, its addition to 19 should occur under less severe conditions and result in less product decomposition.

Dicyanoacetylene and 19 reacted violently when mixed neat at room temperature. The reactants on mixing at 0° turned green immediately, which gradually darkened to give an opaque solution. The color persisted upon warming to room temperature and the reaction mixture became a black oil. A very weak and undefinable esr signal was obtained (Varian, 4502 spectrometer) from a mixture of the reactants in ether at room temperature. No attempt was made to optimize conditions for possible esr studies.

Thin layer chromatographic analysis of the ether soluble portion of the crude reaction products (reaction at -15 to 0° in ether) indicated one major and a multitude of minor components. V.p.c. analysis was unsuccessful due to decomposition. The major component was obtained as a colorless, viscous liquid after column chromatography on silica gel with 3:1 hexane/benzene as the eluting solvent. The yield calculated for a 1:1 adduct was 35%. The infrared spectrum showed nitrile absorption at 4.43 μ. The ultraviolet spectrum had λ_max 256, indicative of a highly conjugated system. The nmr spectrum showed sharp peaks in the olefinic region (a total of 3 hydrogens) and broad multiplets in the aliphatic hydrogen regions (see experimental).

Analysis for carbon (84.28), hydrogen (10.21), and nitrogen (5.36), although totalling 100% did not correspond to any reasonable formula. The mass spectrum showed a parent peak at m/e 183 but it is
questionable whether this was actually a parent peak or a major fragment from a much higher molecular weight substance. The tendency of this product to polymerize precluded further investigation.

Other workers have been unsuccessful in characterizing products from reactions of bicyclo[1.1.0]butane systems with highly electron deficient carbon-carbon multiple bonds. The facile reaction of tetracyanoethylene with 3-methylbicyclo[1.1.0]butanecarbonitrile produced an unidentifiable dark, amorphous solid. The reaction of 1,3-dimethylbicyclo[1.1.0]butane with tetracyanoethylene at 0° gave a blue colored solution from which an esr signal was obtained, but only low molecular weight polymers were found as products.

c. Benzyne

In contrast to the instability of the addition products obtained using \( \mathbf{2} \) and \( \mathbf{6} \), it was believed that the addition of benzyne should result in stable products amenable to characterization.

Benzyne \((\text{C}_6\text{H}_4)\), often represented as \( \mathbf{16} \), is one of the most highly reactive hydrocarbon species known and as such has never been

\[ \mathbf{16} \quad \leftrightarrow \quad \mathbf{22} \quad \leftrightarrow \quad \mathbf{23} \quad \leftrightarrow \quad \mathbf{24} \quad \leftrightarrow \quad \mathbf{25} \]


\[49. \text{M. R. Rifi, ibid., 89, 4442 (1967).}\]
isolated. However, its intermediacy has been well established.
Benzyne undergoes attack by nucleophiles, dimerization and trimerization, and Diels-Alder addition. It has been found to cycloadd to the strained bicyclic hydrocarbons, bicyclo[2.2.1]heptadiene (26) and bicyclo[2.2.1]heptene (27) to give exclusively the exo compounds, 28 and 29, respectively. Addition of benzyne to bicyclo[1.1.0]-

\[
\text{26} + 16 \rightarrow \text{28}
\]

\[
\text{27} + 16 \rightarrow \text{29}
\]

butane has been reported, as previously discussed. Benzyne has also been found to add to benzene.

The electronic structure of benzyne is not completely defined but has been represented as a resonance hybrid of structures 23-25


with structure \(^2\) making the greatest contribution. Molecular orbital calculations of Hoffmann predicted a sizable contribution from resonance structure \(^2\).

When a slurry of three equivalents of the benzyne precursor, benzenediazonium-2-carboxylate, and one equivalent of \(^1\) was refluxed in methylene chloride (40°) for four hours a single adduct (\(^3\)) was obtained in 61% yield after two distillations (b.p. 77-78°/0.5 mm) and silica gel chromatography. V.p.c. analysis of the crude reaction product indicated an approximately 3% impurity of comparable molecular weight. The chemical analysis and molecular weight of 170 obtained from the mass spectral data confirmed a 1:1 adduct.

The infrared spectrum showed bands at 13.80 \(\mu\) and 14.40 \(\mu\) and a pattern in the 5.00-5.70 \(\mu\) region, all of which were characteristic of a monosubstituted aromatic compound. The only absorption in the ultraviolet region was that of a nonconjugated benzene ring. The nmr spectrum (neat) showed a singlet at \(\tau\) 2.94 which integrated for 5

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54. L. Friedman and F. M. Logullo, ibid., 85, 1549 (1965); L. Friedman, ibid., 89, 3071 (1967).
hydrogens, again indicative of a monosubstituted benzene derivative. The remainder of the spectrum consisted of a one hydrogen (H\textsubscript{a}) quartet at \(\tau 6.38\) (\(J_{HA}H_B\), 4.0 cps, \(J_{HA}H_C\) 8.0 cps) a complex doublet at \(\tau 7.24\) (H\textsubscript{C}), a multiplet at \(\tau 7.75\) (H\textsubscript{d}), and a broad six proton multiplet at \(\tau 8.1-9.0\). (The assignment of H\textsubscript{a} and H\textsubscript{d} were confirmed by their absence in the nmr spectrum of the product from 1,7-dideuteriotricyclo[4.1.0.0\textsuperscript{2,7}]heptane.) This portion of the spectrum bore a marked resemblance to that of \(\text{I}\) reported by Tanida \textsuperscript{55} with the exception that the C\textsubscript{7} hydrogen in \(\text{I}\) was buried in the up-field multiplet. Coupling constants of the C\textsubscript{2} proton were consistent with exclusive endo substitution.

In the mass spectrum, in addition to the parent base peak, there was an intense tropylium peak (m/e 91, C\textsubscript{7}H\textsubscript{7}+) as further evidence of a monosubstituted benzene ring. Therefore, benzyne must have added to and abstracted a hydrogen from the tricyclo[4.1.0.0\textsuperscript{2,7}]heptane molecule. Compound \(\text{I}\) contained a cyclopropane moiety as shown by the appearance of maximum in its near-infrared spectrum at

1.657 μ (ε 0.810) characteristic of strained cyclopropane. Aryl C-H stretching overtones appeared at 1.673 μ.

Further evidence for the presence of a highly strained cyclopropane was the rapid uptake by 30 of bromine in carbon tetrachloride and hydrogen over Pd/C, and its slow decolorization of potassium permanganate while remaining unreactive to ozone in methanol and osmium tetroxide in ether.

Final confirmation of structure, including the exclusive endo substitution, was the hydrogenation of 30 to give only endo-2-phenylbicyclo[2.2.1]heptane (32) which was identical in all respects to an authentic sample.

The hydrogenation of endo substituted tricyclo[4.1.0.03,7]-heptane derivatives to endo substituted bicyclo[2.2.1]heptane systems has been previously reported.

B. Tricyclo[4.1.0.03,7]heptane (30)

1. Preparation

This bicyclo[2.1.0]pentane derivative was prepared by the following sequence of conversions.


57. An authentic sample of 32 was kindly furnished by Professor H. C. Brown.

2. Reactions

a. Benzyne

When a slurry of three equivalents of benzenediazonium-2-carboxylate and one equivalent of 20 were refluxed in methylene chloride (40°) for four hours, only unreacted 20 was recovered. An increase in the ratio of reactants to 5:1 and reflux in tetrahydrofuran (66°) still resulted in no observation of addition products.

Similar procedures also resulted in no reaction of benzyne with bicyclo[2.1.0]pentane

b. Dicyanoacetylene

When equivalent amounts of dicyanoacetylene (6) and 20 were stirred under nitrogen for 4 days at room temperature the mixture darkened somewhat but little reaction seemed to have occurred. However, when an equimolar mixture was sealed under nitrogen in a glass ampoule and heated at 70° for 14 hours, a 46% yield of 38 was formed. Extraction of the crude black reaction mixture with ether, followed by removal of the solvent gave 38 as a pale yellow oil which slowly crystallized. V.p.c. analysis indicated approximately 4% impurity.

The low yields, compared with values up to 76% for products obtained from the reaction of 6 with bicyclo[2.1.0]pentane, 62 can be attributed to 38 being a derivative of 20 and thus able to react further with 6. Compound 38 was highly stable at room temperature in contrast to the corresponding bicyclo[2.1.0]pentane adducts.

The assignment of structure to 38 was based on spectroscopic and chemical evidence. Analysis of a sample recrystallized from

petroleum ether, m.p. 58-59°C, and mass spectral data (parent peak at m/e 170) confirmed that 36 was formed from the addition of one equivalent of 6 to 20. The infrared spectrum showed a nitrile absorption at 4.45 µ, while the near-infrared spectrum showed a maximum at 1.658 µ (ε 0.910), similar to that of 30, and characteristic of the presence of a cyclopropyl moiety in a polycyclic system. The ultraviolet spectrum had λ_max 222 nm (ε 8,250) suitable for a monosubstituted maleonitrile.

The nmr spectrum had a single olefinic proton at τ 3.75 (doublet) which was coupled with the single allylic proton at 6.25 (J_AB 2.5 cps). The remainder of the spectrum consisted of multiplets at τ 7.00 (1H), τ 7.40 (1H), and τ 8.00-8.60 (6H). The nmr spectrum was similar to that of 30 but the possibility of a mechanistically feasible nortricyclane structure (39) could not be excluded by spectroscopic data.

Chemical degradation of the adduct, however, confirmed its structure as 38. Ozonolysis proved ineffective in cleaving the

---


maleonitrile double bond, as did osmium tetroxide in a sodium meta-

\[
\begin{align*}
\text{C}\text{H}_2\text{N}_2 & \xrightarrow{\text{H}_2\text{O}_2, \text{THF}} \text{C}\text{H}_2\text{N}_2 \\
\end{align*}
\]

periodate solution. However, it was found that the addition of pyridine to an ether solution of osmium tetroxide and greatly facilitated reaction to give a solid osmate ester pyridine complex.

This complex was decomposed with hydrogen sulfide to give an oil (\(41\)), which was not purified. The infrared spectrum indicated an \(\alpha\)-keto acid, with loss of nitrile functions. Further treatment


with basic hydrogen peroxide resulted in cleavage of the keto acid to give the tricyclic acid (42) which was spectroscopically completely different from an authentic sample of 3-nortricyclane-carboxylic acid (40) (which would have been formed if the adduct were 39). Esterification of 42 gave 43, which mass spectra data and chemical analysis showed had a formula of C₈H₁₂O₂. The tricyclic ester was spectroscopically different from an authentic sample of the methyl ester of 40.

Final confirmation of adduct structure as endo-5-tricyclo-[4.1.0.0³,7]heptyl maleonitrile (38) was the hydrogenation of 43 over 5% Pd/C to give endo-2-carbomethoxybicyclo[2.2.1]heptane (44), identical in all respects to an authentic sample.

III. Mechanism and Stereochemistry - Discussion

Figure 1 contains a summary of reactions of bicyclo[2.1.0]-pentane and bicyclo[1.1.0]butane systems with benzyne (16) and dicyanoacetylene (6). From these data it appears that bicyclo[1.1.0]-butane systems are more reactive toward addition than the bicyclo[2.1.0]pentane systems. The electron withdrawing effect of the

67. This acid was contaminated with small amounts (10-30%) depending on reaction conditions) of an isomeric acid which probably resulted from the base catalyzed epimerization of 37. Esters of these acids were shown to be isomeric by mass spectral measurements.

68. K. Alder, R. Hartmann, and W. Roth, Ber., 93, 2271 (1960).

69. O. Diels and K. Alder, Annalen, 460, 98 (1928).
(* = research presented herein)
cyano group in 12 apparently lowers reactivity. In all cases addition results in cleavage of the same highly strained C-C bridgehead bond. Since, as discussed earlier, the relief of strain energy in the cleavage of the 1,4-bond in bicyclo[2.1.0]pentane (48.1 kcal/mole, 54.1 kcal/mole total strain -6.0 kcal/mole for cyclopentane) is greater than that for cleavage of the 1,3-bond in bicyclo[1.1.0]-butane (38.1 kcal/mole, 63.9 kcal/mole total strain -25.8 kcal/mole for cyclobutane) the reverse order of reactivities might be expected. Similar results are seen in the reactions of these strained molecules with acid. Bicyclo[2.1.0]pentane reacts only partially with glacial acetic acid at 47° for 24 hours, whereas bicyclo[1.1.0]-butane reacts completely at 25° in less than an hour. Here, difference in strain relief was not evidenced in relative rates of reaction. (It was conjectured that perhaps unlike bicyclopentane, bicyclobutane can give a well stabilized ion on protonation.) With respect to the tricyclic system 12, Closs has stated that the trimethylene bridge should be flexible enough not to introduce additional strain over that found in bicyclobutane. The C13-H spin-spin coupling constant of 200 ± 2 cps indicated 40% s-character in the C-H bond orbitals for carbons 1 and 7 of 12. This high degree of s-character is reflected in increased acidity such that n-


butyllithium can remove the C\textsubscript{1} and C\textsubscript{7} hydrogens. In contrast, bicyclo[2.1.0]pentane requires long exposure to amylsodium for removal of the bridgehead hydrogens\textsuperscript{72} indicating less \( s \)-character in the C-H bond orbitals and less \( p \)-character in the 1,4-bond. It appears a combination of strain energy and orbital hybridization effects are involved in determining the reactivities of these systems to addition by such molecules as benzyne and dicyanoacetylene. A considerable amount of more detailed information is needed.

Based on previous reports the most probable mechanism for addition of electron deficient acetylenes to the strained bonds of the tricyclic hydrocarbons under consideration should involve a diradical intermediate. A dipolar intermediate in the addition of benzyne to bicyclo[2.2.1]heptene was excluded on the basis that no products resulting from rearrangements of a polar intermediate were observed.\textsuperscript{73} Until compelling evidence for a diradical intermediate in the formation of both cycloaddition and ene-type products from bicyclo[2.1.0]pentane was published by Gassman\textsuperscript{74} a concerted mechanism was favored for the ene reaction.

\textsuperscript{72} K. T. Mansfield, Ph.D. Dissertation, The Ohio State University, 1967.
\textsuperscript{74} P. G. Gassman and K. T. Mansfield, ibid., \textbf{90}, 1524 (1968).
A diradical intermediate for additions to the bicyclobutane system has been proposed as seen earlier. In the initial report of the addition of benzyne to bicyclobutane a concerted mechanism was favored. However, in a later publication concerning more detailed mechanistic information a diradical intermediate was proposed.

Analogies thus favor a diradical intermediate for formation of the tricyclo[4.1.0.0^2]heptane derivatives from 19 and 20. However, mechanistically, derivatives of tricyclo[4.1.0.0^2]heptane have been obtained via carbene insertion and carbonium ion trapping experiments. In the reaction of benzyne with 19 the forma-

\[
\begin{align*}
\text{D} & \quad \text{D} \\
\text{D} & \quad \text{D}
\end{align*}
\]

\[
\begin{align*}
\text{D} & \quad \text{D} \\
\text{D} & \quad \text{D}
\end{align*}
\]

\[
\begin{align*}
\text{D} & \quad \text{D} \\
\text{D} & \quad \text{D}
\end{align*}
\]

\[
\begin{align*}
\text{D} & \quad \text{D} \\
\text{D} & \quad \text{D}
\end{align*}
\]

\[
\begin{align*}
\text{D} & \quad \text{D} \\
\text{D} & \quad \text{D}
\end{align*}
\]


77. M. Pomerantz, G. W. Gruber, R. N. Wilke, ibid., 90, 5040 (1968).


tion of a carbene would require the intramolecular transfer of the hydrogen initially on the bicyclo[1.1.0]butane bridgehead to the aromatic nucleus. When the addition was carried out with 1,7-dideuteriotricyclo[4.1.0.0²,7]heptane (45) no such deuterium transfer occurred, as shown by nmr spectroscopy (5 aromatic protons versus 7 aliphatic protons) and mass spectroscopy (the presence of C₇H₆D⁺ as the major fragmentation product). This type of mechanism was also eliminated by the stereochemistry of the phenyl group which was proven to be endo. The intermediacy of 46 and 47 would require an exo phenyl group as shown in 48.

The more logical mechanism, which explains endo stereochemistry, requires attack of benzyne on 19 from the same side as the tri-}

![Chemical Diagram](attachment://chemical_diagram.png)
A similar mechanism can be written for the reaction of 20 with dicyanoacetylene. Dicyanoacetylene could attack 20 from the bottom side at the less sterically hindered C-1 position to give the diradical 51. Hydrogen transfer and closure of the new diradical 52 would form 28, of necessity a maleonitrile derivative. Attack at
the more sterically hindered C-7 position would give 59.

In the mechanism shown for addition of benzyne and dicyanoacetylene to 19 and 20, it is seen that the initially formed diradical is converted to a new diradical via a 1,5-hydrogen transfer going through a cyclic six-membered transition state. A 1,4-hydrogen transfer is not possible in diradical 49, since this would involve removal of a bridgehead hydrogen and formation of a double bond at the bridgehead position. However, in diradical 51 there is a methylene hydrogen in the number 2 position available for a 1,4-transfer via a five-membered transition state. The initially formed diradical in the addition of dicyanoacetylene to bicyclo[2.1.0]-pentane has been seen to go through a 1,4-hydrogen transfer to form the ene-product (9). If such a hydrogen transfer occurred in 52 the

![Chemical structures](image)

product formed would be 54. (The removal of a proton activated by a
radical center alpha to it is not possible in 51 or 49 as it is in 52.) The chemical degradation performed on the adduct could not rule out 54. However, analysis of nmr data indicated, but did not prove unequivocally, that this was not the structure.

The great preponderance of evidence for intramolecular transfer of hydrogen radicals via a cyclic six membered transition state argues strongly for the formation of 38. The photochemical rearrangements of N-haloamines (the Hoffman-Loffler-Freytag reaction), alkyl nitrites, alkyl hypohalites, ketones, N-haloamides, and the pyrolysis of alkyl azides are all represented as cases in point. In contrast, there are few examples of 1,4-hydrogen shifts. Such shifts have not been found in the decomposition of the peroxide of


\( \gamma \)-phenylvaleric acid, the photolysis of 3-phenyl-1-propyl nitrite, or in the photochemical isomerizations of N-chloro-N-methyl-2-butylamine and N-chloro-N-ethyl-cyclopentylmethylamime.

With respect to stereochemistry it has previously been shown that the addition of electron deficient carbon-carbon multiple bonds to the bent single bond in bicyclo[2.1.0]pentane occurred via attack on the inside of the flap formed by the fused rings as shown in the reaction of 55 with 56 to form 57. This same backside attack has now been seen to occur with the tricyclo[4.1.0.0\(^3,7\)]-heptane molecule, containing the bicyclo[2.1.0]pentane moiety, and extends to bicyclo[1.1.0]butane systems as now demonstrated with

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90. K. Loffler, Ber., 43, 2025 (1910).


This phenomenon thus appears to be general. Facile additions, even in the presence of additional bridging with considerable attendant steric hindrance to backside attack in the tricyclic structures, indicates overwhelming preference for this stereospecific mode of addition. In contrast, the apparent failure of 58 to react with benzyne has been attributed to steric factors.

\[ \text{CH}_3 \]
\[ \text{CH}_3 \]

In additions to bicyclo[2.1.0]pentane, bicyclo[1.1.0]butane, and their bicyclic derivatives, it has been found that both cycloaddition and ene-type products are formed, with the latter being preferred. However, it is now observed that no cycloaddition products are formed from the tricyclic structures. Again, this is


a natural consequence of requisite backside attack and the rigidity and steric requirements placed on the initially formed diradical by additional bridging. This diradical cannot undergo intramolecular coupling to form cycloadducts. Of necessity it follows the path of hydrogen abstraction via a six membered transition state to give a new diradical which can easily couple. Also steric hindrance from additional bridging has now been shown to control which end of the strained sigma bond undergoes backside attack.
PART TWO

CHEMICAL AND PHYSICAL PROPERTIES OF β-KETO SULFOXIDES

I. Introduction and Historical Review

Although many analogies have been drawn between carbonyl containing compounds and sulfoxides, the electronic structure of sulfoxides is still in doubt. The question of resonance involving the d orbitals of sulfur has never been completely answered. It is thought that the vacant d orbitals of sulfoxides may participate in bond formation by accepting p electrons from the oxygen atom or, with conjugated sulfoxides, from the unsaturated carbon group in an α,β-unsaturated sulfoxide. Thus, resonance structures 59 and 60 are

\[
\begin{align*}
59 & :\overset{\circ}{\equiv} : & 60 & :\overset{\circ}{\equiv} :
R-S-R & \leftrightarrow R-S-R & R-S-R & \leftrightarrow -C=C-S-R & \leftrightarrow -C=C=S-R
\end{align*}
\]

most often represented as 61. The bond dipole moment of the S-O group is smaller by 0.8-1.3D than the 3.8D calculated for a true coordinate covalent bond indicating double bond character. However, in the infrared spectra of sulfoxides, the presence of conjugating vinyl or aryl groups cause only a small increase in the sulfur-oxygen stretching frequency. Ultraviolet spectra show only
a small degree of conjugation between the sulfinyl and other groups.

Spectral data and its interpretation here varied for compounds containing divalent sulfur. One group of investigators has claimed that their spectral evidence showed no significant valence shell expansion of sulfur in the ground state or first few excited states. However, other correlations of carbonyl frequencies and basicities of thiolesters were said to indicate that sulfur participates in resonance interaction in the ground state through 3-d orbitals. So-called substituent interference experiments by Taft and Goodman indicated significant 3-d orbital interaction in the ground states of thiophenols and thiaoanisoles. A comparison of SCF MO calculations with and without inclusions of 3-d orbitals on sulfur in thiophene has indicated only a small d-orbital participation in the \( \pi \)-electronic structure.


A linear free-energy treatment of acidities of phenols containing sulfone, sulfonium, and sulfoxide groups showed that electron-attracting conjugation is greatly enhanced in photoexcited states compared with ground states. The sulfide group participates in both electron-releasing and attracting conjugation in the ground and excited states. The infrared spectrum of dimethyl sulfone is consistent with p-dσ bonding.

According to a LCAO-MO-SCF treatment of the hypothetical compound, hydrogen methyl sulfoxide, resonance structures 64, 65, and 66 were possible for the corresponding α-sulfinyl carbanion.

However, calculations revealed no d-orbital contributions to the higher occupied molecular orbitals to explain delocalization.

Recently, a great deal of interest has been generated in the chemistry of β-keto sulfoxides, since this class of compounds has been found to be readily prepared from the reaction of dimethyl

100. E. L. Wehry, ibid., 89, 41 (1967).
Considering the previous information concerning the nature of the sulfoxide grouping, it might be anticipated that a comparison of chemical and physical properties of β-keto sulfoxides with those of β-diketones would offer additional insight into the extent of analogy between carbonyl and sulfinyl functions.

It is well known that a methylene hydrogen can easily be removed from a β-dicarbonyl system and that a sulfinyl group activates α-hydrogens. Consequently, β-keto sulfoxides should show acidity comparable to that of β-diketones. Research was undertaken to quantitatively measure this property. In addition, since β-keto sulfoxides such as ω-(methylsulfinyl)acetophenone undergo reductive cleavage to form methyl ketones, it was anticipated that alkyla-

tion of β-keto sulfoxides followed by cleavage should offer a synthetic route to ketones of wider variety than those possible with the analogous acetoacetic ester synthesis.

Investigations of β-diketone chemistry suggested the possibility of forming dianion radicals from β-keto sulfoxides. A report by Bauld showed that stable enolate dianion radicals could be generated from dibenzoylmethane (67) and benzoylacetonitrile (71) via reduction of the corresponding anions with alkali metals. Dianion radical (69)

\[
\begin{align*}
\text{NaH} & \quad \text{THF} \\
\text{ANION} & \quad \text{Na} \quad \text{DIANION RADICAL}
\end{align*}
\]

is stable in refluxing THF and can be further reduced to the diamagnetic trianion. In a later report, ESR spectra of these and other paramagnetic enolate systems were discussed with respect to experimental and calculated electron densities. Electron spin resonance studies of β-keto sulfoxide radical dianions should thus


111. N. L. Bauld and M. S. Brown, ibid., 89, 5413 (1967).
offer a direct comparison of the electronic characteristics of sulfanyl and carbonyl functional groups.

Radical anions have been formed from alkali metal reductions of aromatic sulfides, sulfones, and sulfoxides such as structures 72-78. As the oxidation state of sulfur increases, the ease of reduction increases and the total width of the esr spectra narrows due to a greater accommodation of electron spin density on the sulfur groupings. The esr spectrum of diphenyl sulfone radical anion closely resembles that of biphenyl indicating a strong conjugative effect between the two aromatic rings. Attempts to observe an esr spectrum of diphenyl sulfoxide radical anion have been unsuccessful.


in contrast to the highly stable benzophenone radical anion. It seemed reasonable then that the presence of both carbonyl and sulfinyl groups in the \( \beta \)-keto sulfoxides should favor the formation of a stable radical dianion.

II. Experimental Results

A. Ketone Synthesis - Alkylation and Cleavage of \( \beta \)-Keto Sulfoxides

The \( \beta \)-keto sulfoxides, 81 and 82, were prepared by the reaction of appropriate esters, 79 and 80, with dimethyl sulfoxide anion. Addition of 81 to a solution of sodium ethoxide in ethanol gave little

\[
\text{RCO}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{SCH}_2 \rightarrow \text{RCCH}_2\text{SCH}_3 + \text{CH}_3\text{CH}_2\text{O}^-
\]

79, \( R = \emptyset \)  \hspace{2cm} 81, \( R = \emptyset \)

80, \( R = \text{CH}_3(\text{CH}_2)_4 \)  \hspace{2cm} 82, \( R = \text{CH}_3(\text{CH}_2)_4 \)

reaction. When sodium hydride or lithium hydride was used as base in tetrahydrofuran (THF) an immediate evolution of hydrogen was occurred and the alkali metal salt of the \( \beta \)-keto sulfoxide precipitated. Preliminary attempts to alkylate this salt with a slight excess of methyl iodide produced only a 14% yield of 83 (\( R = \text{CH}_3 \)).

When dimethylformamide (DMF) was used as solvent and sodium hydride was the added base, \( \text{I} \) reacted vigorously to yield the soluble salt. Addition of methyl iodide to the DMF solution resulted in immediate reaction at room temperature and a close to quantitative yield of crude monoalkylated \( \beta \)-keto sulfoxide, \( \text{III} \) (\( R = \phi, R' = \text{CH}_3 \)). Since the crude alkylated product was a mixture of diastereomers, purification in high yield by recrystallization proved difficult. It appeared that one of the diastereomers crystallized from ethyl acetate to give a 30% yield of pure alkylated product. The ease with which alkylated \( \beta \)-keto sulfoxides can be cleaved was demonstrated by the reduction of purified \( \text{III} \) (\( R = \phi, R' = \text{CH}_3 \)) with aluminum amalgam which gave a 96% yield of propiophenone.

\[
\text{RCCHSCH}_3 \xrightarrow{\text{Al(Hg)}} \text{RCCH}_2R' \]

Since purification of the alkylated diastereomeric \( \beta \)-keto sulfoxides was so difficult, the direct reductive cleavage of the crude alkylation products appeared attractive.

Table 1 gives the yield of ketone based on starting \( \omega \)-(methyl-sulfinyl)acetophenone for the combined alkylation and cleavage steps. The yields showed that purification of the alkylated \( \beta \)-keto sulfoxide

\[115. \text{In work subsequent to this comparable yields were obtained. G. A. Russell and G. J. Mikol, J. Am. Chem. Soc., 88, 5498 (1966).} \]
The general scope of this synthetic sequence was extended to aliphatic β-keto sulfoxides as illustrated in Table 2, which lists the results obtained from alkylation and cleavage of methylsulfinylmethyl n-pentyl ketone.

From Tables 1 and 2 it is obvious that not only monoalkylation but also dialkylation was possible. This dialkylation can be achieved by either a two-step procedure or a one-step procedure where two equivalents of sodium hydride were added, followed by addition of two equivalents of alkylating agent. The two-step procedure could be used to obtain alkylation with two different alkylating agents thereby allowing the synthesis of rather complex α-substituted ketones.

One alkylation was done both in DMSO and in DMF. In these experiments the yield of ketone was slightly higher in DMSO than in DMF. This slight increase in yield was not sufficient to merit the added problems of rigorously drying the DMSO and of a more complex reaction work-up.

Attempts to alkylate the β-keto sulfoxides with secondary halides (isopropyl bromide and iodide) gave extremely poor yields. Alkylation with 1,4-diiodobutane gave an intractable mixture. None of the desired product was obtained in an attempted Michael reaction of the β-keto sulfoxide anions with acrylonitrile.
Table 1

<table>
<thead>
<tr>
<th>Alkylating Agent</th>
<th>Product R</th>
<th>R'</th>
<th>Alkylation Solvent</th>
<th>Ketone Obtained</th>
<th>% Yield</th>
<th>mp of 2,4-Dinitrophenylhydrazone</th>
<th>Lit mp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃I (1 mole)</td>
<td>CH₃</td>
<td>H</td>
<td>DMF</td>
<td>propiophenone</td>
<td>64</td>
<td>191-192°</td>
<td>191°</td>
</tr>
<tr>
<td>CH₃I (2 moles)</td>
<td>CH₃</td>
<td>CH₃</td>
<td>DMF</td>
<td>isobutyrophenone</td>
<td>54</td>
<td>160-161°</td>
<td>161-162°</td>
</tr>
<tr>
<td>CH₃I (2 moles)</td>
<td>CH₃</td>
<td>CH₃</td>
<td>DMF</td>
<td>isobutyrophenone</td>
<td>50</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>CH₃CH₂I</td>
<td>CH₃CH₂</td>
<td>H</td>
<td>DMF</td>
<td>butyrophenone</td>
<td>70</td>
<td>190-191°</td>
<td>191-192°</td>
</tr>
<tr>
<td>CH₃CH₂CH₂Br</td>
<td>CH₃CH₂CH₂</td>
<td>H</td>
<td>DMF</td>
<td>valerophenone</td>
<td>44</td>
<td>164-165°</td>
<td>165-166°</td>
</tr>
</tbody>
</table>

a) Stepwise carbanion formation and alkylation (see experimental).

b) Two moles of sodium hydride added, followed by two moles of alkylating agent.
Table 2

Alkylation of $\text{CH}_3(\text{CH}_2)_4\text{CCH}_2\text{SCH}_3$ and Cleavage of $\text{CH}_3(\text{CH}_2)_4\text{C-C-S-CH}_3$.

<table>
<thead>
<tr>
<th>Alkylating Agent</th>
<th>Product R</th>
<th>R'</th>
<th>Alkylation Solvent</th>
<th>Ketone Obtained</th>
<th>% Yield</th>
<th>mp of 2,4-Dinitrophenylhydrazone</th>
<th>Lit mp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$I (1 mole)</td>
<td>CH$_3$</td>
<td>H</td>
<td>DMF</td>
<td>3-octanone</td>
<td>62</td>
<td>65-66$^\circ$</td>
<td>64-65$^\circ$</td>
</tr>
<tr>
<td>CH$_3$I (2 moles)</td>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>DMF</td>
<td>2-methyl-3-octanone</td>
<td>59</td>
<td>91-92$^\circ$</td>
<td>92.5$^\circ$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$I</td>
<td>CH$_3$CH$_2$</td>
<td>H</td>
<td>DMF</td>
<td>4-nonanone</td>
<td>57</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>CH$_3$CH$_2$I</td>
<td>CH$_3$CH$_2$</td>
<td>H</td>
<td>DMSO</td>
<td>4-nonanone</td>
<td>69</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
B. Acidity of β-Keto Sulfoxides

The alkylation of β-keto sulfoxides has provided some qualitative estimation of their acidities. It was decided to extend this to a quantitative description by the determination of pKa values. A spectroscopic (ultraviolet) method of measurement was chosen since it would permit working at low concentrations and was applicable to the expected pKa magnitudes. The procedure is based on the following equations similar to those derived by Albert and Serjeant, \textsuperscript{116} and assuming unity for activity coefficients. For a weak acid:

\[ \text{HA}^+ \rightleftharpoons H^+ + A^- \quad K_{eq} = \frac{[A^-][H^+]}{\text{HA}} \]

\[ A_\lambda = C_A^- e_A^- + C_{HA} e_{HA} \]

\[ A_\lambda = \text{absorbance at wavelength } \lambda \]
\[ e = \text{extinction coefficient at wavelength} \]
\[ C = \text{concentration} \]
\[ C = C_A^- + C_{HA} \]
\[ C = \text{total concentration} \]

If the same concentration of acid is used in all measurements then:

\[ Cd = C_A^- d_A^- + C_{HA} d_{HA} \]

\[ d = \text{measured optical density} \]

It can easily be found from the above equations that:

\[ pK_a = pH - \log \frac{(d-d_{HA})}{(d_{A^-} - d)} \]

Taking the antilog and rearranging gives:

\[ d = d_{A^-} - \frac{[H^+](d-d_{HA})}{K_a} \]

From this final equation it can be seen that if a series of values for \( d \) and the corresponding values for \([H^+](d-d_{HA})\) are known it is possible by a least squares treatment of data to obtain a value for the equilibrium constant and thus the \( pK_a \). Accordingly, the optical densities of the \( \beta \)-keto sulfoxides in water solutions of varied pH values (of varied sodium hydroxide concentration) and constant ionic strength were measured at a wavelength where there was minimal overlap of neutral molecule and anion absorptions. (See Experimental Part for details). The results are contained in Table 3 with a list of carbonyl and sulfonyl analogs for comparison.

It is readily seen that a carbonyl group has a greater acidifying influence on an \( \alpha \)-hydrogen than a sulfonyl group, whereas a sulfinyl group has the least. The acidity of the \( \beta \)-keto sulfoxides falls between that of the keto sulfone and the disulfone.

The substitution of an electron-releasing methyl group for a methylene hydrogen in acetylacetone decreases the acidity by a factor of 200, in agreement with the fact that tertiary carbanions
### Table 3

pKa Values for Various β-Disubstituted Carbonyl, Sulfinyl, and Sulfonyl Compounds (Apparent Values)

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅COCH₂SOCH₃ (λₘₐₓ 252)</td>
<td>11.02 ± 0.06 (27.5°)</td>
<td>a</td>
</tr>
<tr>
<td>C₆H₅COCH(CH₃)SOCH₃ (λₘₐₓ 280)</td>
<td>Very weak acid</td>
<td></td>
</tr>
<tr>
<td>CH₃(CH₂)₄COCH₂SOCH₃</td>
<td>11.62 ± 0.07 (26.5°)</td>
<td></td>
</tr>
<tr>
<td>CH₃COCH₂COCH₃</td>
<td>9.0 (25°)</td>
<td>b</td>
</tr>
<tr>
<td>CH₃COCH(CH₃)COCH₃</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>C₆H₅COCH₂COCH₃</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>C₆H₅COCH₂COC₆H₅</td>
<td>8.95</td>
<td>c</td>
</tr>
<tr>
<td>C₆H₅COCH₂SO₂CH₃</td>
<td>10.01</td>
<td>d</td>
</tr>
<tr>
<td>CH₃COCH₂SO₂CH₃</td>
<td>9.90</td>
<td></td>
</tr>
<tr>
<td>C₆H₅COCH₂SO₂C₆H₅</td>
<td>9.83</td>
<td></td>
</tr>
<tr>
<td>CH₃SO₂CH₂SO₂CH₃</td>
<td>14</td>
<td>e</td>
</tr>
</tbody>
</table>

a. Present work.


are less stable than primary. The same influence operates in β-keto sulfoxides and appears to make the acidity of the methylated β-keto sulfoxide too weak for accurate measurement by the present method. As expected, the aromatic β-keto sulfoxide is more acidic than the aliphatic. It would have been interesting to see if any difference would be observed if the phenyl group were substituted on sulfur instead of carbon.

Based on information at hand, the extent of enolization in β-keto sulfoxides must be very small. Resonance stabilization of the anion must be less important than in β-diketones and β-keto sulfones. The large extinction coefficient (14,200) of methylsulfinyl-n-pentyl ketone anion indicates high polarity and relatively little distribution of charge.

The unionized keto sulfoxide has \( \lambda_{\text{max}} = 280 \text{ nm} \) \( (\epsilon = 82.0) \), whereas the enol form of ethyl acetoacetate absorbs at 245 nm \( (\epsilon = 18,000) \) and the keto form at 300 nm \( (\epsilon = 50) \) indicating little tautomerization in β-keto sulfoxides. The infrared spectrum shows little mutual influence of the carbonyl and sulfinyl groups. Also, in sharp contrast to β-diketones which rapidly form stable metal complexes,


β-keto sulfoxides displayed no coordination tendencies. The difference appears to be due to the inability of β-keto sulfoxides to undergo any appreciable enolization.

C. Radical Anion Formation

The β-keto sulfoxides and β-keto sulfones which were chosen for an investigation of possible radical dianion formation are represented by structures 79 and 84-87. The β-keto sulfones were included because of expected increased radical anion stability over that of the corresponding sulfoxides.

A comparison of the various systems appeared attractive.

In a procedure similar to that used for radical dianion formation from enolate systems, the β-keto sulfoxides and sulfones were treated as follows:

121. A saturated solution of cupric acetate and either ω-(methylsulfinyl)acetophenone or ω-(phenylsulfinyl)acetophenone upon prolonged heating gave green crystals (identical infrared spectra) which were soluble in hot benzene. Cleavage must have occurred as further shown by the absence of sulfur in the chemical analysis (C, 67.9%; H, 3.91%). Additional attempts to form metal chelates were similarly unsuccessful.


123. N. L. Bauld, ibid., 86, 2305 (1964); N. L. Bauld and M. S. Brown, ibid., 89, 5413 (1967).
converted to their corresponding anions by reaction with sodium hydride in purified solvents. Subsequent reduction was accomplished by the use of potassium, sodium, or their eutectic alloy. All reactions were carried out in a specially designed vacuum vessel attached to a quartz esr sample tube.

A survey of the literature on radical anions showed that the most commonly employed solvents are tetrahydrofuran (THF) and dimethoxyethane (DME). In preliminary experiments using these solvents, treatment of the anions of \( \text{72} \) or \( \text{84} \) with potassium or sodium-potassium alloy resulted only in an extremely weak esr signal, even at low temperatures (ca. -70°). Variation of reaction conditions produced no improvement. Although the solutions darkened somewhat upon prolonged treatment with the alkali metals, \( \text{72} \) and \( \text{84} \) could be nearly quantitatively recovered after simple neutralization. This was in contrast to the rapid formation and high stability of the radical dianion of dibenzoylmethane in THF. When \( \text{85} \) was similarly treated in THF an immediate red-brown color was observed upon reduction of the anion. A strong esr spectrum was observed, but was only vaguely resolved regardless of concentration or temperature.
Employment of similar procedures with \textsuperscript{79}, \textsuperscript{84}, \textsuperscript{86}, a \textsuperscript{124} acetophenone in diethylene glycol dimethylether (diglyme) at dry-ice bath temperatures resulted in red-brown solutions which gave weak, but symmetrical and somewhat resolved spectra. Temperature variations did not lead to increased signal strength. Within two hours at room temperature all resolution was lost due to a decrease in radical concentration. The spectra obtained, however, were all identical, consisting of 36 main lines (first derivatives) with further unresolved fine structure. Comparison with the spectrum \textsuperscript{125} of peroxyamine disulfonate showed that the spectra covered a 42 gauss region.

The diphenyl substituted sulfone \textsuperscript{87} gave rise to an intense spectrum of nine groups of five lines identical in pattern and coupling constants to a published spectrum of the biphenyl radical anion.\textsuperscript{126} Thus in all cases the spectra appeared to be those of cleavage products. Loss of the phenyl group attached to the sulfonyl rather than the carbonyl group in \textsuperscript{87} was indicated by no observation of the biphenyl radical anion spectrum from \textsuperscript{86}. No biphenyl appeared to be formed from \textsuperscript{84}. Isolation attempts were unsuccessful.

\textsuperscript{124} An unstable acetophenone enolate anion has been reported, but its esr spectrum has not been published; see: N. L. Bauld and M. S. Brown, J. Am. Chem. Soc., \textbf{89}, 5413 (1967).


Several accounts of reductive cleavage of carbon-sulfur bonds have been reported. As previously discussed, β-keto sulfoxides and β-keto sulfones are easily reductively cleaved in the presence of a proton source. Carbon-sulfur bond cleavages appeared in attempted radical anion formation from simple aromatic sulfoxides. Alkali metals have been found to cleave sulfides and sulfones in liquid ammonia. Potassium cleaved dimethyl sulfoxide to the methanesulfonate ion. However, there was still hope that cleavage of the anions of β-keto sulfoxides would not take place upon reduction if proper reaction conditions were used to optimize radical stability.

Radical Formation in HMPA

It has recently been found that hexamethylphosphoramide (HMPA) can dissolve sodium or potassium to give a "solution of electrons."
Based on additional reports concerning the stabilizing influence of $^{133}$HMPA on radicals, it was believed this solvent might be thermodynamically favorable for radical dianion formation.

Treatment of the anion of 72 with sodium-potassium alloy in 25% HMPA/diglyme at room temperature (and below) rapidly gave a red-brown solution exhibiting the same, but much stronger, spectrum as that observed with 100% diglyme. However, in 100% HMPA potassium reduction of the anion produced a broader (ca. 50 gauss) and completely different spectrum consisting of 25 major observable lines plus hyperfine structure. The spectrum was symmetrical about a central line, which indicated the presence of only one radical and the possibility of splitting by an even number of protons. The low intensity of the esr signal under a variety of conditions, and overmodulation prevented an accurate measurement of line widths. The g-value from one determination with peroxylamine disulfonate as a standard was 2.0033 ± .0001.

Another completely different spectrum was obtained from potassium reduction of the anion of 84 in HMPA. The esr signal was of low intensity, but increased resolution revealed a symmetrical spectrum of more than 50 lines. No g-value was determined.

Reduction of the β-keto sulfone (87) anion with potassium or sodium-potassium alloy gave a radical which was slightly more stable

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that obtained from the β-keto sulfoxides. The highly resolved ESR spectrum which covered about 57 gauss represented a more intense ESR signal. The measured g-value was 2.0030 ± .0001. The spectrum had the same pattern as that of the corresponding keto sulfoxide (8k), but was more compressed. This is reasonable in view of expected increased electron spin density on the sulfonyl group over that of the sulfinyl group. This would reduce the relative electron spin density on the carbon atoms and consequently decrease the magnitude of the hydrogen splitting constants. The spectrum from 86 bore a similar relationship to that from 72.

When the anion of 87 was generated with potassium hydride rather than sodium hydride, followed by reduction with potassium, a simpler spectrum resulted. The pattern again covered a 57 gauss range but consisted of only twenty-nine observable broad lines compared with more than 50 for the spectrum obtained with sodium present. The g-value was found to be 2.0031 ± .0001, experimentally the same as for the radical formed in the presence of sodium ions.

In order to determine the extent of structural degradation, attempts were made to recover starting sulfoxides or sulfones. After treatment of 87 with sodium hydride and one equivalent of potassium in HMPA, it was possible to achieve 50% recovery of the sulfone by simple hydrolysis and neutralization. This indicated that the reduction process was incomplete since hydrolysis should not afford recovery without prior oxidation of the radical. The method of oxidation and chelation by anhydrous nickel chloride used to recover
β-diketones from their enolate radical anion form was totally unsuccessful in retrieving β-keto sulfoxides or sulfones. Only a very large excess of alkali metal in the solution of anions would give rise to the single resonance line observed from a solution of these metals in HMPA alone. The large amount of metal could be consumed without resulting in increased intensity of the spectra. The radicals were difficult to form and much decomposition was suspected even at low temperatures, in contrast to the ease of formation and high stability found in β-diketone systems. Since experimental conditions could not be designed to increase signal intensity, maximum resolution was not obtained. Recovery difficulties, decomposition, and the very small concentration of radicals formed (even from large amounts of reactants) offered little assurance that the spectra obtained were actually of β-keto sulfoxides and sulfones. However, with HMPA as the solvent, a different and symmetrical spectrum was observed for each compound. No evidence of biphenyl formation was found. Thus it appeared that although decomposition was occurring, the decomposition products were not subsequently converted into observable radicals as evidenced in diglyme.

Assuming that the spectra obtained were of β-keto sulfoxides and sulfones, some comparisons can be made with the spectra of

enolate radical anions of β-diketones. The published esr spectrum of 88 generated from reaction of sodium with the anion of dibenzoyl-

\[ \text{O} \quad \text{O} \quad \]

\[ \text{H} \quad \text{H} \quad \]

methane consisted of seven poorly resolved lines. However, electrolytic reduction in dimethylformamide gave a well resolved spectrum (ca. 30 lines) with \( a_H = 2.75 \) for the two equivalent para-hydrogens and \( a_H = 2.20 \) for the four equivalent ortho-hydrogens. The spectra observed from the corresponding β-keto sulfoxide and β-keto sulfone systems were considerably more complex than that of 88. The presence of sulfur results in a nonsymmetrical molecule with a greater number of nonequivalent hydrogens. Hence, the hyperfine structure and even the overall pattern of the spectra are different. Also the spectra of 91 and the corresponding sulfone are much more complex than the broad-line septet observed for 90 in which the methyl, ortho, and para hydrogens are nearly equivalent.

\[ \text{O} \quad \text{O} \quad \]

\[ \text{H}_3 \quad \text{H}_3 \quad \]

\[ \text{O} \quad \text{O} \quad \]

\[ \text{S} \quad \text{H}_3 \quad \]

Spectra of $88$ and $90$ showed no observed splitting from the number 3 proton in agreement with MO calculations.

The spectra of the 3-deuterated and undeuterated β-diketone radicals were identical. Analogously, identical spectra were obtained from $87$ and the corresponding β-keto sulfone containing two methylene deuteriums. As in β-diketone radical dianions, there appears to be little odd electron density on the methylene carbon, and any splittings are apparently unresolved. Also, the absence of odd electron density on the phenyl group of 3-phenylacetylacetone radical dianion, as shown by its esr spectrum, was attributed to inhibition of the system to attain coplanarity. In contrast, the radical dianion of $85$ exhibited increased ease of formation and stability due to phenyl substitution in methylene position. The broad unresolved spectrum resulted from the splitting by many non-equivalent protons. Perhaps the structural influence of sulfur permits greater coplanarity of the central phenyl group.

The breadth of esr lines found for enolate radical dianions from β-diketones were unusually large. A study of solvent effect on their visible spectra indicated very tight ion pairing. Although no metal splitting was observed in the esr spectra, ion agglomeration effects gave rise to hyperfine structure modulation and line broadening. As previously discussed, when sodium was excluded as a counter anion in the radical dianion formation, the former hyperfine structure appeared to merge to give a spectrum of fewer but broader lines (23 vs 6 lines over a 13.0 g region).
The g-value (2.0031 ± 0.0001) for 87 with only potassium as the counter ion was experimentally the same as that obtained with sodium present. Previous examples have been reported in which sodium but no potassium splitting has been observed. Since sodium (and potassium) has a nuclear spin of $\frac{3}{2}$, a four fold splitting should result. The splitting due to sodium in the spectrum of the naphthalene radical anion was reported to be $1.05 ± 0.003$ gauss. The sodium splitting constant in the spectrum of the cyclooctatetraenide radical anion was 0.9 gauss. The spectrum of benzophenone ketyl showed a sodium splitting of 1.0 gauss. Only line broadening and not splitting was observed with potassium as the counter ion, presumably due to the small magnetic moment of K and faster electron exchange.

The apparent sodium splitting in the spectrum of 87 is 1.1 gauss. However, the spectrum was obtained from a solution containing both sodium and potassium and thus may be a composite. Also, the pattern observed may be due to metal splitting by two ions since the radical under observation is also a dianion.

Due to the complexity and weakness of the spectra obtained, splitting constants could not be determined and assigned.


Experimental

Part One

Instrumental Techniques

Melting points were taken on a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord as neat liquids, solutions, or powdered solids in potassium bromide disks. Near-infrared spectra were obtained on a Cary Model 14 Recording Spectrometer from 1M solutions in A.R. carbon tetrachloride. Ultraviolet spectra were recorded on the same instrument. Nuclear magnetic resonance spectra were obtained on Varian Associates A-60, A-60-A, and HA-100 spectrometers and reported τ (τ) units relative to tetramethylsilane (τ = 10.00). Electron spin resonance spectra were obtained from a dual cavity Varian Model V-4502 spectrometer using peroxylamine disulfonate as a standard. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, or by M-H-W Laboratories, Garden City, Michigan. Aerograph Hi-Fi's, Models 600-A and 600-D, and Aerograph Autoprep, Model 700 were used for analytical and preparative gas chromatography. The columns employed will be referred to in the text.
**SOLVENTS**

Commercial grade solvents (except for A.R. benzene) were distilled before use in chromatography. Anhydrous ether was purchased from J. T. Baker Co. Pentane was purified by stirring over three successive portions of concentrated sulfuric acid followed by filtration through sodium carbonate and distillation.

**REAGENTS**

Dimethyl acetylenedicarboxylate (Aldrich Co.) was used both with and without prior distillation. Anthranilic acid (J. T. Baker Co.) and isoamyl nitrite (Matheson Co.) were not further purified.

**7,7-DIBROMONORCARANE (21)**

This compound was prepared from cyclohexene by the procedure of Doering

\[ \text{b.p.} \ 82^\circ (1.5 \text{ mm}) \]

**TRICYCLO[4.1.0.0^2,7]HEPTANE (19)**

Preparation of this hydrocarbon by the treatment of 21 with methyl lithium in ether followed the procedure of Moore and Ward

\[ \text{b.p.} \ 82^\circ (1.5 \text{ mm}) \]

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200 ml. of anhydrous ether was placed under a dry nitrogen atmosphere and cooled to 0° in a salt-ice-water bath. Methyl lithium (330 ml. of a 5.18% ether solution, Foote Chemical Co.) was added via syringe at approximately 200 ml. per hr. to maintain the temperature between 0° and 5°, with vigorous mechanical stirring. Stirring was continued for 0.5 hr. after addition was complete. An additional 114 g. of 21 was similarly treated. The resulting reaction solutions were poured into 1 l of an ice-water mixture. The layers were separated and the water portion was extracted with ether. The combined ether solutions were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The ether was removed by distillation through a packed column and the residue was distilled at 80-130°, at atmospheric pressure. Careful redistillation of this crude distillate on a spinning band column at atmospheric pressure afforded 17.0 g. (20%) of 19, b.p. 111-112°. Vpc analysis on a 15% TEG column at 50° indicated a 3-4% impurity which was presumably the tricyclo[4.1.0.03,7]heptane isomer. The parent peak in the mass spectrum appeared at m/e 94. Infrared and nmr data were consistent with that previously reported.

REACTION OF DIMETHYL ACETYLENEDICARBOXYLATE (3) WITH (19)

A mixture of 2.0 g. (22 mmole) of 19 and a 4.0 g. (28 mmole) of 3 was sealed under nitrogen in a glass ampoule and heated in a bomb at 96° for nine hours. Distillation of the crude viscous reaction mixture gave 0.42 g. of recovered 19 and 1.28 g. of 3. The residue
(4.21 g.) was resistant to distillation. Thin layer chromatography on silica gel (with 10% ether/chloroform and 3:1 benzene/ethyl acetate) indicated four components plus a considerable amount of polymeric material. Column chromatography on silica gel with a benzene-ether solvent system gave two major fractions, which still contained some polymeric material. Attempts to crystallize the oils obtained were unsuccessful. The infrared spectrum of the main component showed strong carbon-hydrogen absorptions at 3.2, 3.3, and 3.4 μ and a strong ester carbonyl absorption at 5.75 μ. The ultraviolet spectrum had λmax 258 μ with a strong shoulder at 277 μ. The nmr spectrum (CDCl3) had a multiplet at 4.0-4.8, a singlet at 6.3 (methoxy group), and a multiplet at 7.8-8.7. Nmr data on the second component was similar. A chemical analysis and mass spectrum were not obtained due to product decomposition and purification difficulties. Variations of reaction conditions and the use of cyclohexane as a reaction solvent produced the same results.

**ACETYLENEDICARBOXAMIDE**

This diamide was prepared from 1 by a procedure similar to that of Blomquist. To a rapidly stirred solution of 40 ml. of methanol, 120 ml. concentrated ammonium hydroxide, and 120 ml. saturated methanolic ammonia was added 30 g. of 1 at -35° over a

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45-minute period. After completion of the addition, the mixture was stirred for one hour at 0°. The product was filtered, washed with water, methanol, and ether and dried to yield 76% of diamide, m.p. 217-220°. Further purification was not effected since loss of material during recrystallization was larger than the gain in yield of dicyanoacetylene in the next step.

**DICYANOACETYLENE (6).**

In a procedure similar to that of Blomquist, dehydration of 11.0 g. of acetylenedicarboxamide with 60 g. of phosphorous pentoxide in 80 g. of fine sand at 180-210° (2 mm) for 0.5 hr. yielded 0.8-1.4 g. (11-19%) of 6. Substitution of dry nitrogen for carbon dioxide in this procedure gave only slightly reduced yields. The use of carbon dioxide even with a silica gel drying tube contaminated 6 with water. An alternative procedure reported to give high yields of 6 was not investigated.

**REACTION OF DICYANOACETYLENE WITH 19**

Dicyanoacetylene (6) reacted vigorously with 19 at room temperature, and rapidly at 0°. A solution of 1.0 g. (10.6 mmole) of 19 in 3.0 ml. of anhydrous ether was cooled in a dry ice-isopropanol bath. To this was added 0.80 g. (10.5 mmole) of 6 and the solution was allowed to stand for two hours just above its freezing point (ca. -15°). Extraction of the crude reaction product with ether followed

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by removal of the solvent left 1.2 g. of yellow oil, 800 mg. of which was soluble in Skelly B. The insoluble portion was shown by thin layer chromatography on silica gel with hexane-benzene to contain dicyanoacetylene and a multitude of minor products. Chromatography of the soluble portion (800 mg.) on silica gel with 3:1 hexane-benzene gave 607 mg. (3% of a 1:1 adduct) of a nonvolatile colorless oil. The oil could not be crystallized and slowly decomposed to an ether insoluble gel even when stored under nitrogen in a refrigerator. Apparent decomposition prevented vpc analysis. However, silica gel tlc with three solvent systems indicated a pure substance. The infrared spectrum showed a strong carbon-hydrogen stretching absorption, a single strong nitrile absorption at 4.43 µ, weak bands at 6.02, 6.19, and 6.30 µ, and a strong band at 13.88 µ. The near-infrared spectrum indicated no cyclopropyl hydrogens. The ultraviolet spectrum (methanol) had λ_max 256 m_ν (ε 8,530 if a 1:1 adduct) and a shoulder at 239 m_ν. The nmr spectrum (CCl_4) showed a quartet of sharp peaks of equal height from τ 3.13 to 3.62 (1H) with a separation of 11, 8 and 11 cps and a quartet of broad peaks in a 1:2:2:1 ratio in the region τ 3.89 to 4.5 (2H) separated by 10, 16, and 10 cps. The coupling constants of this pattern were not assigned due to lack of further information. Broad multiplets appeared at τ 5.8-6.8 (1H) and τ 7.6-8.6 (6H). An analysis found for C, 84.28; H, 10.21; and N, 5.36 did not correspond to a reasonable formula. The mass spectrum indicated a parent peak at m/e = 183. The adduct was recovered unchanged after stirring in a
benzene solution of the aromatizing agent DDQ.

**ADDITION OF BENZYNE (16) TO 19**

The benzyne precursor, benzenediazonium-2-carboxylate, was prepared from anthranilic acid, isoamyl nitrite and a catalytic amount of trichloroacetic in dry THF at room temperature. The salt was isolated by decanting off the solvent and washing with THF followed by methylene chloride. A slurry of the diazonium salt (from 9 g. of anthranilic acid) in 30 ml. of methylene chloride was refluxed (40°) with 2.00 g. (2.12 mmole) of 19 for four hours. Gas evolution ceased and the mixture became dark brown. The methylene chloride was removed by distillation through a packed column. The residue was extracted with ether and washed with a saturated sodium carbonate solution to remove benzoic acid. Removal of the ether followed by distillation of the residue gave a fraction (0.165 g.) boiling at 110-115° (1 atm) which was shown by vpc and infrared data to consist of chlorobenzene. Continued distillation gave 2.7 g. of a second fraction, b.p. 87-91° (1.1 mm) which vpc analysis on a 5% SE-30 column showed to contain approximately 4% impurity of comparable molecular weight plus some higher molecular weight impurities. Chromatography on silica gel with pure Skelly B gave 2.2 g. (61%) of product, b.p. 77-78° (0.55 mm) containing approximately 3% impurity. Preparative vpc with a 20% SE-30 on 60/80

Chrom W column (10') afforded an analytical sample of endo-2-phenyltricyclo[4.1.0.0^3,7]heptane (30).

**Anal. Calcd. for C_{13}H_{14}; C, 31.71; H, 8.29.**

**Found: C, 91.83; H, 8.27.**

When the reaction was completed on the same scale with THF rather than methylene chloride as the solvent, no chlorobenzene was formed and 1.4 g. (39%) of 30 was obtained after chromatography. The infrared spectrum showed bands at 13.80 and 14.40 μ and a pattern of absorptions in the 5.00-5.70 μ region characteristic of a monosubstituted aromatic compound. The ultraviolet spectrum showed a nonconjugated benzene ring. The nmr spectrum (neat) showed a singlet at τ 2.94 (5H), a quartet at τ 6.38 (1H), a complex doublet at τ 7.24 (1H), a multiplet at τ 7.75 (1H), and a broad multiplet at τ 8.1-9.0 (6H). The near-infrared spectrum showed maxima at 1.657 (0.810) and 1.673 μ. The parent peak in the mass spectrum appeared at m/e 170. An intense peak at m/e 91 was also present. The reaction product reacted rapidly with bromine in carbon tetra-chloride and slowly decolorized aqueous potassium permanganate but was unreactive to ozone in methanol at room temperature and osmium tetroxide in ether.

**HYDROGENATION OF ENDOR-2-PHENYLTRICYCLO[4.1.0.0^3,7]HEPTANE (30)**

A solution of 170 mg. (1 mmole) of 30 in 10 ml. of ethanol over 50 mg. of prereduced 5% palladium on carbon rapidly absorbed 1.0 equivalent of hydrogen. Filtration of the catalyst followed
by solvent removal yielded 170 mg. (99%) of \(^3\). Vapor phase chromatography on a 5% SE-30 column revealed only one product. The near-infrared spectrum showed no cyclopropyl hydrogens. The nmr spectrum had a singlet at \(\tau 2.86\) (5H), a broad five peak multiplet at \(\tau 6.60-7.00\) (1H), and multiplets at \(\tau 7.5-7.8\) (2H), \(\tau 7.95-8.30\) (2H), \(\tau 8.40-8.80\) (6H). The nmr and infrared spectra were identical to an authentic sample of \(^3\) furnished by Professor H. C. Brown. (The sample supplied by Professor Brown contained 13% 2-phenylnor-tricycle and was purified by preparative chromatography on a 10' 20% XF-1150 on Chrom W column at 135\(^0\).)

\(1,7\)-DIDEUTERIOTRICYCLO[4.1.0.0\(^2,7\)]HEPTANE (45)

The preparation of this compound was similar to that of the monodeuterated substance prepared by Closs.\(^{144}\) Tricyclo[4.1.0.0\(^2,7\)]-heptane, 3.0 g. (32 mmole), was added to 38 ml. of a solution of n-butyllithium\(^{145}\) freshly prepared from 4.3 g. (0.62 mole) of lithium and 34.25 g. (0.25 mole) of n-butylbromide in 150 ml. of anhydrous ether. This solution was allowed to stand for six hours and then quenched with 1.28 g. of deuterium oxide. The lithium deuteroxide was removed by filtration and most of the ether was removed through a packed column. The procedure was repeated three additional times with the remaining hydrocarbon. Subsequent distillation gave


0.80 g. of product which mass spectral data indicated was greater than 90% deuterated.

**REACTION OF 1,7-DIDEUTERIOTRICYCLO[4.1.0.0²,7]HEPTANE WITH BENZENE**

The procedure was the same as for the undeuterated compound. From 800 mg. of 32, 387 mg. (27%) of deuterated adduct was obtained after chromatography on silica gel. The nmr spectrum (CCl₄) showed a singlet at τ 6.84 (5H), a broad singlet at τ 7.20 (1H), and a multiplet at τ 8.15-9.0 (6H). The peaks at τ 6.38 and τ 7.75 in the spectrum of the undeuterated adduct had disappeared. The mass spectrum showed a parent peak at m/e 172 and the major fragmentation peak at m/e 92 (C₇H₆D⁺), compared with an intense peak at m/e 91 for the undeuterated adduct.

**7-t-BUTOXYNORBORNADIENE (34)**

This compound was prepared on the same scale and with the same yields according to a previously reported procedure.  

**7-ACETOXYNORBORNADIENE (35) AND ANTI-7-NORBORNENOL (36)**

These compounds were prepared on three times the literature scale and with similar yields by a previously reported procedure. The alcohol was sublimed at 90° (15 mm).

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TRICYCLO[4.1.0.0^3,7]HEPTANE (20)

The tosylate (37) was prepared by allowing a solution of 35.6 g. (2.324 mmole) of 36 and 70.0 g. (0.367 mole) of tosyl chloride in 200 ml. of pyridine to stand twelve hours in a refrigerator. The mixture was poured into 1.0 l of ice water containing 200 ml. of concentrated hydrochloric acid and extracted with chloroform. The extracts were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the solvent gave a yellow oil (80%) which crystallized upon cooling and trituration with Skelly B. Due to its tendency to decompose, 37 was not re-crystallized. A solution of 37 in 50 ml. of THF was added over 15 minutes to 20.0 g. (0.52 mole) of lithium aluminum hydride in 600 ml. of THF while maintaining room temperature. After the mixture was stirred for an additional two hours, 40 ml. of water was added dropwise and stirring continued for 0.5 hr. Filtration was followed by removal of the THF through a packed column. The residue was distilled through a 6' Vigreux column at atmospheric pressure with collection of the distillate at 90-110°. Redistillation at 94-103° gave 8.0 g. (26% from 36) of a mixture of 20 and norbornene in the approximate ratio of 3:2 by vpc analysis (1% TEG) as previously reported. 148 Elution of this mixture with purified pentane from 100 g. of a 10% saturated silver nitrate alumina column gave 3.07 g. of pure 20. The nmr spectrum (neat)

showed a broad multiplet at δ 7.40-9.35. When sodium borohydride was used in place of lithium aluminum hydride only a small yield of 20 plus norbornene in the same ratio was obtained, in contrast to previously reported results.

ATTEMPTED REACTION OF 20 WITH BENZYNE

No addition products from 20 and benzyne were observed when the previously described reaction procedure was followed. The starting hydrocarbon was recovered unchanged. The use of 5 equivalent of benzyne precursor with 1.0 g. of 20 produced after silica gel chromatography an amount of material sufficient only for an infrared and mass spectrum. The infrared spectrum showed both aromatic and aliphatic hydrogens. However, the mass spectrum had a parent peak at m/e 146 in contrast to 170 necessary for a 1:1 adduct. No further investigation was undertaken.

ADDITION OF DICYANOACETYLENE (6) to 20

A mixture of 400 mg. (5.26 mmole) of 6 and 500 mg. (5.31 mmole) of 20 was sealed under nitrogen in a glass ampoule and heated for 14 hours at 70°. Extraction of the crude reaction mixture with 20 ml. of ether followed by removal of the solvent gave 410 mg. (46% of 38) as a light brown oil which slowly crystallized upon cooling and trituration with Skelly B. Under reaction conditions of 80°

for ten hours and 60° for twenty hours, the yield was approximately 2%. Thin layer chromatography on silica gel with benzene and ether-Skelly B showed only one component plus some polymeric material. The product was dissolved in four successive 25 ml. portions of Skelly B at room temperature. Slow cooling of the combined solutions in a dry ice bath gave as small white needles, m.p. 58-59°.

**Anal.** Calcd. for C_{11}H_{10}N_2: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.59; H, 5.77; N, 16.27.

Homogeneity of the crystalline material was shown by vpc analysis on a FS-1265 column at 200°. However, the residue in the mother liquor after two additional crops of crystals were removed indicated that the crude reaction product was contaminated with approximately 5% impurity. The infrared spectrum had a nitrile absorption at 4.43 μ and a weak double bond absorption at 6.23 μ. The near infrared spectrum showed maxima at 1.658μ (ε 0.909) and 1.676 μ. The ultraviolet spectrum (methanol) had λ_{max} 222 μ (ε 8,250). The nmr showed a single olefinic proton at τ 3.75 (doublet) which was coupled with a single allylic proton at τ 6.25 (J_{AB} 2.5 cps) as determined via spin decoupling. The remainder of the spectrum consisted of multiplets at τ 7.00 (1H), τ 7.40 (1H), and τ 8.00-8.60 (6H). The parent peak in the mass spectrum appeared at m/e 170.
CONVERSION OF ENDO-TRICYCLO[4.1.0.0^{3,7}]HEPTYL-5-MALEONITRILE (38)
TO ENDO-5-CARBOMETHOXYTRICYCLO[4.1.0.0^{3,7}]HEPTANE (43)

After standing at room temperature for twelve hours, a solution of 200 mg. (1.07 mmole) of 38 and 300 mg. (1.08 mmole) of osmium tetroxide in 15 ml. of ether and 4 ml. of pyridine produced a light brown crystalline precipitate. The precipitate was washed with three 5-ml. portions of ether and slurried with 6 ml. of THF. A slow stream of hydrogen sulfide was passed through the slurry for 0.5 hr. and the mixture was allowed to stand for an additional 0.5 hr. The precipitated osmium dioxide was removed by filtration. The residue remaining after solvent removal was dissolved in 4 ml. of 5% sodium hydroxide solution, followed by addition of 0.5 ml. of 30% hydrogen peroxide with cooling. After standing at room temperature for two hours, the solution was washed with ether. The aqueous solution was made slightly acidic (pH 6) with 10% hydrochloric acid and extracted with ether. Removal of the ether after drying over anhydrous magnesium sulfate gave 48 mg. of a clear oil. The infrared spectrum showed the presence of a carboxylic acid function. Analysis on a 37% FFAP on 46/60 Chrom W vpc column at 190° indicated two products. The minor component was assumed to be the exo-acid and represented 10-30% of the mixture depending


on reaction conditions. The acids were not separated but were con­verted quantitatively to their methyl esters with diazomethane. Separation of the esters on a 25% XF-1150 preparative column gave 14 mg. of the major component and 3 mg. of the minor one. The mass spectrum of the major ester, shown to be endo-5-carbomethoxytricyclo­-[4.1.0.03,7]heptane (43) showed a parent peak at m/e 152.


Found: C, 70.78; H, 7.97.

The infrared spectrum (neat) of this ester was not superim­posable on that of an authentic sample of 3-carbomethoxynortricyclane­carboxylic acid. An nmr spectrum was obtained on a small amount of ester formed from a repetition of the degradation sequence. Al­though this sample contained approximately 10% impurity, the spec­trum was similar to that of the original adduct and not to that of a nortricyclane structure.

An accurate mass measurement (found: m/e 152.083557; calcd: m/e
152.0834) of the minor ester component showed it to be isomeric with 43.

HYDROGENATION OF ENDO-5-CARBOMETHOXYTRICYCLO[4.1.0.03,7]HEPTANE (43) TO ENDO-2-CARBOMETHOXYNORBORNANE (44)

Into a 5-ml. side arm flask fitted with rubber septums was placed 20 mg. of 43, 4 mg. of 5% Pd/C, and 3 ml. of ether. The

152. K. Alder, R. Hartmann, and W. Roth, Ber., 93, 2271 (1960).
flask was flushed with hydrogen and a positive hydrogen pressure was introduced via a syringe. Vpc analysis on a 2% XF-1150 column indicated hydrogenation was 80% complete after overnight stirring. The catalyst was removed by centrifugation and 10 mg. of fresh catalyst was added. Completion of hydrogenation in 20 minutes gave 12 mg. of product which was purified by means of a 3% PDEAS (1/2" x 8') vpc column at 86°. The nmr and infrared spectra were identical with those of an authentic sample of 44. The nmr spectrum was obtained on an A-60-A spectrometer coupled with a transient averaging computer (27 scans, 250 sec each). 154

AUTHENTIC ENDO-2-CARBOETHOXYNORBORNANE

A known sample of 1.0 g. (7.25 mmole) of endo-5-norbornene-2-carboxylic acid was quantitatively hydrogenated over 80 mg. of 5% Pd/C in 20 ml. of ethanol in less than one hour. The saturated acid was converted to its methyl ester, with diazomethane in ether. The nmr spectrum had a singlet at $\tau 6.63$ (3H), a broad multiplet at $\tau 7.30-8.47$ (3H) and a multiplet at $\tau 8.47-9.47$ (8H).

ATTEMPTED REACTION OF BICYCLO[2.1.0]PENTANE (2) WITH BENZYNE

No benzyne adduct could be detected after 2.0 g. of bicyclo-[2.1.0]pentane was refluxed with 5 equiv. of benzenediazonium


154. Appreciation is expressed to D. S. Patton and R. Cryberg for recording this and other nmr spectra.
carboxylate in methylene chloride or in THF until gas evolution had ceased. Only unreacted hydrocarbon was recovered. Also, no reaction was observed when 1.0 g. of 2 was stirred seven hours with 7.5 g. of o-bromofluorobenzene and 1.0 g. of lithium \(^{155}\) in 5 ml. of ether.

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Part Two

A. Alkylation and Reduction of β-Keto Sulfoxides

SOLVENTS

Dimethylformamide was distilled from calcium hydride before use. Dimethylsulfoxide was distilled from calcium hydride and stored over Linde type 5A molecular sieves.

ω-(METHYSULFINYL)ACETOPHENONE AND METHYL SULFINYL-METHYL-n-PENTYL KETONE

These were prepared by the published procedure. 156

METHYLATION OF ω-(METHYSULFINYL)ACETOPHENONE IN DMF

Sodium hydride (0.264 g., 0.011 mole) was washed free of mineral oil with dry pentane under a nitrogen atmosphere. Dimethylformamide (30 ml.) was added to the dry sodium hydride powder. To this stirred slurry was added a solution of 2.0 g. (0.011 mole) of ω-(methylsulfinyl)acetophenone in 10 ml. of DMF. Vigorous hydrogen evolution ensued and the reaction was controlled by cooling. When the conversion of the β-keto sulfoxide to the anion was complete, 1.56 g. (0.011 mole) of methyl iodide was added dropwise with cooling.

The reaction mixture was stirred for 0.5 hr. at room temperature, diluted with 100 ml. of water and the aqueous solution was extracted with chloroform. The chloroform extracts were washed with water and dried over anhydrous magnesium sulfate. After removal of the drying agent, the chloroform was stripped off on a rotary evaporator and the residual yellow oil was triturated with a small amount of cold ether to yield a solid product. Recrystallization of this material from ethyl acetate yielded 0.65 g. (30%) of pure IIIa as colorless needles, m.p. 77-78°.

**Anal.** Calcd. for C₁₀H₁₂O₂S:  C, 61.20;  H, 6.16;  S, 16.34.  
**Found:**  C, 61.49;  H, 6.31;  S, 16.51.

**METHYLATION OF ω-(METHYLSULFINYL)ACETOPHENOINE IN DMSO**

Dry sodium hydride (0.66 g., 0.0275 mole) was prepared as described above and slurried with 40 ml. of dry DMSO. While maintaining the reaction temperature at 20°, 5.0 g. (0.0275 mole) of ω-(methylsulfinyl)acetophenone in 10 ml. of DMSO was added. When hydrogen evolution ceased, 3.9 g. (0.0275 mole) of methyl iodide was added and the reaction was stirred for 0.5 hr. The reaction mixture was diluted with 150 ml. of water, extracted with chloroform and the chloroform extracts were dried over anhydrous magnesium sulfate. The drying agent was filtered off and the chloroform was removed under vacuum. The residue was seeded and triturated with cold ether-pentane. Recrystallization from ethyl acetate yielded 3.77 g. (70%) of ω-(methylsulfinyl)propiophenone (IIIA), m.p. 77-78°.
PROPIOPHENONE

\( \text{\textcopyright-(Methylsulfinyl)propiophenone} \) (0.34 g., 7.73 mmole) dissolved in 25 ml. of 10% aqueous tetrahydrofuran (THF) was reacted with 0.47 g. of freshly prepared amalgamated aluminum for 10 minutes. The reaction mixture was filtered and the inorganic products were washed with THF. The THF was removed on a rotary evaporator. The residue was diluted with ca. 5 ml. of water and extracted with ether. The ethereal extracts were dried over anhydrous magnesium sulfate. Removal of the drying agent and solvent gave 0.225 g. (95%) of propiophenone.

GENERAL PROCEDURE FOR COMBINED ALKYLATION AND CLEAVAGE STEPS

The alkylations were carried out as described above for the methylation of \( \text{\textcopyright-(methylsulfinyl)acetophenone} \) except no attempt was made to crystallize or purify the crude alkylation product obtained upon removal of the solvent. This crude alkylation product was dissolved in 10% aqueous THF and reduced as described above for the preparation of propiophenone with the exception that the resulting ketones were extracted with pentane rather than with ether. The pentane solution was washed with water, dried over anhydrous magnesium sulfate and the pentane removed on a rotary evaporator. The crude ketones were distilled and the purity of the distillation product was checked by vapor phase chromatography.
DIALKYLIATION - THE PREPARATION OF ISOBYROPHENONE - A. TWO-STEP PROCEDURE

ω-(Methylsulfinyl)acetophenone (5.0 g., 0.0275 mole) was methylated in DMF as described above using sodium hydride (0.66 g., 0.0275 mole) and methyl iodide (3.9 g., 0.0275 mole). After ca. 0.5 hour reaction time, the reaction mixture was transferred via syringe to a second reaction flask containing 0.66 g. (0.0275 mole) of sodium hydride. When evolution of hydrogen ceased, the second equivalent of alkylating agent was added (in this case 3.9 g. of methyl iodide) and the reaction mixture was stirred for ca. 45 minutes. Reduction with aluminum amalgam and distillation of the product yielded 2.21 g. (54%) of isobutyrophenone, b.p. 68-72° (1 mm). A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol-ethyl acetate, m.p. 160-161° (lit. m.p. 161-162°).157

DIALKYLIATION - THE PREPARATION OF ISOBYROPHENONE. B. ONE-STEP PROCEDURE

ω-(Methylsulfinyl)acetophenone (5.0 g., 0.0275 mole) was added to a slurry of sodium hydride (0.32 g., 0.055 mole) in 50 ml. of DMF and 3.9 g. (0.0275 mole) of methyl iodide was added. After 0.5 hr. an additional 3.9 g. of methyl iodide in 50 ml. of DMF was added and the reaction mixture was stirred for 40 minutes. Reduction and isolation were completed as described above to yield 2.05 g. (50%) of isobutyrophenone.

**PROPIOPHENONE**

Propiophenone was prepared as outlined in the general procedure from 5.0 g. (0.0275 mole) of \(\omega\)-(methylsulfinyl)acetophenone. Distillation of the product yielded 2.37 g. (64%) of propiophenone, b.p. 62-66° (1.5 mm), 2,4-dinitrophenylhydrazone, m.p. 191-192° (lit. m.p. 191°).  

**BUTYROPHENONE**

Butyrophenone was prepared on the usual scale (0.0275 mole) as described in the general procedure using ethyl iodide as the alkylating agent and allowing the alkylation one hour reaction time. Distillation of the product gave 2.83 g. (70%) of butyrophenone, b.p. 75-80° (1.5 mm), 2,4-dinitrophenylhydrazone, m.p. 190-191° (lit. m.p. 191-192°).

**VALEROPHENONE**

Valerophenone was prepared in the described manner from \(\omega\)-(methylsulfinyl)acetophenone except with n-propyl bromide as the alkylating agent and at reaction time of 22 hours at 55°. Distillation of the crude product gave 1.97 g. (44%) of valerophenone, b.p. 82-86° (0.5 mm), 2,4-dinitrophenylhydrazone, m.p. 164-165° (lit. m.p. 165-166°).  


OCTANONE

3-Octanone was prepared by the general procedure described above except the reduction with aluminum amalgam required one hour in refluxing THF. Distillation of the crude product gave 62% of 3-octanone, b.p. 55-58° (1.5 mm), 2,4-dinitrophenylhydrazone, m.p. 65-66° (lit. 161 m.p. 64-65°).

2-METHYL-3-OCTANONE

The procedure described for two-step dialkylation was followed in the preparation of this ketone. This procedure was modified to have a reduction time of one hour in refluxing THF. Distillation of the product gave 59% of ketone, b.p. 70-74° (1.5 mm), 2,4-dinitrophenylhydrazone, m.p. 91-92° (lit. 162 m.p. 92.5°).

4-NONANONE

The general procedure was followed, allowing an alkylation time of one hour and a reduction time of one hour in refluxing THF. Distillation gave 75% of product, b.p. 85-88° (2.0 mm).

4-NONANONE

The same alkylation procedure was followed using DMSO as the solvent. The reaction mixture was poured into three times its volume of water and extracted with chloroform. The chloroform extracts were washed three times with water and the chloroform extracts were washed three times with water and the chloroform


evaporated. No attempt was made to isolate the intermediate keto sulfoxide. Reduction was completed as above. Methylsulfinylmethyl n-pentyl ketone (5 g., 0.0284 mole), sodium hydride (0.68 g., 0.0294 mole), and ethyl iodide (4.43 g., 0.0284 mole) yielded upon distillation 2.81 g. (70%) of 4-nonanone.

B. Acidity of β-Keto Sulfoxides

The procedure for determining pKa values was similar to that of Albert and Serjeant. Optical densities of β-keto sulfoxide solutions at various pH values were measured in triply distilled water at a wavelength corresponding to minimum overlap of the unionized and anionic keto sulfoxide. Carbonate free standardized sodium hydroxide solutions were used to obtain the desired pH. Preliminary experiments determined the λmax and extinction coefficients of the ionized and unionized β-keto sulfoxides. The measurement of optical density in a strongly basic solution gave an estimation of the pKa value. The range of pH values chosen extended from one unit greater to one unit less than the estimated pKa. This pH range brought about the greatest change in optical densities.

The β-keto sulfoxides tended to decompose slowly in the basic medium as shown by a decrease in optical density upon standing. Consequently, solutions of the keto sulfoxide of known concentration were mixed in equal volumes with solutions of standardized sodium hydroxide.

hydroxide (from accurate dilution from more concentrated solutions) one minute prior to spectroscopic measurement. Thus, the solutions measured had concentrations of keto sulfoxide and sodium hydroxide equal to one-half the original concentration. The required amount of sodium chloride was added to maintain a constant ionic strength. (I = \tfrac{1}{2}C_1Z^2 where C_1 = molar concentration of ion, Z = its valency).

The pH of each solution was calculated from the hydroxide ion concentration using the Kw value (ionization constant of water) at the appropriate temperature. All absorption measurements were completed on a Cary Model 14 recording spectrophotometer in the ultraviolet region.

Equation I as derived in Section B of the Discussion was used to calculate the pKa values. The data and results obtained for

\[ d = d_A^- - \frac{[H^+](d-d_{HA})}{K_a^c} \]

where \(d\) = total optical density measured
\(d_A^-\) = optical density of the anion
\(d_{HA}\) = optical density of unionized acid
\(K_a^c\) = concentration equilibrium constant

\(\omega\)-(methylsulfinyl)acetophenone and methylsulfinylmethyl-n-pentyl ketone are contained in Tables 4 and 5. This method did not seem applicable for the pKa determination of \(\omega\)-(methylsulfinyl)propiophenone.

Table 4

pKa Measurements of β-Keto Sulfoxides

<table>
<thead>
<tr>
<th>Compound: C₆H₅COCH₃SOCH₃</th>
<th>λ_max = 252 μ (ε 13,200)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wavelength of Measurements:</strong></td>
<td>287.5 μ</td>
</tr>
<tr>
<td><strong>Cell length:</strong></td>
<td>1.00 cm.</td>
</tr>
<tr>
<td>d_HA = 0.095 (at 6.080 x 10⁻⁵ M)</td>
<td>d_A = 0.574</td>
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<tr>
<td>Temperature = 27.5°C</td>
<td>I = 0.50</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>[H⁺]</th>
<th><a href="d-d_HA">H⁺</a></th>
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<tbody>
<tr>
<td>3.025 x 10⁻¹¹</td>
<td>3.327 x 10⁻¹²</td>
</tr>
<tr>
<td>1.210 x 10⁻¹¹</td>
<td>2.698 x 10⁻¹²</td>
</tr>
<tr>
<td>6.05 x 10⁻¹²</td>
<td>1.815 x 10⁻¹²</td>
</tr>
<tr>
<td>2.42 x 10⁻¹²</td>
<td>0.932 x 10⁻¹²</td>
</tr>
<tr>
<td>1.21 x 10⁻¹²</td>
<td>0.502 x 10⁻¹²</td>
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</table>

pKa = 11.02 ± .06 by least squares calculations on above data.
Table 5

*pKa* Measurements of β-Keto Sulfoxides

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<thead>
<tr>
<th>Compound:</th>
<th>CH₃(CH₂)₄COCH₂SOCH₃</th>
<th>λₘₐₓ = 280 µ (ε 82.08)</th>
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<tr>
<td>Wavelength of Measurements:</td>
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<tr>
<td>Cell length:</td>
<td>100 cm.</td>
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</tr>
<tr>
<td>d₁H₂A</td>
<td>0.00 (at pH 6.90, at 4.839 x 10⁻⁵ M)</td>
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</tr>
<tr>
<td>d₁A</td>
<td>0.688</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>26.5°C</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Kₘ</td>
<td>1.14 x 10⁻¹⁴</td>
<td></td>
</tr>
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<tr>
<th>d</th>
<th>[-CH₂]</th>
<th>[H⁺]</th>
<th><a href="d-d%E2%82%81H%E2%82%82A">H⁺</a></th>
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<tbody>
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<td>0.045</td>
<td>4.00 x 10⁻⁴ M</td>
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<td>1.283 x 10⁻¹²</td>
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<tr>
<td>0.128</td>
<td>1.00 x 10⁻³</td>
<td>11.4</td>
<td>1.459</td>
</tr>
<tr>
<td>0.230</td>
<td>2.00 x 10⁻³</td>
<td>5.70</td>
<td>1.311</td>
</tr>
<tr>
<td>0.380</td>
<td>5.00 x 10⁻³</td>
<td>2.28</td>
<td>0.866</td>
</tr>
<tr>
<td>0.485</td>
<td>1.00 x 10⁻²</td>
<td>1.14</td>
<td>0.553</td>
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<tr>
<td>0.640</td>
<td>1.00 x 10⁻¹</td>
<td>0.114</td>
<td>0.073</td>
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pKa = 11.60 ± 0.07 by least squares calculations on above data.
C. Radical Dianion Formation

ω-(METHYL SULFINYL)ACETOPHENONE (79)

ω-(Methylsulfinyl)acetophenone was prepared by the published procedure.

ω-(PHENYL SULFINYL)ACETOPHENONE (84)

ω-(Phenylmercapto)acetophenone was prepared by the published procedure. Oxidation of this β-keto sulfide to the β-keto sulfoxide (84) was effected with sodium metaperiodate. A mixture of 14.8 g. (0.069 mole) of sodium metaperiodate and 15.0 g. (0.066 mole) of ω-(phenylmercapto)acetophenone in 125 ml. of water and 125 ml. of THF was stirred overnight with initial cooling, in an ice bath. Most of the THF was removed on a rotary evaporation, and the aqueous residue was extracted with chloroform. After drying over anhydrous magnesium sulfate the chloroform was removed to give 15.2 g. (94.5%) of solid product. Colored impurities were removed by washing with a small amount of cold ether. Recrystallization from ethanol gave white crystals, m.p. 78-79° (lit. m.p. 76-77°).


U-\text{(METHYL SULFINYL)ACETOPHENONE (85)}

Benzylphenyl sulfoxide was prepared by the published method. A mixture of 5.0 g. (0.023 mole) of benzylphenyl sulfoxide and 1.1 g. (0.046 mole) of sodium hydride (washed free of mineral oil with pentane) in 200 ml of THF was refluxed for one hour. After cooling to room temperature, 3.47 g. (0.023 mole) of ethyl benzoate was added and the solution was stirred overnight followed by reflux for an additional hour. Water (30 ml.) was added and the solution was neutralized with dilute hydrochloric acid. The THF was removed on a rotary evaporator and the aqueous portion was extracted with chloroform. Drying over anhydrous magnesium sulfate followed by removal of the solvent gave 5.6 g. (76%) of a crude solid. White crystals were obtained from absolute ethanol, m.p. 139-140°. The nmr spectrum showed a multiplet at $\tau$ 2.2-2.8 (15H) and a singlet at $\tau$ 3.4 (1H). The chemical analysis for C$_{20}$H$_{18}$O$_2$S was correct for hydrogen and sulfur, but was off 0.59% for carbon. An analytical sample was not resubmitted since no further investigation of this material was contemplated.

w-\text{(METHYL SULFONYL)ACETOPHENONE (86)}

A solution of 3.0 g. (0.016 mole) of 72 and 2.4 g. of 30% by weight hydrogen peroxide in 20 ml. of acetic acid was stirred for one hour just above its freezing point (ca. 15°). After stirring

for an additional twelve hours at room temperature, most of the solvent was removed in vacuo. Recrystallization of the residue from ethanol gave 2.2 g. (69%) of 86, m.p. 106-107° (lit. m.p. 107.5-108°). 169

\( \omega-(\text{Phenylsulfonyl})\text{acetophenone} (87) \)

\( \omega-(\text{Phenylsulfonyl})\text{acetophenone} (87) \) was obtained by hydrogen peroxide oxidation of the corresponding \( \beta \)-keto sulfide according to the published procedure. 170

DEUTERATION OF \( \omega-(\text{Phenylsulfonyl})\text{acetophenone} (87) \)

A solution of 1.0 g. (3.85 mmole) of 87 was stirred over 0.09 g. of oil free sodium hydride in 20 ml. of THF until hydrogen evolution had ceased. The anion solution was quenched with 3.0 ml. of deuterium oxide to which 0.30 ml. of acetyl chloride was added. The THF was removed on a rotary evaporator and the residue was extracted with chloroform. The chloroform was removed after drying over anhydrous magnesium sulfate and the entire procedure was repeated three times. Final recrystallization from carbon tetrachloride gave 0.6 g. of the dideuterated compound. Dideuteration of the methylene carbon was confirmed by the nmr spectrum of this sample which showed only aromatic protons.


SOLVENTS

THF, DME, and diglyme were purified by distillation from lithium aluminum hydride and stored over Linde Type 5-A molecular sieves. HMPA (Eastman) was distilled from calcium hydride and metallic sodium.

RADICAL DIANION GENERATION

Esr spectra were obtained using a Varian V-4502 spectrometer. The vessel used to prepare esr samples consisted of two 25 ml. round bottom reaction flasks joined by means of glass tubing to a quartz esr sample tube. One of the round bottom flasks had a 5 ml. side-arm bulb attached to hold the alkali metal. Access was afforded through a ground glass joint. The vessel was connected to a vacuum pump through a hollow plug stopcock. Samples were prepared by charging the side-arm bulb with alkali metal, one of the main bulbs with the substrate and sodium hydride, and the other bulb with solvent. The solvent was freeze-degassed and the system was evacuated. After allowing 0.5 to 1 hr. for anion formation the alkali metal was added. In certain experiments, potassium was distilled into the main reaction bulb before transferring the anion solution. The radical dianion solution was poured into the sample tube and the esr spectrum was recorded.

REDUCTIONS IN THF, DME, AND DIGLYME

Preliminary experiments using THF or DME as the solvent indicated little alkali metal reduction of the anions 79 and 84.

171. Appreciation is expressed to Professor Jack Calvert for use of the esr spectrometer.
Neutralization of the anion solution followed by removal of the solvent gave almost quantitative recovery. Reduction of a $4 \times 10^{-3} \text{M}$ solution of the anion of $\text{Bz}$ with an excess of Na-K alloy gave rise to a broad unresolved spectrum. Dilution gave no increased resolution.

In diglyme, $10^{-3}$ to $10^{-1} \text{M}$ solutions of $\text{Bz}$, $\text{Dz}$, and acetophenone gave rise to the same spectra when treated with an excess of sodium hydride followed by potassium or sodium-potassium alloy regardless of temperature variations. A $1.5 \times 10^{-4} \text{M}$ solution of $\text{Bz}$ when treated with 0.03 g. of sodium hydride and an excess of sodium-potassium alloy gave rise to the esr spectrum of biphenyl.

**REDUCTIONS IN HMPA**

The spectra obtained were superimposed upon that of peroxylamine disulfonate (7.5 mg./ml. of saturated sodium carbonate) as a standard.

In all cases alkali metal reductions gave red-brown solutions. The green solution obtained from acetophenone eventually turned red-brown.

All spectra of the reduction product of $\text{m-}(\text{phenylsulfonyl})$-acetophenone ($\text{Bz}$) and its deuterated analog were obtained from $7.7 \times 10^{-2} \text{M}$ solutions at room temperature. The microwave frequency, as measured by a calibrated wavemeter, for the radical dianion obtained from $\text{Bz}$ with both sodium and potassium ions present was $9549.4 \text{Mc}$. The frequency used when only potassium was the counter ion was $9560.4 \text{Mc}$. After optimizing conditions the spectrum of the
dideuterated compound was obtained using a frequency of 9563.4 Mc.

The spectrum of \( \omega-(\text{phenylsulfinyl})\text{acetophenone} \) (\( 84 \)) was obtained from a \( 4.1 \times 10^{-2} \) M solution at room temperature. The frequency was not measured.

The spectrum from \( \omega-(\text{methylsulfinyl})\text{acetophenone} \) (\( 79 \)) was recorded from a \( 5.5 \times 10^{-2} \) M solution. The measured frequency was 9551.1 Mc.

A \( 8.4 \times 10^{-2} \) M solution of \( \omega-(\text{methylsulfonyl})\text{acetophenone} \) (\( 86 \)) in HMPA gave rise to the spectrum obtained. The frequency was not measured.

**RECOVERY ATTEMPTS**

Following the same procedure used for esr sample preparation, 1.0 g. (3.85 mmole) of \( 87 \) was treated with 0.094 g. of sodium hydride and 0.015 g. (3.85 mmole) of potassium in 5 ml. of HMPA. After all the metal had dissolved, the red-brown solution was neutralized with 10\% sulfuric acid. The solution became pale yellow. The addition of 20 ml. of water precipitated 0.55 g. of \( 87 \). A very small amount of the 2,4-DNP of acetophenone, sufficient for an infrared spectrum and mixed melting point, was obtained from the aqueous solution. After reaction of 0.5 g. of \( 87 \) with 0.047 g. of sodium hydride in 3.0 ml. of HMPA, followed by neutralization, the addition of 20 ml. of water precipitated 0.43 g. of the starting sulfone. Only the 2,4-DNP of \( 87 \) was obtained from the chloroform extracts of the aqueous solution.
CALCULATION OF g-VALUES

Peroxylamine disulfonate (Aldrich Co.) was used as a standard for magnetic field calibration and g-value determinations. The esr spectrometer was equipped with a dual cavity which permitted simultaneous recording of sample and standard spectra. The dual cavity was calibrated by placing identical samples in each channel to determine the difference in magnetic field and recorder pen offsets. Frequencies were measured with a calibrated wavemeter.

The expression used to calculate the unknown g-value is:

\[ g = 2.0055 \left( 1 - \frac{\Delta H}{H} \right) \]

Here \( \Delta H \) is the shift of the unknown resonance field with respect to peroxylamine disulfonate and was positive for the higher field shifts observed. The g-value of peroxylamine disulfonate is 2.0055. The field at which the center line of the standard resonates, \( H \), was calculated from:

\[ H = \frac{hv}{g \mu_0} \]

\( h \) = Planck's constant, \( 6.6252 \times 10^{-27} \) erg·sec
\( \nu \) = measured frequency (Mc)
\( g \) = g-value of standard, 2.0055
\( \mu_0 \) = moment of Bohr magneton, \( 0.9273 \times 10^{-23} \) erg·gauss