STUDY OF THE McFADYEN-STEVEN'S ALDEHYDE SYNTHESIS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

By

EDWARD GEORGE CAFLISCH, JR., B.S.
The Ohio State University

1954

Approved by:

Melvin S. Heiferman
Adviser
ACKNOWLEDGEMENT

I wish to thank Dr. Melvin S. Newman, who suggested this problem and whose guidance was invaluable throughout this investigation; my family for their encouragement; and the Union Carbide and Carbon Corporation who made my fellowship possible.
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INTRODUCTION

Many methods for the preparation of aldehydes are known. In actual practice, however, the preparation of a desired aldehyde in high yield is often difficult. One of the newer methods, the McFadyen-Stevens procedure, for converting an acid to the corresponding aldehyde has been successfully used for the preparation of several aromatic and heterocyclic aldehydes. The acid (I) is converted in the usual manner to the hydrazide (II), and this in turn to the sulfonylhydrazone (III). The aldehyde (IV) is then rapidly formed when

\[ \text{ArCO}_2\text{H} \rightarrow \text{ArCOOR} \rightarrow \text{ArCONNH}_2 \rightarrow \text{ArCONHNHSO}_2\text{Ar'} \]

I II III

a large excess of solid sodium carbonate is added in one batch to a hot solution of the sulfonylhydrazone (III) dissolved in ethylene glycol. The reaction conditions are described in detail, but little information

\[ \text{ArCONHNHSO}_2\text{Ar'} + \frac{1}{2}\text{Na}_2\text{CO}_3 \rightarrow \text{ArCHO} + \text{N}_2 + \text{NaSO}_2\text{Ar'} + \frac{1}{2}\text{CO}_2 + \frac{1}{2}\text{H}_2\text{O} \]

III IV

is available about the reaction mechanism and the side reactions. This lack of information prompted the following investigation. Although the first aim originally was to modify the experimental conditions so that the desired reaction would take place under milder conditions and at a more measurable rate, this dissertation deals for the most part with the investigation of some unusual aspects of this reaction. Before discussing the details of this work the previous work will be briefly reviewed to provide the background necessary to understand the importance of these aspects.

REVIEW OF PREVIOUS WORK

General Procedure.—Acids (I) or their esters are usually the starting materials for the McFadyen-Stevens procedure, probably because of the availability of these compounds. The acids are esterified, and the esters reacted with hydrazine hydrate in refluxing ethanol. The resulting hydrazides (II) are treated with arylsulfonyl chlorides in cold pyridine to produce the desired sulfonhydrazides (III). The alternate procedure of treating hydrazine or benzene-

\[
\text{ArCO}_{2}H \rightarrow \text{ArCOOR} \quad \text{NH}_{2}\text{NH}_{2} \cdot \text{H}_{2}O \rightarrow \text{ArCONHNH}_{2} \quad \text{Ar' SO}_{2} \text{Cl} \rightarrow \text{ArCONHNHSO}_{2}\text{Ar'}
\]

sulfonhydrazide with an acyl chloride often gives diacylation.

The sulfonhydrazides III are written as symmetrically-substituted hydrazine derivatives, because benzenesulfonylbenzhydrazide gave no reaction with benzaldehyde in refluxing alcohol. Compounds with the unsymmetric structure normally react with aldehydes to produce hydrazones. An unsymmetrically substituted hydrazine derivative is also not expected to form the stable sodium salt that was later prepared from benzenesulfonylbenzhydrazide. The position of substituents on the nitrogens of the hydrazide will be indicated as N or N'. N refers to the acylated nitrogen and N' to the unsubstituted nitrogen of the hydrazide from which the name is derived.

The best yields of aldehydes were usually obtained when about a four-equivalent excess of sodium carbonate was added, all at once, to

the sulfonhydrazide (III) dissolved in the ethylene glycol (or glycerol) and maintained at about 160°. One case was reported, however, in which the use of one equivalent of sodium carbonate gave better results than when an excess was used. The reaction was very rapid. At the moment the evolution of nitrogen seemed to subside (30-180 sec.), the reaction mixture was rapidly cooled. Prolonged heating seriously decreased the yields of aldehyde. The solvents, pyridine, quinoline, and cyclohexanol were not so satisfactory as ethylene glycol or glycerol. Glycerol has not received much use. The yields of the aldehydes were affected little by the quantity (5 to 20 parts) of the solvent. Sodium carbonate was more satisfactory than potassium carbonate, while sodium borate or acetate, or organic bases were ineffective. Later, borax was found in one case to give better results than sodium carbonate. Barium carbonate and calcium carbonate were not as satisfactory as sodium carbonate. Instead of adding solid alkali to the hot solution of the sulfonhydrazide (III), several workers put alkali (usually

3. References 9, 16, 17 of Table I; 1, 2, 4, 12, 16 of Table II; and 1, 3 of Table III.
5. Y. Tamamushi, J. Pharm. Soc. Japan 60, 184 (1940); Chem. Abstracts 34, 54471 (1940).
6. References 9, 16, 17 of Table I; 1, 2 of Table II; and 3 of Table III.
potassium carbonate) into the reaction mixture before the reaction temperature was attained. Several sulfonyl chlorides (benzene-,
2,5-dichlorobenzene-,\(^1\) and 4-methylbenzene-\(^2\)) have been used with no particular effect on the yield. The 2,5-dichlorobenzene-sulfonylhydrazides, however, could be decomposed slower at a lower temperature.

Reaction Scope.—The McFadyen-Stevens procedure has been successfully used (see Tables I and II) with a large number of aromatic aldehydes (yields usually 65-80\%) and heterocyclic aldehydes (yields usually 30-65\%). Highly substituted benzenaldehydes and polynuclear aldehydes have been prepared, but this method has not been tried on a diortho-substituted benzenaldehyde or a dialdehyde. All reported attempts to prepare ortho- or para-nitro substituted benzenaldehydes\(^1,3,4\) have failed, but in every other case of an aromatic aldehyde some desired product was obtained. The general rule of parallel behavior of a pyridine derivative and the corresponding nitrobenzene derivative was believed\(^4\) to apply to the following observation: 3-nitrobenzenaldehyde and pyridine-3-carboxaldehyde were obtained in fair yield, but no 4-nitrobenzenaldehyde or pyridine-4-carboxaldehyde was produced by the normal McFadyen-Stevens procedure. Pyridine-2-carboxaldehyde (VI) was obtained in fair yield, but this exception to the parallel behavior

\[
\begin{align*}
V & \quad \leftrightarrow \quad VI \\
\text{CONHNHSO}_2C_8H_5 & \quad \rightarrow \quad \text{CHO}
\end{align*}
\]

2. References 3-6, 8, 9, 11, 16, 17 of Table I; 9, 17 of Table II; and 3 of Table III.
3. A. Albert, ibid., 1225 (1948).
### TABLE I

Aromatic Aldehydes from McFadyen-Stevens Procedure

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Yield, %</th>
<th>Time, min.</th>
<th>Temperature</th>
<th>Equivalents of Na₂CO₃</th>
<th>Volume (L) of ethylene glycol per mole hydrazide</th>
<th>Reference</th>
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<tbody>
<tr>
<td>C₆H₅CHO</td>
<td>73</td>
<td>1.25</td>
<td>160</td>
<td>5</td>
<td>1.5-6.1</td>
<td>1</td>
</tr>
<tr>
<td>4-C₆H₅CHO</td>
<td>74</td>
<td>8.3</td>
<td>110</td>
<td>4</td>
<td>2.8</td>
<td>1</td>
</tr>
<tr>
<td>2-FC₆H₅CHO</td>
<td>81</td>
<td>4.0</td>
<td>160-165</td>
<td>1.1</td>
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<td></td>
</tr>
<tr>
<td>3-FC₆H₅CHO</td>
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<td>80-110</td>
<td>5</td>
<td></td>
<td>1</td>
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<tr>
<td>4-FC₆H₅CHO</td>
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<td>2-FC₆H₅CHO</td>
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<td>160</td>
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<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>3-CH₃C₆H₅CHO</td>
<td>61</td>
<td>3.8</td>
<td>160</td>
<td>5.8</td>
<td></td>
<td>3</td>
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<td>2-HOC₆H₅CHO</td>
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<td>0.7</td>
<td>160</td>
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</tr>
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<tr>
<td>4-(1'-CH₃OC₆H₅O)C₆H₅CHO</td>
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<td>1.3</td>
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<td>5.5</td>
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<td></td>
</tr>
<tr>
<td>4-(2'-CH₃OC₆H₅O)C₆H₅CHO</td>
<td>78</td>
<td>4.5</td>
<td>165</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-C₆H₅CH₃SC₆H₅CHO</td>
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<td>1</td>
<td>160</td>
<td>3.8</td>
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<td>2-(1'-HOC₆H₅O)C₆H₅CHO</td>
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<td>3.8</td>
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<td>2-C₆H₅CH₃CH₂C₆H₅CHO</td>
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<td>150</td>
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<tr>
<td>2-NO₂C₆H₅CHO</td>
<td>67</td>
<td>4</td>
<td>30-205</td>
<td>4.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- f₂,5-Dichlorobenzenesulfonyl chloride used.
- *Modified procedure with surface used.
- x₄-Methylbenzenesulfonyl chloride used.
- #Glycerol used instead of ethylene glycol.
- !Potassium carbonate used instead of sodium carbonate.
- †Heated slowly with alkali in solution.

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Yield, %</th>
<th>Time, min</th>
<th>Temperature, °C</th>
<th>Equivalents of Na₂CO₃</th>
<th>Volume (l.) of ethylene glycol per mole hydrazide</th>
<th>Reference</th>
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<td>3-NO₂C₆H₄CHO</td>
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<td>2.5</td>
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<td>6</td>
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<td>3.0</td>
<td>160-165</td>
<td>1.1</td>
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<td>4-NH₂C₆H₄CHO</td>
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<td>4.0</td>
<td>160-165</td>
<td>1.1</td>
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<td>3-C₆H₅NH₂</td>
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<td>165</td>
<td>1.2</td>
<td>2.6</td>
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<td>5-Br-2-C₆H₄CHO</td>
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<td>3-F-4-C₆H₄CHO</td>
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<td>155</td>
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<td>3-CH₃-2-C₆H₄CHO</td>
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<td>150-160</td>
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<td>2.3</td>
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<td>6.3</td>
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<tr>
<td>3,5-(CH₃O)₂C₆H₄CHO</td>
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<td>155</td>
<td>6.0</td>
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<td>2-C₆H₅NH₂-1-NO₂C₆H₄CHO</td>
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<td>13</td>
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<td>0.5</td>
<td>160</td>
<td>3.1</td>
<td>3.3</td>
<td>18</td>
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</tbody>
</table>

* Methylbenzenesulfonyl chloride used.
# Heated slowly with alkali in solution.
^Glycerol used instead of ethylene glycol.
*Potassium carbonate used instead of sodium carbonate.
*Modified procedure with surface used.
### TABLE I - Continued

Aromatic Aldehydes from McFadyen-Stevens Procedure

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Yield, %</th>
<th>Time, min.</th>
<th>Equivalents of Na₂CO₃</th>
<th>Volume (l) of ethylene glycol per mole hydrate</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>3,4,5-(CH₃O)₃C₆H₂CHO</td>
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<td>1.2</td>
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<tr>
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<td>CH₃O</td>
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<td>CH₃O</td>
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<td>5.0</td>
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<table>
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<th>Yield, %</th>
<th>Time, min.</th>
<th>Temperature, °C</th>
<th>Equivalents of Na₂CO₃</th>
<th>Volume (l.) of ethylene glycol per mole hydrazide</th>
<th>Reference</th>
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<td>160</td>
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<td>30-160</td>
<td>5.0</td>
<td>1.1#</td>
<td>2</td>
</tr>
<tr>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>31</td>
<td>2</td>
<td>160</td>
<td>1.0</td>
<td>1.5#</td>
<td>5</td>
</tr>
<tr>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>0</td>
<td>2-3</td>
<td>160</td>
<td>4.8</td>
<td>1.4</td>
<td>6</td>
</tr>
<tr>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>traces</td>
<td>3</td>
<td>155</td>
<td>4.4</td>
<td>3.8</td>
<td>7</td>
</tr>
<tr>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>44</td>
<td>3-5</td>
<td>160</td>
<td>5.3</td>
<td>3.5</td>
<td>8</td>
</tr>
<tr>
<td><img src="https://via.placeholder.com/150" alt="image" /></td>
<td>56</td>
<td>2-3</td>
<td>160-165</td>
<td>5.3</td>
<td>7.5</td>
<td>7</td>
</tr>
</tbody>
</table>

#Heated with alkali in solution
#Glycerol used instead of ethylene glycol.
*Modified procedure with surface used.

5. A. Dornow and H. Bormann, ibid., 82, 216 (1949).
### TABLE II - Continued

Heterocyclic Aldehydes from McFadyen-Stevens Procedure

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Yield, %</th>
<th>Time, min.</th>
<th>Temperature, °C</th>
<th>Equivalents of Na₂CO₃</th>
<th>Volume (1.) of ethylene glycol per mole hydrazide</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45^x</td>
<td>3</td>
<td>150</td>
<td>6.4</td>
<td>1.5</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>33^x</td>
<td>3</td>
<td>160</td>
<td>6.4</td>
<td>1.7</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>13^x</td>
<td>3</td>
<td>160</td>
<td>6.4</td>
<td>1.7</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>25^x</td>
<td>3</td>
<td>160</td>
<td>6.4</td>
<td>1.6</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3</td>
<td>150</td>
<td>8.2</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>3.0</td>
<td>165</td>
<td>1.2</td>
<td>2.6</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>7</td>
<td>170</td>
<td>5.2</td>
<td>0.8#</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>7</td>
<td>170</td>
<td>5.2</td>
<td>0.8#</td>
<td>12</td>
</tr>
<tr>
<td>N=N-CHO</td>
<td>58</td>
<td>7</td>
<td>170</td>
<td>5.2</td>
<td>0.8#</td>
<td>12</td>
</tr>
<tr>
<td>N=N-CH₃(CH₃)₂</td>
<td>61</td>
<td>7</td>
<td>170</td>
<td>5.2</td>
<td>0.8#</td>
<td>12</td>
</tr>
</tbody>
</table>

^x: Methylbenzenesulfonyl chloride used.

*Modified procedure with surface used.

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Yield, %</th>
<th>Time, min.</th>
<th>Temperature</th>
<th>Equivalents of N₂CO₃</th>
<th>Volume (l.) of ethylene glycol per mole hydrazide</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(^\cap)CHO</td>
<td>51</td>
<td>7</td>
<td>170</td>
<td>5.2</td>
<td>0.8#</td>
<td>12</td>
</tr>
<tr>
<td>N(_\equiv)CHO</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>C(^\equiv)CHO</td>
<td>25</td>
<td>15</td>
<td>160</td>
<td>4.5</td>
<td>1.3</td>
<td>14</td>
</tr>
<tr>
<td>N(_\equiv)S(^\equiv)CHO</td>
<td>30</td>
<td>15</td>
<td>160</td>
<td>4.5</td>
<td>1.3</td>
<td>14</td>
</tr>
<tr>
<td>C(_\equiv)S(^\equiv)CHO</td>
<td>40</td>
<td>2-3</td>
<td>160</td>
<td>4.8</td>
<td>1.4</td>
<td>15</td>
</tr>
<tr>
<td>CH₃-N(_\equiv)N=0-CHO</td>
<td>50</td>
<td>2</td>
<td>160</td>
<td>5</td>
<td>1.3#</td>
<td>16</td>
</tr>
<tr>
<td>S(_\equiv)CHO</td>
<td>63*</td>
<td>0.5</td>
<td>160</td>
<td></td>
<td>1.7</td>
<td>17</td>
</tr>
</tbody>
</table>

\(^{h}\)Borax used instead of sodium carbonate.

\(^{\#}\)Glycerol used instead of ethylene glycol.

\(^{x}\)Methylbenzenesulfonyl chloride used.

rule (no 2-nitrobenzaldehyde was found) was explained through the possible hydrogen bonding of the ring nitrogen with one of the hydrazine hydrogens in the sulfonhydrazide (V). This explanation is rather questionable, since hydrogen bonding can not protect the aldehyde VI once formed. Pyridine-4-carboxaldehyde was shown to be produced under the normal reaction conditions but completely decomposed before isolation. This fact was demonstrated by placing thiosemicarbazide in the reaction mixture so that the thiosemicarbazone formed before the aldehyde decomposed. The parallel behavior rule would thus predict that the nitrobenzaldehydes also were formed, and the isolation of a small quantity of 4-nitrobenzaldehyde will be mentioned later. The parallel behavior rule should not be extended too far, as it is somewhat limited; for example the ionization constants of the carboxylic acids of two series are in inverse order (see Table IV).

The McFadyen-Stevens procedure has little applicability in the aliphatic series. The method has been tried for aldehydes with phenyl or heterocyclic rings in the alpha position but not for an aliphatic aldehyde with no alpha hydrogen or an aldehyde like trifluoroethanal (see Table III). Cyclopropanecarboxaldehyde and tetrahydrofuran-2-carboxaldehyde are the only aliphatic aldehydes that have been obtained by this method, and only traces of the latter were found. The success for cyclopropanecarboxaldehyde was attributed to the well-

### TABLE III

**Aliphatic Aldehydes from McFadyen-Stevens Procedure**

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Yield, %</th>
<th>Time, min.</th>
<th>Temperature, °C</th>
<th>Equivalents of Na₂CO₃</th>
<th>Volume (1.) of ethylene glycol per mole hydrazone</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CHO</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>(CH₃)₂CHCHO</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>(C₆H₅)₂CHCHO</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>CH₃ - N - CH₂CHO</td>
<td>0</td>
<td>3-5</td>
<td>160</td>
<td>5</td>
<td>3.5</td>
<td>2</td>
</tr>
<tr>
<td>CH₃ - S - CH₂CHO</td>
<td>0</td>
<td>3-5</td>
<td>160</td>
<td>5.3</td>
<td>3.5</td>
<td>2</td>
</tr>
<tr>
<td>H₂ - CH₂OH</td>
<td>traces</td>
<td>&gt;3</td>
<td>30-105</td>
<td>5.0¹</td>
<td>3.0#</td>
<td>3</td>
</tr>
<tr>
<td>CH₂CH₂</td>
<td>16</td>
<td>1</td>
<td>165</td>
<td>4.5</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>C₆H₅CH=CHCHO</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

¹ Methylbenzensulfonyl chloride used.
² Heated with alkali in solution.
³ Potassium carbonate used instead of sodium carbonate.
⁴ Glycerol used instead of ethylene glycol.

### TABLE IV

Ionization Constants of Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>K x $10^4$</th>
<th>Acid</th>
<th>K x $10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-NO$_2$C$_6$H$_4$COOH</td>
<td>67.1$^\circ$</td>
<td>3-NO$_2$C$_6$H$_4$COOH</td>
<td>3.21$^\circ$</td>
</tr>
<tr>
<td>4-NO$_2$C$_6$H$_4$COOH</td>
<td>5.76$^\circ$</td>
<td>COOH</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### TABLE V

Yields in the McFadyen-Stevens and Kalb-Gross Procedures

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>McFadyen-Stevens Yield, %</th>
<th>McFadyen-Stevens Reference</th>
<th>Kalb-Gross Yield, %</th>
<th>Kalb-Gross Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_5$CHO</td>
<td>73</td>
<td>2</td>
<td>64</td>
<td>3</td>
</tr>
<tr>
<td>2-HO$_2$C$_6$H$_4$CHO</td>
<td>55</td>
<td>2</td>
<td>37</td>
<td>3</td>
</tr>
<tr>
<td>2-NO$_2$C$_6$H$_4$CHO</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>3-NO$_2$C$_6$H$_4$CHO</td>
<td>42</td>
<td>2</td>
<td>23</td>
<td>3</td>
</tr>
<tr>
<td>4-NO$_2$C$_6$H$_4$CHO</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>4-NH$_2$C$_6$H$_4$CHO</td>
<td>36$^\circ$</td>
<td>2</td>
<td>34</td>
<td>3</td>
</tr>
<tr>
<td>2-C$_6$H$_5$NHC$_6$H$_4$CHO</td>
<td>80</td>
<td>5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>3,4,5-(CH$_2$O)$_3$C$_6$H$_2$CHO</td>
<td>84</td>
<td>6</td>
<td>59</td>
<td>3</td>
</tr>
</tbody>
</table>

*Modified Procedure of this paper.

known unsaturated character of the cyclopropyl ring.\(^3\) The only attempt
to make an \(\alpha,\beta\)-unsaturated compound, that of 3-phenylpropenal,\(^2\)
failed, but there was some question about the structure of the
hydrazide. Unsaturated hydrazides (VII) are rather unstable and have a
tendency to cyclize to pyrazolidones\(^3-6\) (VIII). The possibility of

\[
\begin{align*}
\text{RCH} = \text{C} - \text{CR'} \text{CONHNH}_2 & \quad \text{VII} \\
\text{R} & \quad \text{NH} \\
\text{CH} & \quad \text{NH} \\
\text{R} & \quad \text{CO} \\
\end{align*}
\]

obtaining an unsaturated aldehyde if this cyclization does not occur
seems reasonable since unsaturated compounds work in some of the reactions
which are similar to the McFadyen-Stevens aldehyde synthesis.

Analogous Reactions.—Arylsulfonylarylhydrazines (IX) have been

\[
\begin{align*}
\text{ArCONHNHSO}_2\text{Ar'} + \frac{1}{2}\text{Na}_2\text{CO}_3 & \rightarrow \text{ArCHO} + \text{N}_2 + \text{NaSO}_2\text{Ar'} + \frac{1}{2}\text{CO}_2 + \frac{1}{2}\text{H}_2\text{O} & \text{III} \\
\text{ArNHNHSO}_2\text{Ar'} + \text{OH}^- & \rightarrow \text{ArH} + \text{N}_2 + \text{CO}_2\text{Ar'} + \text{H}_2\text{O} & \text{IX} \\
\end{align*}
\]
cleaved by alkali, producing aromatic hydrocarbons\(^2,7-10\) (X) in a manner
analogous to the above preparation of aldehydes (IV). Cycloheptatri-

5. E. Muckermann, J. prakt. Chem. (2) 82, 523 (1911).
7. R. Escales, Bér. 18, 893 (1885).
enones\textsuperscript{1} (XII) were obtained from the corresponding 2-benzenesulfonyl hydrazides (XIII) possibly tautomeronized to unsaturated hydrazides (XIV) before the pyrolytic cleavage to the olefins (XV).

Another analogous reaction is the preparation of aldehydes by the mild alkaline oxidation of benzhydrazide derivatives\textsuperscript{3-10} (II).

\[
\text{ArCONHNH}_2 + 2 \text{OH}^- \rightarrow \text{ArCHO} + \text{N}_2 + 2 \text{H}_2\text{O} + 2 \text{e}^- \\
\text{IV}
\]

Similarly the oxidation of substituted hydrazines (XVI) gave hydrazides (X).

\[
\text{ArNHNH}_2 + 2 \text{OH}^- \rightarrow \text{ArH} + \text{N}_2 + 2 \text{H}_2\text{O} + 2 \text{e}^- \\
\text{X}
\]

\begin{itemize}
\item 3. T. Curtius, Ber. 32, 2559 (1900).
\item 4. A. Darapsky, J. prakt. Chem. (2) 76, 464 (1907).
\item 5. A. Darapsky, Ber. 40, 3033 (1907).
\item 7. L. Kalb and D. Gross, Ber. 59, 727 (1926).
\end{itemize}
The preparation of aldehydes from benzhydrazide derivatives (II) seems to offer a short cut to the McFadyen-Stevens procedure. In the few cases in which these two aldehyde preparations could be compared the McFadyen-Stevens procedure always gave the better yield (see Table V). The extra step required for the McFadyen-Stevens procedure is usually accomplished in very high yield.

The analogy can be extended to several other reactions such as the Wolff-Kishner reduction. These similarities will be discussed in the section on proposed mechanisms, since the proposed intermediates are involved.

Reaction Products.—The desired aldehydes (IV) were usually isolated by extraction and distillation, by steam distillation, or by conversion to a derivative. The benzenesulfinate anion (XVII, Ar = C₈H₅⁻) was isolated in only two cases, once by being converted to 2,4-dinitrodiphenylsulfone and once by being converted to 2,5-dioxodiphenylsulfone. The collection of the nitrogen and carbon dioxide was not reported. No case of a failure to obtain a violent reaction has been reported but a little unreacted sulfonhydrazide (III) has been reclaimed in a few cases. The following compounds were isolated as by-products: 4-nitrobenzoic acid (58% yield, crude), pyrazine-2-

carboxylic acid,\(^1\) pyrazine-2-carboxamide,\(^1\) \(\text{N},\text{N}'\)-di-2-pyrazinoyl-
hydrazine\(^1\) (21\% yield), benzenesulfonhydrazide\(^2\) (from an attempt to
make 4-hydroxy-2-methylpyrimidine-5-carboxaldehyde), and diphenyl-
disulfide.\(^1,3\) In two cases other functional groups attached to
the aldehydes (IV) underwent some reaction.\(^4,5\) The starting sul-
onhydrazides (III) were not completely accounted for in any reported
case.

**Side Reactions.**—The isolation of pyrazine-2-carboxylic acid and
\(\text{N},\text{N}'\)-di-2-pyrazinoylhydrazine\(^1\) provides some support for the earlier
proposal\(^6\) that 4-nitrobenzoic acid (rather than 4-nitrobenzaldehyde)
and benzenesulfonic acid were obtained from the side reaction in
which diacylhydrazines (XVIII) were formed from the sulfonhydrazides
(III). The diacylhydrazines (XVIII) were then hydrolyzed to the

\[
\text{II} \quad \text{XVIII}
\]

\[
2 \text{ArCONHNHSO}_2\text{Ar}^1 + 2 \text{OH}^- \rightarrow (\text{ArCONH}^-)\text{II} + 2 \text{SO}_2\text{Ar}^1 + \text{N}_2 + 2 \text{H}_2\text{O}
\]

\[
\text{XVIII}
\]

\[
(\text{ArCONH}^-)\text{II} + 2 \text{OH}^- \rightarrow 2 \text{ArCOOH} + \text{NH}_2\text{NH}_2
\]

\[
\text{XVIII}
\]

corresponding acids (I) and hydrazine. Some evidence originally cited
for this side reaction was that the mild alkaline oxidation of
4-nitrobenzhydrazide (II, Ar = 4-\(\text{NO}_2\text{C}_6\text{H}_4\)) did not give the expected
4-nitrobenzaldehyde (see page 15). Instead, \(\text{N},\text{N}'\)-bis-(4-nitrobenzoyl)-

---

hydrazine (XVIII, \(Ar = \text{4-NO}_2\text{C}_6\text{H}_4^-\)) was formed. The pH of the oxidation

\[
2 \text{ArCONNH}_2 + 4 \text{OH}^- \rightarrow (\text{ArCONH}_2^-)_{\text{2}} + \text{N}_2 + 4 \text{H}_2\text{O} + 4 e^-
\]

medium used with benzhydrazides (II) is important, as acids or amides may be obtained when the medium is strongly alkaline or neutral (or acidic) respectively. These acids and amides were not formed from the decomposition of aldehydes and acylhydrazones.

The decomposition of the desired aldehydes is a very important side reaction in the McFadyen-Stevens procedure. A few extra minutes of heating seems to almost completely destroy many of the aldehydes. Nothing, however, was mentioned concerning the exact nature of this decomposition.

**Proposed Mechanisms.** — The intermediates XIX were postulated for the conversion of the sulfonhydrazides (III) to aldehydes (IV).

Similar intermediates (XX) were postulated for the preparation of aromatic hydrocarbons (X) from arylsulfonylarylhydrazines (IX). These two reaction paths have been cited as examples of 1,2-elimination.

---

1. L. Kalb and D. Gross, Ber. 59, 727 (1926).
The intermediate for benzaldehyde (XIX, Ar = C₆H₅⁻) has never been reported, and is assumed to be very unstable. Phenyldiimine¹⁻⁴ (XX, Ar = C₆H₅⁻) also has not been isolated, but the oxidation of 4-bromophenylhydrazine⁴ with p-benzoquinone at -60° gave a substance that was believed to be 4-bromophenyldiimine (XX, Ar = 4-BrC₆H₅⁻). This substance could be reduced to 4-bromophenylhydrazine, or, on being heated to room temperature, gave nitrogen and bromobenzene. Diimines (XX) were the proposed intermediates for several other reactions⁵ including the reduction of diazonium salts and the Wolff-Kishner reduction.⁶

This review is brief, but includes the facts pertinent to this investigation. Many of the observations that seemed to have little relationship to each other will be mentioned again in the following discussion of the results of this investigation. These isolated observations were invaluable in providing a basis for some of the proposals.

1. W. Vauble, Ber. 33, 1711 (1900).
4. S. Goldschmidt, ibid., 46, 1529, 2300 (1913).
RESULTS AND DISCUSSION

Starting Materials.—Maximum yields in all the separate steps of the McFadyen-Stevens aldehyde synthesis would be required in order to obtain the best yield of an aldehyde. The aim of this work, however, was to study only the last step, the alkaline cleavage of acylbenzenesulfonylhydrazides. These latter compounds are not normally available, but usually can be prepared in high yield by standard methods. These standard methods were used with fair success for the compounds required for this study, but no special attempt was made to raise the yields by using a very exhaustive procedure for the isolation of the products or by modifying the reaction conditions.

Use of Strong Bases.—The very fast reaction rate and the high sensitivity of the yield of benzaldehyde to the reaction time were two problems which made the study of the McFadyen-Stevens procedure difficult. The reported procedure required about a four-equivalent excess of sodium carbonate and a temperature of 160°. The proposition that the use of a stronger base would eliminate the need for the large excess of base and the high temperature was considered. This modification could give a more measurable reaction rate and decrease the sensitivity to reaction time. Potassium t-butylate in refluxing t-butyl alcohol (b.p. 82°) failed to decompose benzenesulfonyl-benzhydrazide, while potassium n-butylate, a weaker base, in refluxing n-butyl alcohol (b.p. 117°) caused an evolution of nitrogen. The higher boiling point of n-butyl alcohol, rather than the strength of the base or solvent effects, seemed to be the reason for the difference.
All of the strong bases (II) converted benzenesulfonylbenzhydrazide (I) to the sodium or potassium salts (III), but the salts did not seem to decompose unless the temperature was high. These very strong bases, 

$$C_{6}H_{5}CONHNSO_{2}C_{6}H_{5} + RO^{-} + M^{+} \rightarrow C_{13}H_{11}N_{2}O_{3}S^{-} + M^{+} + ROH$$

However, were expected to rapidly decompose the desired aldehydes at high temperatures. Since the strong bases seemed to offer more disadvantages than advantages, their use was abandoned.

**Discovery of Surface Effect.**—In the reported procedure solid sodium carbonate was added in one portion to a solution of the acylarylsulfonhydrazide in ethylene glycol at 150-160°. At the end of the reaction time (1-5 min.) water was added and the aldehyde isolated. In repeating this procedure no difficulty was had in obtaining a yield of benzaldehyde which was very close to the reported value (73%; 75 seconds, 160°). The benzenesulfonic acid, which reportedly was produced in quantity and identified as 2,4-dinitrodiphenylsulfone, was reacted with p-benzoquinone to yield 2,5-dihydroxydiphenylsulfone (86% yield). The yield of nitrogen also was slightly higher than the yield of aldehyde. The object of repeating this preparation of

1. The interpretation of these observations is not changed by the later discovery of the surface effect; for the mixture in which potassium t-butyllate was tested was heterogeneous.


4. O. Hinsberg, Ber. 27, 3259 (1894).

benzaldehyde was to provide a basis for comparing results. N'-Benzenesulfonfnylbenzhydrazide (in ethylene glycol) did not decompose when heated in the absence of alkali.

The tests with stronger bases showed that the sodium or potassium salts of N'-benzenesulfonfnylbenzhydrazide are fairly stable at room temperature. The use of these salts seemed to offer the possibility of two advantages over the usual procedure: no excess base would be present, and the nitrogen would be free of carbon dioxide. Sodium N'-benzenesulfonfnylbenzhydrazide was prepared in high yield and was found to be very stable at room temperature. Treatment with hydrochloric acid regenerated N'-benzenesulfonfnylbenzhydrazide. The solid form of this salt may be only one ionic form, but alkylation, which will be mentioned later, showed that in solution the salt acts as a mixture. The potassium salt was also prepared, but the higher solubility of this salt made recrystallization difficult.

A suspension of sodium N'-benzenesulfonfnylbenzhydrazide in ethylene glycol started to evolve nitrogen at about 70°. The salt slowly dissolved as the temperature was raised, and, when the last disappeared, the gas evolution also stopped. The gas evolution, however, became brisk again when a little activated charcoal was added. Copper dust, zinc dust, Super Cel (diatomaceous earth), glass wool, and other materials, which will be mentioned later, had the same effect on similar runs. These solids caused no gas evolution with hot ethylene glycol alone. Some aldehyde was formed in each case. The evolution of nitrogen thus appeared to be surface catalyzed. The addition of an excess of potassium carbonate dissolved in hot ethylene glycol to a hot solution of N'-benzenesulfonfnylbenzhydrazide in the same solvent
caused little gas evolution unless some surface like glass wool was present. This was not just a case of supersaturation of the nitrogen, as the yield of benzaldehyde was affected. The reported procedure was then modified as follows: sodium N'-benzenesulfonylbenzhydrazide was added in one portion to hot ethylene glycol which contained a solid to provide surface. The reaction was stopped by cooling in an ice bath. The use of Pyrex glass wool (4-7 min. at 160-165°C) gave a 3-5% higher yield of benzaldehyde than the reported value (73%). The yield of benzaldehyde was only slightly affected by prolonged heating, but the high temperature and short reaction time were still advantageous (see Figure 1 and Table VIII). Apparently the large excess of solid sodium carbonate, which was required in the reported procedure, was partly needed to provide surface. The quantity of sodium carbonate had to be large enough so that complete solution did not occur before the main portion of the desired reaction was over. Potassium carbonate probably was not so satisfactory because of a higher solubility, and thus a larger quantity was needed to provide surface for the same length of time. A serious disadvantage of the reported procedure was the high sensitivity of the yield to time which apparently was caused by the reaction of this excess alkali with the desired aldehyde (yield decreased to 10% after 16 minutes at 140–190°C). The reported modifications in which the sodium carbonate was dissolved before the mixture was heated thus defeated the purpose of the excess alkali, and, in the only case in which a comparison can be made, this modification led to a lower yield.\textsuperscript{1,2} Of course the vessel walls

and the stirrer provided some surface.

Effect of Time and Temperature on Yield of Benzaldehyde

Figure 1

Effect of Surface on Alkali Requirement.—When N'-benzenesulfonyl-benzhydrazide and then sodium carbonate were added to a stirred suspension of powdered soft glass in hot ethylene glycol one equivalent of sodium carbonate was found sufficient to give the same yield of benzaldehyde as obtained from the use of the salt. Again the yield was found to be only slightly effected by prolonged heating (see Table IX). An equilibrium between the sulfonhydrazide I and the Salt III probably exists in which some of the base II is free to react in side

\[
C_6H_5\text{CONHNHSO}_2C_6H_5 + OR^- \rightleftharpoons C_{13}H_{11}N_2O_3S^- + H_2OR
\]

reactions, and thus a slightly better yield should be obtained if a slight excess of sodium carbonate were used. This excess would replace
any base used in side reactions, and allow complete pyrolysis of the salt. A very large excess of alkali apparently would be advantageous if aldehydes were not so easily decomposed; for it was later shown that the best yield of 2-hydroxybenzaldehyde was obtained when 5 equivalents of sodium carbonate was used. 2-Hydroxybenzaldehyde does not undergo the Cannizzaro reaction. The use of 1.1 equivalents of sodium carbonate was found to give the optimum yield (81%) of benzaldehyde, (see Table IX).

**Improved Procedure for Benzaldehyde.**—The above study of modifications of the reported McFadyen-Stevens procedure resulted in the following improved procedure; N'-Benzenesulfonylbenzhydrazide was added to a stirred suspension of powdered soft glass in ethylene glycol. This mixture was maintained at 160-165°. Sodium carbonate (1.1 equivalents) was then added and after four minutes the mixture was rapidly cooled in an ice bath. The benzaldehyde (81% yield) was isolated in the usual manner.

**Search for By-products.**—The 81% yield left 19% of the benzene-sulfonylbenzhydrazide unaccounted for. The evolution of nitrogen seemed to have little relation to the yield of aldehyde except at the very beginning of the reaction, and a yield of nitrogen close to 100% was often obtained after several minutes at 160°. This high yield of nitrogen indicated that very little unreacted sulfonhydrazide, benzamide, N,N'-dibenzoylhydrazine, or hydrazine were left in the reaction mixture. The last two were products predicted for a postulated side reaction (see page 17). This side reaction and the Cannizzaro reaction should produce benzoic acid (both require considerable sodium carbonate), but no benzoic acid or benzyl alcohol were found in the
reaction mixture. No benzene, benzaldehyde or carbon monoxide were found in the evolved nitrogen. The possibility of acetal formation between ethylene glycol and benzaldehyde was ruled out by the following facts. When benzaldehyde was extracted from a typical run, 2,4-dinitrophenylhydrazine reagent and the Bryant-Smith titration indicated the same yield. The 2,4-dinitrophenylhydrazine reagent gave higher results than the titration when used on a solution known to contain some acetal (IV). The hydrazine reagent apparently hydrolyzed the acetal. A small amount of acetal IV, however, was obtained by distillation of the extracted benzaldehyde. This acetal probably formed during the distillation of the lower boiling benzaldehyde. No evidence was found for the reaction of benzene-sulfinic acid with benzaldehyde.¹

\[
\text{C}_6\text{H}_5\text{CHO} + \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2 + \text{H}_2\text{O}
\]

obtained by distillation of the extracted benzaldehyde. This acetal probably formed during the distillation of the lower boiling benzaldehyde. No evidence was found for the reaction of benzene-sulfinic acid with benzaldehyde.¹

\[
\text{C}_6\text{H}_5\text{CHO} + \text{HSO}_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH(OH)SO}_2\text{C}_6\text{H}_5
\]

Little can be concluded from the completely negative results of this search for by-products, since the possibility can not be excluded that the failures were experimental errors.

**Improved Procedure with Other Aldehydes.**—The conditions which were found to give the best yield of benzaldehyde were tested on a series of other aldehydes. The extra step of isolating the salts of the sulfonhydrazides was omitted; for the use of the salts offered no advantage. In several cases the conditions were varied slightly,

since the optimum conditions varied from those for benzaldehyde (see Table IX). The effect of surface and the need of only about one equivalent of sodium carbonate were demonstrated in almost every case by improved yields. The reported procedures were repeated for several of these aldehydes, and in each case only the reported yields were obtained. With 2-hydroxybenzaldehyde, however, no improvement was found when only one or two equivalents of sodium carbonate was used, but this aldehyde is resistant to the Cannizzaro reaction. Small yields (3-4%) of the hydrazone were obtained from N'-benzenesulfonyl-4-nitrobenzhydrazide, but none was found when sodium N'-benzenesulfonyl-4-nitrobenzhydrazide was pyrolyzed. The modification\(^2\) using thiosemicarbazide in the reaction mixture gave a 15% yield of 4-nitrobenzaldehyde thiosemicarbazone. These derivatives were very crude and there was some question about their composition. The 4-aminobenzaldehyde-2',4'-dinitrophenylhydrazone was also fairly crude and may have contained some polymerized product. Copper dust and charcoal were again shown to be inferior to glass in catalyzing the reaction. The greatest improvement was with heterocyclic aldehydes; for example the yield of pyridine-2-carboxaldehyde was almost doubled.

**Explanations for Surface Catalysis.**—The exact need for the surface catalyst is not understood. Surfaces are known to affect many reactions, but little is actually known about reactions occurring in heterogeneous mixtures. The proposition that the surface catalyzes

---


A free radical reaction was considered. Ultraviolet light did not cause any evolution of nitrogen from N'-benzenesulfonylbenzhydrazide dissolved in hot ethylene glycol. This radiation also did not seem to influence the rate of evolution of nitrogen or the yield of benzaldehyde when sodium N'-benzenesulfonylbenzhydrazide was pyrolyzed in hot ethylene glycol with the walls of the glass vessels as the surface. Ethylene glycol is not the type of solvent that usually works well in a chain reaction, since this solvent tends to be an inhibitor. The by-products usually found in free radical reactions were not reported, but simply may have been missed. Benzaldehyde is quite sensitive to the attack of free radicals. Free radical promoters, such as the peroxides, were not used for this reason. Silver benzoate in triethylamine was found to cause the evolution of an equivalent amount of nitrogen from sodium N'-benzenesulfonylbenzhydrazide dissolved in 100% methanol at room temperature. Benzaldehyde may have been formed and then reduced the silver ion. In spite of these facts, the possibility that the reaction has a free radical mechanism will be discussed later.

The quantity of surface did not seem important except when limited to the walls of the vessel, and even a Teflon (tetrafluoroethylene polymer) vessel allowed some evolution of nitrogen. The large variety of substances that catalyze the reaction is unusual. The surfaces may be acting similar to boiling chips; and indeed ethylene glycol has some tendency to become supersaturated with nitrogen. The very low reactivity of molecular nitrogen, however,

1. M. S. Newman and P. F. Beal, J. Am. Chem. Soc., 72, 5163 (1950), found that this reagent was needed in only catalytic quantities in the Wolff Rearrangement.
causes the formation of nitrogen to be almost irreversible. Another unlikely possibility is that the cleavage of the sulfonhydrazide resulted in the rupture of the nitrogen to nitrogen bond and that a surface was needed for the recombination of the nitrogen atoms.

The catalytic effect of surface was also noted on the rate of evolution of gas from the pyrolysis of N,N'-bis-(benzenesulfonyl)-hydrazine and sodium N'(2,4-dinitrophenyl)-benzenesulfonylhydrazide. This effect may also be important in many other reactions where nitrogen is lost.

**MECHANISM DISCUSSION**

**Loss of Proton.**—The first step in the reaction mechanism is apparently the loss of a proton from the sulfonhydrazide. Sodium N'-benzenesulfonylbenzhydrazide is stable at room temperature but decomposes on heating at a rate (evolution of nitrogen) very similar to the rate of decomposition of the benzenesulfonylbenzhydrazide with sodium carbonate under the same conditions. Two hydrogens in N'-benzenesulfonylbenzhydrazide are activated. Both are located on the nitrogen atoms, and either one might come off as a proton. The one on the nitrogen adjacent to the benzenesulfonyl group is expected to be the most active, since sulfonamides have more acidic hydrogens than the corresponding amides. The situation is probably most accurately described as an equilibrium of compounds

---

1. The possibility that these were only cases of super saturation was not excluded.

I and VII and the ions V, VI and VIII. Any one or all of these ions may be involved in the aldehyde synthesis and the choice probably depends on the comparative ease of the respective reaction paths.

\[
\begin{align*}
C_6H_5CONHHSO_2C_6H_5 + H_2O & \quad \rightarrow \quad \text{V} \\
C_6H_5CONHHSO_2C_6H_5 + OH^- & \quad \rightarrow \quad \text{I} \\
C_6H_5CONHHSO_2C_6H_5 + OH^- & \quad \rightarrow \quad \text{VI} \\
C_6H_5CONHHSO_2C_6H_5 + OH^- & \quad \rightarrow \quad \text{VII} \\
C_6H_5CONHHSO_2C_6H_5 + OH^- & \quad \rightarrow \quad \text{VIII}
\end{align*}
\]

**Alkylation of the Sulfonhydrazide Salt.**—An attempt was made to obtain supporting evidence for this proposed equilibrium by isolating the products from the alkylation of sodium N′-benzenesulfonyl-benzhydrazide with either methyl sulfate or methyl iodide at room temperature. In both cases similar mixtures of methyl derivatives were found. Three monomethyl derivatives and two dimethyl derivatives are possible (IX-XIII). Only three compounds were isolated from the alkylation reaction mixture, but small quantities of the other two may have been missed. The yields and corrected melting points of these isolated compounds are indicated following.

1. Methylphenylsulfone and benzoic acid were the products when the alkylation was carried out at 80-90°C.
the structures (IX, XI, XIII) that are tentatively assigned to these compounds. This assignment of structures was based on the following considerations. All the compounds had sharp melting points, and analysis indicated the correct empirical formula in each case. The infrared spectra were of little help in confirming these assignments.

Structure X.—This structure was assigned to the compound (m.p. 145-145.5°) which was the only product isolated from the benzylation and benzenesulfonylation of methylhydrazine. N-Methylbenzhydrazide

\[
\text{CH}_3\text{NNH}_2 + \text{C}_6\text{H}_5\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{CON}([\text{CH}_3])\text{NH}_2 \\
\text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CON}([\text{CH}_3])\text{NHSO}_2\text{C}_6\text{H}_5 \\
\text{XIV} \\
\text{C}_6\text{H}_5\text{CHO} \rightarrow \text{C}_6\text{H}_5\text{CON}([\text{CH}_3])\text{N=CHC}_6\text{H}_5 \\
\text{XV}
\]

(XIV) has been reported as an unstable oil and was not isolated in this work. The presence of some of this compound, however, was demonstrated by reacting a portion of the reaction mixture (from benzoylation) with benzaldehyde. Benzaldehyde N-benzoylemethylhydrazone (XV) was obtained in 38% yield. This yield was low but identical to the yield of the only product (X) obtained from the benzenesulfonylation. An attempt to make IX by benzenesulfonylation and then benzoylation of methylhydrazine failed.

Structure IX (C_6H_5CONN(CH_3)SO_2C_6H_5).—The monomethyl compound with m.p. 188-189.2° was assigned the structure IX (rather than XI which has a methoxy group) since analysis indicated no methoxy and 67% of the required N-methyl. None of the methoxy or N-methyl

1. A. Michaelis and E. Hadanock, Ber., 41, 3285 (1908).
determinations on this series of compounds were quantitative, but the methods should qualitatively identify the respective groups.

Structure XI (C₈H₅C(OCH₃)=NNHSO₂C₆H₅).—This structure had to be assigned to the remaining monomethyl derivative (m.p. 164.5-166°). This assignment was supported by a methoxy determination which was 2% of the required value, but some N-methyl was found.

Structure XIII (C₈H₅C(OCH₃)=NN(CH₃)SO₂C₆H₅).—The dimethyl compound with m.p. 91-92.5° was assigned the structure XIII (rather than XII which had no methoxy group) since the methoxy group determination was 50% of the required value.

The occurrence of XI and XIII (or X and XII) as a pair in the reaction mixture was reasonable since the alkylation of the "amide" portion of N-benzenesulfonylbenzhydrazide would be expected to consistently give methoxy (or N-methyl) as the main or only product. The assignment of the above structures was not unequivocal, but none of the data conflicted with this proposal, except for XI.

Loss of Benzenesulfinate Anion.—There are many possibilities for the rest of the mechanism, which vary from one simultaneous cleavage to a many-step process. There is no advantage in writing equations for all of these processes, for there is very little information which can serve as a guide. One reaction path was postulated by earlier workers because apparent similarities suggested a common mechanism for several separate reactions (see page 18). This discussion will be limited mainly to an elaboration of this previously postulated reaction path.
The loss of the benzenesulfinate anion as the second step seems reasonable. The hydrazide salt (III) already has a negative charge and is not likely to lose a second proton or a cation of any kind. The higher stability of the benzenesulfinate anion over that of the benzoyl carbanion makes the former the likely choice if the cleavage is heterolytic. The loss of the benzenesulfinate anion produces a neutral intermediate that is probably not stable and immediately breaks down into the aldehyde and nitrogen. In agreement with this proposed mechanism N,N'-dibenzoylhydrazine was found stable under McFadyen-Stevens conditions, while N,N'-bis-(benzenesulfonyl)-hydrazine decomposed to benzenesulfinic acid and nitrogen on heat alone (the evolution of the gas was surface catalyzed). The ease of the loss of the benzenesulfinate anion is also shown by the instability of benzenesulfonhydrazide which has a great tendency to lose hydrazine and form N,N'-bis(benzenesulfonyl)-hydrazine. Difficulty was had in even recrystallizing the benzenesulfonhydrazide. On heating, benzenesulfonhydrazide also loses nitrogen, but the exact products are not known.\(^1\)

The conventional form of 1,2 elimination\(^2\) would require that the benzenesulfinate anion could be lost from only one of the possible hydrazide salt anions. This anion (VI) is not the one produced from

\[ C_{6}H_{5}CONSO_{2}C_{6}H_{5}Na^{+} \rightarrow [C_{6}H_{5}CONH_{2}] + SO_{2}C_{6}H_{5} \]

\[ C_{6}H_{5}CHO + N_{2} \]


the loss of the hydrogen expected to be the most acidic, but has a structure that is stabilized by resonance. In the formation of benzene from N'-phenylbenzenesulfonhydrazide the importance of the anion XXII that is necessary for 1,2-elimination is expected to be less, since this anion is stabilized by resonance with the phenyl ring. In both cases an ortho- or para-nitro group (on Ar of XXVI or XXVII) would be expected to aid rather than hinder this step.

nitrobenzaldehydes is unsatisfactory. There are two theoretically possible 1,2-elimination mechanisms which should be considered here, as these paths give a possible explanation for some of the observed facts. The first involves a shift of a hydrogen to produce the same intermediate (XIX and XXIV) as the 1,2-elimination. The second involves the shift of a pair of electrons rather than a hydrogen, to produce a dative bond (intermediates XX, XXI and XXV). These intermediates with dative bonds probably lack some of the resonance stabilization that occurs in the intermediates XIX and XXIV.

\[
\text{C}_6\text{H}_5\text{CON}=\text{NH} \leftrightarrow \text{C}_6\text{H}_5\text{C}(=\text{N})\text{NNH} \quad \text{XIX}
\]

The choice between the types of elimination becomes very important in postulating the products which each of the monomethyl derivatives IX-XI will give under the McFadyen-Stevens conditions.

IX. \( \text{C}_6\text{H}_5\text{CON}-(\text{CH}_3)\text{SO}_3\text{C}_6\text{H}_5 \)

X. \( \text{C}_6\text{H}_5\text{CON}-(\text{CH}_3)\text{NHSO}_2\text{C}_6\text{H}_5 \)

XI. \( \text{C}_6\text{H}_5\text{C}(\text{OCH}_3)\text{NNHSO}_2\text{C}_6\text{H}_5 \)

The decomposition of the intermediates (XIX, XX or XXI) may be explained by a homolytic fission in which the benzoyl radical is formed. This benzoyl radical then could extract a hydrogen from the solvent, ethylene glycol, or react with the hydrogen from XIX, XX or XXI

\[
\text{XIX, XX or XXI} \rightarrow \text{C}_6\text{H}_5\text{CO}^\cdot + \text{N}_2 + \text{H}^\cdot \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{N}_2
\]

the other half of the intermediate. This free radical reaction may be the surface catalyzed step and becomes the rate determining step in the absence of sufficient surface.

The heterolytic decomposition of the intermediate is also possible but will not be discussed. Much of this discussion is speculation, and, until more information is available about this reaction, the analogous reactions, and heterogeneous reactions in general, the selection of a mechanism is impossible.
EXPERIMENTAL DETAILS

The melting point determinations were carried out in a Hershberg melting point apparatus. All the temperatures are in degrees Centigrade, and the temperatures that are marked "corrected" were measured by total immersion thermometers that had been calibrated by the National Bureau of Standards. Manual temperature control was used for all the heating baths. The analyses of the composition of the compounds were carried out by the Clark Microanalytical Laboratory, Urbana, Illinois. Dr. Albert Antoine and Mr. Stanley Kopczynski deserve many thanks for measuring the infrared absorption spectra given in Appendix I. These spectra were measured on portions (muddled in Nujol) of the samples which were submitted for the composition analyses. A Baird Associates, Inc., Infra-red Recording Spectrophotometer was used. Characteristic infrared group frequencies were used as a basis for assigning some of the absorption peaks to groups believed to be present in each molecule.

Esters.—The acids were esterified using a mixture of 95% ethanol (120 to 500 ml. per mole acid), benzene (60 to 160 ml. per mole acid) and a catalytic quantity of sulfuric acid or hydrogen chloride. The reaction was forced to completion by distillation of the water-ethanol-benzene azeotrope through a column fitted with a head for returning to the column the water-poor upper layer of the distillate. When no more water came off (occasionally more catalyst was needed), the solvent was removed by distillation on a steam bath.

and the ester residue dissolved in ether. This solution was extracted with aqueous sodium bicarbonate, dried, and distilled under vacuum.

The following acids were treated in this manner: benzoic- (student material), 3-nitrobenzoic- (Eastman No. 558, 86% yield), 4-nitrobenzoic- (Eastman No. 183, 99% yield), furan-2-carboxylic- (Quaker Oats, 84% yield), and pyridine-3-carboxylic-acid (Eastman No. 2266 converted to the hydrochloride, 58% yield).

**Hydrazides.**—The esters were refluxed with an excess hydrazine hydrate (Mathieson) in 95% ethanol (200 ml. per mole) for several hours. Most of the solvent was then removed by distillation on a steam bath, and the hydrazide that solidified on cooling was collected by filtration. The hydrazides were recrystallized from water or 95% ethanol only in a few cases. The yields are given in Table VI. The procedures for two special cases are given below.

**2-Hydroxybenzhydrazide.**—Methyl 2-hydroxybenzoate (Orr, Brown, and Price) was treated as above (see Table VI), but too long a reflux period gave N,N'-bis-(2-hydroxybenzoyl)-hydrazine, m.p. 311° in 24% yield. The very low solubility of the latter compound in 95% ethanol made its separation from 2-hydroxybenzhydrazide very easy. A material, m.p. 99-100.5°, believed to be 2-hydroxybenzonitrile (10% yield), also separated out from the reaction mixture on standing. This material was soluble in sodium bicarbonate and reprecipitated on the addition of hydrochloric acid. Refluxing with 20% sodium hydroxide solution gave 2-hydroxybenzonic acid (identified by mixed melting point).

---

TABLE VI

Hydrazides from Esters

<table>
<thead>
<tr>
<th>Hydrazide</th>
<th>Excess N₂H₄, %</th>
<th>M.P., °C.</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CONHNH₂</td>
<td>10</td>
<td>112-112.5</td>
<td>89</td>
</tr>
<tr>
<td>3-NO₂C₆H₄CONHNH₂</td>
<td>70</td>
<td>153-155</td>
<td>93</td>
</tr>
<tr>
<td>4-NO₂C₆H₄CONHNH₂</td>
<td>10</td>
<td>212-214</td>
<td>85</td>
</tr>
<tr>
<td>2-HOC₆H₄CHO</td>
<td>10</td>
<td>147.5-148.3</td>
<td>50</td>
</tr>
<tr>
<td>CONHNH₂</td>
<td>50</td>
<td>75.5-76.5</td>
<td>88</td>
</tr>
<tr>
<td>N(CONHNH₂)</td>
<td>32</td>
<td>159.5-161</td>
<td>89</td>
</tr>
</tbody>
</table>

2,4,6-Trimethylbenzhydrazide—2,4,6-Trimethylbenzoyl chloride, 1.56 g. (0.0086 mole), was added dropwise to 1.5 g. (0.053 mole) of anhydrous hydrazine in 3 ml. pyridine (0.8 U.) with shaking and cooling in an ice bath. After about ten minutes the excess hydrazine and pyridine were removed by distillation under vacuum. The residue, which promptly solidified, was fractionally recrystallized from a mixture of water and ethanol, giving first a low melting material, then a little of a higher melting material, and finally more of the low melting material.

2. T. Curtius and O. Trachmann, ibid. (2) 51, 169 (1895).
3. Eastman No. 1716 has m.p. 153-155°C.
5. Eastman No. 3341 has m.p. 210-211°C.
8. T. Curtius and E. Mohr, Ber. 31, 2493 (1898).
The high melting material, N,N'-bis-(2,4,6-trimethylbenzoyl)-hydrazine (about 2% yield) was recrystallized from 95% ethanol; colorless solid m.p. 251-252.8° (corrected). The infrared absorption spectrum is given in Appendix I.

Anal. Calcd. for C_{20}H_{24}N_{2}O_{4} (m.w. 324.41): C, 74.0; H, 7.5; N, 8.6. Found: C, 73.8; H, 7.3; N, 8.7.

The low melting material (m.p. about 153°) was obtained in almost 98% yield, but the recrystallization from 60% ethanol was not satisfactory to provide a sample for analysis. This material was shown by later use to be the desired 2,4,6-trimethylbenzyldrazide.

Benzenesulfonyldrazides. — The hydrazides were treated as in the examples given below. The yields are given in Table VII.

N'-Benzensulfonylfurane-2-carbohydrazide. — Benzensulfonyl chloride (Eastman No. 32), 19.3 g. (0.11 mole), was added dropwise with stirring to 12.6 g. (0.10 mole) of furane-2-carbohydrazide in 80 ml. of pyridine cooled in an ice bath. After stirring three hours at room temperature, the reaction mixture, which then contained an orange precipitate, was poured on a mixture of ice and 40 ml. concentrated hydrochloric acid. After standing overnight, the wet solid (58 g.) was collected by filtration, washed with water, and recrystallized from 95% ethanol; colorless solid, m.p. 185.5-187.2° (corrected; with decomposition). Further crops raised the yield to 89%. The infrared absorption spectrum is given in Appendix I.

Anal. Calcd. for C_{11}H_{10}N_{2}O_{4}S (266.27): C, 49.6; H, 3.8; N, 10.5; S, 12.0. Found: C, 49.9; H, 3.7; N, 10.6; S, 12.2; m.w. 280, 296 (ebullioscopic methanol)
<table>
<thead>
<tr>
<th>Benzenesulfonylhydrazide</th>
<th>M.P., °C</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{H}_5\text{CONHNHSO}_2\text{C}_6\text{H}_5$</td>
<td>194-195</td>
<td>98</td>
</tr>
<tr>
<td>2-NO$_2\text{C}_6\text{H}_4\text{CONHNHSO}_2\text{C}_6\text{H}_5$</td>
<td>158.5-159.5</td>
<td>89</td>
</tr>
<tr>
<td>3-NO$_2\text{C}_6\text{H}_4\text{CONHNHSO}_2\text{C}_6\text{H}_5$</td>
<td>216-216.5</td>
<td>81</td>
</tr>
<tr>
<td>4-NO$_2\text{C}_6\text{H}_4\text{CONHNHSO}_2\text{C}_6\text{H}_5$</td>
<td>199-200</td>
<td>69</td>
</tr>
<tr>
<td>4-NH$_2\text{C}_6\text{H}_4\text{CONHNHSO}_2\text{C}_6\text{H}_5$</td>
<td>200.5-203</td>
<td>29</td>
</tr>
<tr>
<td>2,4,6-(CH$_3$)$_3\text{C}_6\text{H}_2\text{CONHNHSO}_2\text{C}_6\text{H}_5$</td>
<td>205.6-206</td>
<td>56</td>
</tr>
<tr>
<td>$\text{CONHNHSO}_2\text{C}_6\text{H}_5$</td>
<td>184.5-186.5</td>
<td>90</td>
</tr>
<tr>
<td>$\text{CONHNHSO}_2\text{C}_6\text{H}_5$</td>
<td>185.5-187.2</td>
<td>89</td>
</tr>
</tbody>
</table>

$N'$-Benzenesulfonyl-$4$-aminobenzhydrazide.—Benzenesulfonyl chloride, 17.6 g. (0.10 mole), was added dropwise with stirring to 16.6 g. (0.11 mole) of 4-aminobenzhydrazide (m.p. 222-225°C) in 80 ml. of pyridine cooled in an ice bath. After stirring two hours at room temperature, the reaction mixture was poured on a mixture of ice and 20 ml. of concentrated hydrochloric acid. An oil separated.

5. T. Curtius, J. Prakt. Chem. (2) 95, 336 (1917).
from this mixture and solidified on standing. The solidified oil was collected by filtration (26 g.), washed with water, and recrystallized from a little 95% ethanol yielding first the desired product (29% yield) and then a very soluble material. The N'-benzenesulfonyl-4-amino-benzhydrazide was recrystallized from 95% ethanol; colorless solid m.p. 200.5-203° (corrected). The infrared absorption spectrum is given in Appendix I.

Anal. Calcd. for C₁₃H₁₃N₃O₃S (291.32): C, 53.6; H, 4.5; S, 11.0. Found: C, 53.8; H, 4.5; S, 11.2.

N'-Benzenesulfonyl-2,4,6-trimethylbenzhydrazide.—Benzenesulfonyl-chloride, 1.0 g. (0.0056 mole), was added dropwise with shaking to 0.5 g. (0.0028 mole) of 2,4,6-trimethylbenzhydrazide in 2 ml. pyridine cooled in an ice bath. After standing an hour, the reaction mixture which then contained a precipitate, was poured on a mixture of ice and concentrated hydrochloric acid. An oil separated from this mixture and later solidified. After several hours the solid was collected by filtration, washed with water (56% yield), and recrystallized from 60% ethanol; colorless solid, m.p. 205.6-206° (corrected; with decomposition). The infrared spectrum is given in Appendix I.

Anal. Calcd. for C₁₆H₁₈N₃O₃S (318.39): C, 60.3; H, 5.7; N, 8.8. Found: C, 60.4; H, 5.8; N, 8.9.

Use of Stronger Bases.—N'-Benzenesulfonylbenzhydrazide was treated with sodium hydroxide in refluxing ethanol (b.p. 78°), but no evolution of nitrogen occurred. On cooling, sodium N'-benzenesulfonyl-benzhydrazide precipitated. No evolution of nitrogen also occurred when potassium t-butyrate in refluxing t-buty alcohol (b.p. 32°) was used,
but in this case the potassium salt precipitated on the addition of the base to the hot solution of the sulfonhydrazide. N'-Benzenesulfonylbenzhydrazide was precipitated (90% yield) from solutions of these salts in water by the addition of hydrochloric acid. Nitrogen\(^\text{o}\) (0.011 mole) was slowly evolved after potassium n-butylate (0.041 mole from 1.6 g. potassium) was added to 3.0 g. (0.011 mole) of N'-benzenesulfonylbenzhydrazide in refluxing butanol (b.p. 117°). No benzaldehyde, benzoic acid, or benzyl alcohol were found in the reaction mixture. Acidification of the reaction mixture gave a small quantity of an unidentified substance, m.p. 230°.

**Sodium N'-benzenesulfonylbenzhydrazide.**—Sodium, 2.4 g. (0.10 mole), was dissolved in 50 ml. of 100% ethanol under an atmosphere of nitrogen. This solution was added to 28 g. (0.10 mole) of N'-benzenesulfonylbenzhydrazide dissolved in 800 ml. of hot 100% ethanol, and the mixture cooled allowing the salt to slowly crystallize out. Colorless needles (93% yield) were obtained by filtration and washing with a little ethanol. The mother liquors in some cases were concentrated (under vacuum to prevent decomposition) to improve the yield. The infrared absorption spectrum is given in Appendix I.

Anal. Calcd. for C\(_{13}\)H\(_{11}\)N\(_2\)NaO\(_3\)S (298.30): C, 52.4; H, 3.7; N, 9.4; S, 10.8. Found: C, 51.0; H, 4.1; N, 9.2; S, 10.6; non-alkaline ash, 23.0 (calcd. for Na\(_2\)SO\(_4\), 23.8).

Sodium N'-benzenesulfonylbenzhydrazide, 2.00 g., was dissolved in 10 ml. of water and the solution filtered through a sintered glass
 funnel. N'-Benzenesulfonylbenzhydrazide (solubility about 0.016 g. per 100 ml. of water) and other insoluble material amounted to less than 0.01 g. Acidification with hydrochloric acid yielded the hydrazide in 96% yield. Duplicate results were obtained on a sample of salt that had stood seventeen months. This latter sample did not lose weight when dried under vacuum (< 0.1 mm.) over phosphorus pentaoxide for four hours (duplicate results).

General Results Using Salt.—Glass wool was tried as the first surface in the temperature range, 135-145°C, with a 5-30 minute reaction time. The type of vessel and stirrer varied with the size of the run and other requirements. In each case sodium N'-benzenesulfonylbenzhydrazide was added to the hot ethylene glycol which contained the glass wool. At the end of the reaction time the reaction mixture was cooled rapidly in an ice bath. Water was then added and the aldehyde extracted with ether. An aliquot of this extract was carefully concentrated¹ and then used to determine the yield of aldehyde by the Bryant-Smith² titration (hydroxyamine hydrochloride reagent and standard sodium hydroxide solution). A fluorescent lamp was found very helpful in obtaining reproducible end-points. These runs gave poor yields, but there seemed to be little difficulty in getting duplicate results (see Table VIII). The yields still dropped with time but to a very small extent.

The quantity of evolved nitrogen was measured in several of these runs but seemed to have little relation to the yield of aldehyde. A

1. Failure to distill the ether slowly caused in one case a loss of benzaldehyde equivalent to a 1.4% yield.

yield of nitrogen close to 100% was obtained if the reaction time were long enough (4-5 minutes at 160-165°C). The apparatus which worked best for adding the salt while collecting the nitrogen is shown in Figure 2. The powdered salt was placed in the inverted cylindrical addition tube with the plunger extended through the middle. The top was then packed slightly to keep the material from falling out when the tube was put in place. The tube was weighed before and after discharge. The plunger permitted a faster discharge than a piston. Later the apparatus shown in Figure 4 was found very useful for adding small quantities of sodium carbonate by turning the side joint which tipped the attached cup.

The nitrogen from 27.7 g. (0.093 mole) of sodium N'-benzene-sulfonylbenzhydrazide was passed through an efficient Dry Ice-acetone cooled trap. The ultraviolet absorptrum of the few drops of liquid that was collected by the trap showed no more than traces of benzaldehyde and benzene. Ethanol (95%) was used as both the solvent and the blank (see Figure 3). In another case the gas was analyzed for carbon monoxide, but none was found. The infrared absorption spectrum of this gas also showed no carbon monoxide since there was just one strong peak at 7.39 μ and two small peaks at 4.43 μ and 12.02 μ. These absorption peaks do not fit any expected gas.

Since the fairly mild conditions used above (5-30 minutes at 135-145°C) did not give improved yields of benzaldehyde, the temperature range, 160-165°C, with shorter reaction times was investigated using

1. The author greatly acknowledges the micro gas volumetric analyses conducted by Dean Walton, The Ohio State University.
**TABLE VIII**

Pyrolysis of Sodium N'-Benzenesulfonylbenzhydrazide

<table>
<thead>
<tr>
<th>Millimole of hydrazide salt*</th>
<th>Volume (l.) of ethylene glycol per mole hydrazide</th>
<th>Time, min</th>
<th>Temperature, °C</th>
<th>Yield by Bryant-Smith titration, %</th>
<th>Yield as 2,4-dinitrophenylhydrazone, %</th>
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*Glass wool was used for the surface except where other materials are indicated.

*Powdered charcoal was used for the surface.

*Barium carbonate was used for the surface.

*Barium hydroxide was used for the surface.
TABLE VIII—Continued

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<th>Millimole of hydrazide salt*</th>
<th>Volume (l.) of ethylene glycol per mole hydrazide</th>
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<th>Temperature, °C</th>
<th>Yield by Bryant-Smith titration, %</th>
<th>Yield by 2,4-dinitrophenylhydrazine, %</th>
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*Glass wool was used for the surface except where other materials are indicated. Charcoal, barium carbonate, barium hydroxide, and Pyrex glass wool as surfaces (see Table VIII). The glass wool gave consistently better results than charcoal or barium carbonate. This seemed to indicate that the mildly alkaline nature of the glass wool was not the important feature for the catalysis. The barium ion did not seem to precipitate any of the sulfonhydrazide ion. Throughout this study no effect due to changes in quantity of the solvent or surface (unless limited to vessel walls) was noted. A 10% yield of benzaldehyde was obtained when sodium N'-benzenesulfonylbenzhydrazide was
Apparatus for salt addition and nitrogen collection

Figure 2
UNKNOWN MIXTURE FROM DRY ICE TRAP IN 500 ML 95% ETHANOL

0.001% BENZALDEHYDE IN 95% ETHANOL (BY VOLUME)

1% ETHYLENE GLYCOL IN 95% ETHANOL (BY VOLUME)

0.1% BENZENE IN 95% ETHANOL (BY VOLUME)
heated five minutes at 160-165°C without a solvent.

Pyrolysis of Sodium N'-benzenesulfonylbenzhydrazide.—A series of runs were made to determine more definitely the effect of reaction time on the yield of benzaldehyde (see Figure 1, and Table VIII). Sodium N'-benzenesulfonylbenzhydrazide (about 0.0020 mole) was carefully weighed on a small piece of paper and then added to 5 ml. of ethylene glycol in a 2.5 cm. x 15 cm. test tube heated in a glycerol bath and stirred by about 0.2 g. of pyrex glass wool. The glass wool was held in the eye of a mechanical stirrer. Care was used to scrape down any material which stuck to the walls of the tube. At the end of the desired time the glycerol bath was quickly replaced by an ice bath. The reaction mixture was filtered through a sintered glass funnel into a methanol solution that was 0.05 M in 2,4-dinitrophenylhydrazine and 0.5 M in hydrochloric acid. The tube, stirrer, and funnel were then rinsed with 0.5 M hydrochloric acid in methanol. After standing several hours, the benzaldehyde 2,4-dinitrophenylhydrazone was collected by filtration, washed by allowing 5-10 ml. of the acidic methanol solution to filter through without suction and dried to constant weight.

Accuracy of Determinations.—The above analytical procedures were tested using freshly distilled (alkaline washed) benzaldehyde dissolved in 95% ethanol. Duplicate results on aliquots of this solution were obtained for each of the following methods: 2,4-dinitrophenylhydrazine in methanol reagent (values about 1% high), aqueous 2,4-dinitrophenylhydrazine reagent1 (± 1%), and the Bryant-Smith

titration (about 1% low). Throughout this work there are a number of
determinations with values lower than expected from the trend of
other values, but few if any gave high values. The heating baths were
not controlled by thermostats, thus small variations in the temperature
accounted for some deviation in the experimental results.

Benzaldehyde.—Anhydrous sodium carbonate was carefully weighed
on a piece of paper and then added to a mixture of about 0.0018 mole
N'-benzenesulfonyl benzhydrazide, 0.2 g. of powdered soft glass (finer
than 30 mesh) and 5 ml. of ethylene glycol in a 2.5 cm. x 15 cm. test
tube heated in a glycerol bath and stirred mechanically. The mixture
was then worked up as above using the 2,4-dinitrophenylhydrazine
reagent. The yields are shown in Table IX.

Pyridine-3-carboxaldehyde.—N'-Benzenesulfonylpyridine-3-carbo-
hydrazide (0.00110 mole) was treated with sodium carbonate, (about
0.00060 mole) 0.1 g. powdered soft glass, and 3 ml. of ethylene glycol
in a manner similar to the above preparation of benzaldehyde. The
yields are shown in Table IX. The pyridine-3-carboxaldehyde 2',4'-
dinitrophenylhydrazone was recrystallized from 95% ethanol; orange
solid, m.p. 258.5-259.5° (corrected). The infrared absorption
spectrum is given in Appendix I.

Anal. Calc'd. for C₁₂H₁₀N₅O₄ (287.23): C, 50.2; H, 3.1; N, 24.4.
Found: C, 50.2; H, 3.1; N, 23.8.

2,4,6-Trimethylbenzaldehyde.—N'-Benzenesulfonyl-2,4,6-trimethyl-
benzhydrazide (about 0.00033 mole) was treated with sodium carbonate,
0.05 g. powdered soft glass and 1.5 ml. of ethylene glycol in a
manner similar to the above preparation of benzaldehyde. The yield
### Table IX

Aldehydes Using the Modified Procedure

<table>
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<tr>
<th>Aldehyde</th>
<th>Yield, %</th>
<th>Time, min.</th>
<th>Temperature, °C</th>
<th>Equivalents of Na₂CO₃</th>
<th>Volume (l.) CO₂</th>
<th>Millimoles of Hydrazide</th>
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<tr>
<td>2,4,6-(CH₃)₃C₆H₂CHO</td>
<td>36</td>
<td>3.0</td>
<td>165</td>
<td>1.16</td>
<td>2.6</td>
<td>1.16</td>
</tr>
<tr>
<td>4-CHO (36)</td>
<td>61</td>
<td>2.0</td>
<td>165</td>
<td>1.1</td>
<td>2.8</td>
<td>1.09</td>
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<tr>
<td></td>
<td>64</td>
<td>3.0</td>
<td>165</td>
<td>1.1</td>
<td>2.8</td>
<td>1.08</td>
</tr>
<tr>
<td>5-CHO (36)</td>
<td>61</td>
<td>3.0</td>
<td>165</td>
<td>1.16</td>
<td>2.6</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>3.0</td>
<td>165</td>
<td>1.16</td>
<td>2.6</td>
<td>1.16</td>
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<td>165</td>
<td>4.7</td>
<td>2.9</td>
<td>1.72</td>
</tr>
</tbody>
</table>

*Powdered soft glass was used for the surface except where other materials are indicated.

*No surface other than Na₂CO₃.

*Yield by distillation.

*Activated charcoal was used for the surface.

*Copper dust was used for the surface.

*Thiosemicarbazide was used to prevent decomposition.
was 38% (see Table IX). The 2',4',6-trimethylbenzaldehyde 2',4'-di-
nitrophenylhydrazone was recrystallized from 95% ethanol; red solid, m.p. 256-257° (corrected). The infrared absorption spectrum is given in Appendix I.

**Anal. Calcd. for C_{15}H_{16}N_{4}O_{4} (328.32): N, 17.5. Found: N, 17.1.**

**Other Aldehydes.**—2-Hydroxy-, 3-nitro-, 4-nitro-, and 4-amino-
benzaldehyde and furane-2-carboxaldehyde were prepared in a manner similar to the above examples determining the yields in each case as the corresponding 2,4-dinitrophenylhydrazone. The yields are given in Table IX.

**Effect of Ultraviolet Light.**—A Vycor (quartz) test tube containing 0.51 g. (0.0017 mole) N'-benzenesulfonylbenzhydrazide, a Vycor test tube containing 0.51 g. (0.0017 mole) sodium N-benzenesulfonylbenzhy-
drazide, and a Pyrex test tube (wrapped with several layers of paper) also containing 0.50 g. (0.0017 mole) of the salt, were placed in a glycerol heating bath under a strong ultraviolet light source. Each tube contained 10 ml. of ethylene glycol and was equipped with a birefringometer. The only surfaces were the walls of the test tubes. The temperature was raised slowly until solution was complete, and then the tubes were kept at 160-162°. No nitrogen was evolved from the first tube, but the other two gave nitrogen at about equal rates. A 95% yield of nitrogen was obtained after 15 min. at 162° from the Vycor tube, but an accident prevented a final reading for the shielded tube. The yields of benzaldehyde were respectively 81% and 78% (crude).

**Silver Benzoate Catalyst.**—A 0.50 M solution of silver benzoate dissolved in triethyl amine was added with stirring in small portions
to 0.66 g. (0.0022 mole) sodium N'-benzenesulfonylbenzhydrazide dissolved in 10 ml. of 100% methanol at room temperature. An apparatus similar to that shown in Figure 2 was used with the addition tube replaced by a dropping funnel. Each addition of reagent caused a temporary evolution of nitrogen. After 8.2 ml. (0.0041 mole) had been added over a four hour period 0.0019 mole (85% yield) of nitrogen was obtained. During this time a black silver mirror formed on the stirrer and reaction vessel. No precipitate was formed when a little of the reaction mixture was added to 2,4-dinitrophenylhydrazine reagent. On standing, a white precipitate formed in the reaction mixture. The reaction mixture was placed in ether but did not completely dissolve. Extraction with sodium bicarbonate solution also did not dissolve all of this precipitate. The insoluble material seemed to be a silver salt. The aqueous extract was filtered and heated to drive off ether, methanol, and triethylamine. Acidification gave 0.36 g. (0.0029 mole) benzoic acid, m.p. and mixed m.p. 120-122°. Triethylamine was the only material found on distillation of the ether solution and was identified as the picrate, m.p. and mixed m.p. 172-173°.

Supersaturation of Nitrogen.—Ethylene glycol, 25 ml., was placed in a glass tube (see Figure 5) supported in a high pressure bomb. The bomb was swept out with nitrogen twice, and shaken for six hours at 20° under a nitrogen pressure of 1875 p.s.i. The bomb was then vented and carefully opened so that the ethylene glycol was in the end of the glass tube with the female joint. This was quickly, but carefully, connected to the addition tube shown in Figure 4. Glass
powder was dumped from the cup to cause the evolution of about 40 ml.
of nitrogen gas from the supersaturated ethylene glycol.

Methylation of N'-Benzenesulfonylbenzhydrazide.—Methyl sulfate
(0.55 mole) was added dropwise with stirring to
3.8 g. (0.050 mole) of N'-benzenesulfonylbenzhydrazide and sodium
hydroxide (0.050 mole) dissolved in 100 ml. of water at room tempera
ature. The mixture remained alkaline until the last of the methyl
sulfate was added. After another hour of stirring, the precipitate,
which formed during the reaction, was collected by filtration and
mixed well with sodium hydroxide solution to be sure all base-soluble
material was dissolved. The insoluble portion was collected by
filtration and recrystallized from 95% ethanol to give colorless
dimethyl derivative, m.p. 91-92.5°C (corrected) in about 9% yield.

The infrared absorption spectrum is given in Appendix I. This material seemed to be N-benzenesulfonyl-N'-\(1\)-methoxybenzylidene)-N-methyl-

hydrazine (I).

Anal. Calcd. for \(C_{15}H_{16}N_2O_3S\) (304.36): C, 59.2; H, 5.3; N, 9.2;
S, 10.5; OCH\(_3\), 0.0 or 10.2. Found: C, 59.5; H, 5.6; N, 8.9; S,
10.7; OCH\(_3\), 5.1.

I. \(C_6H_5C(OCH_3)\equiv\text{NN(CH}_3\text{)}SO_2C_6H_5\)

II. \(C_6H_5CONHN(CH_3)SO_2C_6H_5\)

III. \(C_6H_5C(OCH_3)\equiv\text{NNHSO}_2C_6H_5\)

The base-soluble material was reprecipitated with hydrochloric acid and fractionally recrystallized from 95% ethanol yielding two monomethyl derivatives. The first crops (57% yield; sharp melting) were recrystallized from 95% ethanol; colorless solid, m.p. 186-
189.2°C (corrected). The infrared absorption spectrum is given in appendix I. This material seemed to be N'-benzenesulfonyl-N'-
methylbenzhydrazide (II).

Anal. Calcd. for \(C_{14}H_{14}N_2O_3S\) (290.33): C, 57.9; H, 4.9; N, 9.6;
S, 11.0; \(\text{-CH}_3\) (on N), 0.0 or 5.2. Found: C, 57.9; H, 4.9; N, 9.1; 9.3;
S, 11.5; \(-\text{OCH}_3\), 0.0; \(-\text{CH}_3\) (on N), 3.5, m. v. 340, 346 (ebullioscopic methanol).

The other crops were a second monomethyl derivative (21% yield; sharp melting) and were also recrystallized from 95% ethanol; colorless solid, m.p. 164.5-166°C (corrected). The infrared absorption spectrum is shown in Appendix I. This material seemed to be N-benzenesulfonyl-
N'-\(1\)-methoxybenzylidene)-hydrazine (III).
Methylphenylsulfone. — Methyl sulfate, 15 ml. (0.16 mole) was added dropwise with stirring to 5.5 g. (0.020 mole) of N'-benzene-sulfonylbenzhydrazide in 40 ml. of water at 80-90°. This temperature is slightly above the point where the salt of this hydrazide starts to evolve nitrogen. Sodium hydroxide was also added dropwise in order to keep the mixture just slightly basic. After a total of 2.5 hours the mixture was cooled and an oil separated and later solidified. This solid was collected by filtration and the reaction mixture extracted with ether. The precipitate and the residue from the concentration of the ethereal extract were recrystallized from cyclohexene yielding methylphenylsulfone in 72% yield; m.p. 86.2-86.7° (corrected).

Anal. Calcd. for C\textsubscript{14}H\textsubscript{14}N\textsubscript{2}O\textsubscript{3}S (290.33): C, 57.9; H, 4.9; N, 9.6; S, 11.0; -CH\textsubscript{3}, 0.0 or 10.7. Found: C, 57.1; H, 4.8; N, 9.8; S, 11.2; -CH\textsubscript{3}, 0.2, 0.4; -CH\textsubscript{3} (on N) 0.85.

About the same results were obtained when methyl iodide was used instead of methyl sulfate.

Methylphenylsulfone.—Methyl sulfate, 15 ml. (0.16 mole) was added dropwise with stirring to 5.5 g. (0.020 mole) of N'-benzene-sulfonylbenzhydrazide in 40 ml. of water at 80-90°. This temperature is slightly above the point where the salt of this hydrazide starts to evolve nitrogen. Sodium hydroxide was also added dropwise in order to keep the mixture just slightly basic. After a total of 2.5 hours the mixture was cooled and an oil separated and later solidified. This solid was collected by filtration and the reaction mixture extracted with ether. The precipitate and the residue from the concentration of the ethereal extract were recrystallized from cyclohexene yielding methylphenylsulfone in 72% yield; m.p. 86.2-86.7° (corrected).

Acidification of the reaction mixture gave almost a quantitative yield of benzoic acid, m.p. and mixed m.p. 122-122.5°.

N'-Benzenesulfonyl-N-Methylbenzhydrazide.—Sodium hydroxide solution (0.10 mole) was added with stirring to 7.2 g. (0.050 mole) of methylhydrazine sulfate,\textsuperscript{1} partially dissolved in 20 ml. of pyridine. Benzoyl chloride (Coleman and Bell), 7.0 g. (0.050 mole) was then added.

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dropwise with stirring and cooling in an ice bath. After several
minutes 9.0 g. (0.050 mole) of benzenesulfonyl chloride was also
added dropwise. The reaction mixture was poured into water and the
precipitate recrystallized from 95% ethanol; colorless solid, m.p.
145-145.3° (corrected). Further crops raised the yield to 38%. The
infrared absorption spectra is given in Appendix I. Attempts to isolate
N-methylbenzhydrazide as a pure compound failed.¹

Anal. Calcd. for C₁₄H₁₄N₂O₃S (290.55): C, 57.9; H, 4.9; N, 9.7;
S, 11.0. Found: C, 58.2; H, 5.1; N, 9.7; S, 10.7; m.w. 240, 250.
(EBulliOsCopic benzene); -CH₃, 0.37; -CH₃(onN), 3.89.

Benzaldehyde N-Benzoylmethylhydrazone.—Methylhydrazinesulfate,
1.4 g. (0.010 mole) was treated with 1.4 g. (0.010 mole) of benzoyl
chloride as in the above reaction. After several minutes 1.2 g.
(0.012 mole) of benzaldehyde (Coleman and Bell) was added dropwise.
The reaction mixture was then poured into very dilute hydrochloric
acid and the precipitate recrystallized from 60% ethanol; colorless
solid, m.p. 81.5-82.5° (reported¹ m.p., 82°), 38% yield.

Attempted Decomposition of N,N'-Dibenzoylhydrazine.—Anhydrous
sodium carbonate, 0.11 g. (0.0010 mole), and a little powdered soft
glass were quickly added (using apparatus of Figure 3) to 0.24 g.
(0.0010 mole) of N,N'-dibenzoylhydrazine² dissolved in 5 ml. of
ethylene glycol at 160-170°. Very little nitrogen was evolved over a
two and one-half hour period. On addition of the reaction mixture to

1. A. Michaelis and E. Hadamcz, Ber. 41, 3288 (1908).

1943, p. 208.
water and acidification, most of the \( N,N' \)-dibenzoylhydrazine was reclaimed. Similar results were obtained using sodium \( N,N' \)-dibenzoylhydrazine in ethylene glycol (to \( 200^\circ \)) and glycerol (to \( 280^\circ \)). 2,4,-Dinitrophenylhydrazine reagent was used at several points to show the absence of aldehyde.

**Benzenesulfonhydrazide and \( N,N' \)-Bis-(benzenesulfonyl)-hydrazine.**

An attempt to repeat the rather indefinite procedure\(^1\) for the preparation of benzenesulfonhydrazide gave a considerable quantity of \( N,N' \)-bis-(benzenesulfonyl)-hydrazine. The recommended procedure involved the addition of sufficient ethanol to the aqueous hydrazine mixture to dissolve the benzenesulfonyl chloride as fast as it was added. A good yield of benzenesulfonhydrazide, however, was obtained when 44 g. \((0.25 \text{ mole})\) of benzenesulfonyl chloride was added in a steady stream with rapid stirring to 16 g. \((0.50 \text{ mole})\) of anhydrous hydrazine in 100 ml. of 100% ethanol cooled in an ice bath. The precipitate that formed during the reaction was filtered off after a few more minutes and recrystallized from 95% ethanol; colorless solid, m.p. 92-94\(^\circ\). All attempts to raise the melting point to the reported 104-106\(^\circ\) value failed; for even recrystallization converted considerable benzenesulfonhydrazide to \( N,N' \)-bis-(benzenesulfonyl)-hydrazine. The compounds were easily separated, since benzenesulfonhydrazide was much less soluble and remained as an oil when a small quantity of hot 95% ethanol was used. \( N,N' \)-Bis-(benzenesulfonyl)-hydrazine crystallized well from 95% ethanol as a colorless solid, m.p. 219.5-220\(^\circ\). Pyridine was never tried as a reaction medium; for the reaction of benzenesulfonyl chloride.

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sulfonyl chloride with the ethanol or water was very limited.

Pyrolysis of \(N,N'\)-Bis-(benzenesulfonyl)-hydrazine.—The pyrolysis of this compound has been reported,\(^1\) but the products were not clearly defined. \(N,N'\)-Bis-(benzenesulfonyl)-hydrazine, 1.0 g. (0.0033 mole) was placed in 10 ml. of ethylene glycol and the temperature raised to 140-145°. Solution took place rapidly, and a gas was evolved slowly. The addition of powdered glass greatly increased the rate of gas evolution, but the reaction still was not complete at the end of ten minutes. The reaction mixture was added to 30 ml. of water and a precipitate formed. This precipitate did not completely dissolve on adding sodium hydroxide, so was collected with the powdered glass on a sintered glass funnel. Acidification of the filtrate with hydrochloric acid yielded 0.202 g. of crude starting material, m.p. 211-213°.

\(p\)-Benzoquinone\(^2\) was used to precipitate the benzenesulfonic acid from the acidic filtrate as crude 2,5-dihydroxydiphenyl sulfone,\(^3\) m.p. 193-195°, (25% yield based on the unreclaimed starting material). This was a good yield considering the instability of benzenesulfonic acid. The insoluble material (< 0.1 g.) which was collected with the powdered glass was recrystallized from 95% ethanol, m.p. 59-60°. This solid depressed the melting point of diphenyldisulfone (m.p. 42-44°) which was prepared by refluxing benzenesulfonic acid with dilute hydrochloric acid.

\(^1\) T. Curtius and F. Lorenzen, J. prakt. Chem. (2) \(58\), 160 (1898)
\(^3\) O. Hinsberg, Ber. \(27\), 3259 (1894).
SUMMARY

Eighty-one examples of the McFadyen-Stevens aldehyde synthesis are tabulated in Tables I, II and III. The reported procedure, which involved the addition of a large excess of sodium carbonate to an acylaryl sulfonfnyldrazide in hot ethylene glycol, was reviewed. The yields from this procedure decreased rapidly on prolonged heating. An investigation of the reaction indicated the following facts:
1. the reaction is catalyzed by almost any surface; 2. the excess sodium carbonate is not necessary when the reaction is catalyzed by a surface; 3. the yield is only slightly affected by time when only one equivalent of sodium carbonate and a surface are used; and 4. a high temperature (165°C) and short reaction time (4 min.) are still advantageous. The modified procedure, which involves the addition of slightly more than one equivalent of sodium carbonate to a suspension of powdered glass in a solution of the acylaryl sulfonfnyldrazide in hot ethylene glycol, was used with a series of aldehydes. The aldehydes, their best yields (in %) by this modified procedure and their highest previously reported yields (in %) respectively are listed below:

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Modified Procedure</th>
<th>Previously Reported</th>
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<tbody>
<tr>
<td>C₆H₅CHO</td>
<td>81, 73</td>
<td></td>
</tr>
<tr>
<td>2-NOC₆H₄CHO</td>
<td>59, 55</td>
<td></td>
</tr>
<tr>
<td>3-NO₂C₆H₄CHO</td>
<td>52, 42</td>
<td></td>
</tr>
<tr>
<td>4-NO₂C₆H₄CHO</td>
<td>4, 0</td>
<td></td>
</tr>
<tr>
<td>4-NH₂C₆H₄CHO</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>2,4,6-(CH₃)₃C₆H₂CHO</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>

The previously proposed reaction path was elaborated in light of recent work, but insufficient evidence still prevents the selection...
this mechanism over any of the others. A part of this mechanism study was the alkylation of sodium N'-benzenesulfonylbenzhydrazide. Two monomethyl derivatives and one dimethyl derivative were formed. A third monomethyl derivative was prepared from methylhydrazine. Structures were tentatively assigned to these compounds.

**FUTURE WORK**

An essential part of proving a mechanism is the isolation of all the side-products. Very few have been found in the MCFadyen-Stevens procedure. A greater effort should thus be made to account for all of the starting material.

The effect of using other benzenesulfonyl chlorides should be investigated. 2,5-Dichlorobenzenesulfonylbenzhydrazide was found to give the same yield of benzaldehyde as the corresponding benzenesulfonyl compound at a much lower temperature. The reaction rate was much slower, and this compound may thus be more suitable for a rate study. The improved procedure should be tested on the compounds made from these other benzenesulfonyl chlorides. Substituents placed on the two benzene rings of benzenesulfonylbenzhydrazide affect the relative acidity of the two activated hydrogens, and thus may determine the yield to some extent. For example, if the failure to obtain 4-nitrobenzaldehyde from benzenesulfonyl-4-nitrobenzhydrazide was that the "amide" hydrogen was now more acidic than the "sulfonamide" hydrogen, then the difficulty could be overcome by using N'-(4-nitrobenzenesulfonyl)-4'-nitrobenzhydrazide.

The decomposition of the aldehyde has been a factor in determining the yield of most of the examples of the reported MCFadyen-
Stevens procedure. The improved procedure eliminates this factor, and may allow the demonstration of a correlation of the yields to the ionization constants of the corresponding acids.

The brief study of suitable solvents carried out by McFadyen and Stevens should be extended. The possibility of solvation effects and the role in a free radical mechanism should receive special attention.

An attempt to extend the scope of the reaction to aldehydes like trifluoroethanal and 2,2-dimethylpropanal (no alpha-hydrogen), and to dialdehydes should be made. The preparation of unsaturated aldehydes also needs reinvestigation.

The fact that glass gave the best results opens the possibility that a better surface still may be found. A survey should be made of other reactions in which a gas is evolved to see if the addition of a surface catalyst will result in better yields.

The study of the preparation, structure, and decomposition of the methyl derivatives, although not directly associated with the McFadyen-Stevens procedure, should be a very interesting investigation.
Figure 1

Figure 6

Figure 7

APPENDIX I

INFRARED ABSORPTION SPECTRA

\[ \text{C}_6\text{H}_5\text{CONHNHSO}_2\text{C}_6\text{H}_5 \]
APPENDIX I

INFRARED ABSORPTION SPECTRA

Figure 8

Figure 9

$\text{C}_6\text{H}_5\text{CONHN(CH}_3\text{)}_2\text{SO}_2\text{C}_6\text{H}_5$

$\text{C}_6\text{H}_5\text{CONHN(CH}_3\text{)}_2\text{NSO}_2\text{C}_6\text{H}_5$

Wave numbers in cm$^{-1}$

Wave length in microns
APPENDIX I

INFRARED ABSORPTION SPECTRA

\[ C_6H_5C(\text{OCH}_3) = \text{NNH}_2 \text{SO}_2 \text{C}_6\text{H}_5 \]

\[ C_6H_5C(\text{OCH}_3) = \text{NN} (\text{CH}_3) \text{SO}_2 \text{C}_6\text{H}_5 \]

\[ \text{SO}_2 \]

\[ \text{NUJO} \]

\[ \text{NH} \]
Figure 12

Figure 13
Figure 14

Figure 15
The infrared absorption spectra of the methyl derivatives (II-IV, VI) were not helpful in confirming the assignment of structures. There were, however, some features of these spectra which deserve comment. Each compound had an absorption peak in the range 1710-1635 cm.⁻¹ (5.85-6.11 μ) where the Amide I peak is found. These absorption peaks for compounds IV and VI, perhaps, may be attributed to the CH₃O-C=N group whose absorption is intensified by the methoxy group. This effect of the methoxy is well-known in the CH₃O-C=O group. The occurrence of the absorption peak for compound IV in the Amide II range (1590-1480 cm.⁻¹ or 6.29-6.75 μ), however, was not expected. No absorption peaks were found in this range for compounds III and VI, but this absence for compound III was not expected since compound III was made from methyl hydrazine. The spectral similarities of compound IV to compound I or compound II suggested that compound

1. The author is grateful to Dr. James L. Johnson, Upjohn Corp., Kalamazoo, Michigan for criticizing these spectra.

2. Compound V has not been isolated.

3. The –C=N group generally absorbs at 1665-1660 cm.⁻¹ (6.00-6.02 μ).
IV might be a polymorph of compound I or II. Spectra of Nujol mulls cannot be used to identify polymorphs, since the crystalline structure effects the spectra. The spectra of solutions of 0.100 g. of these compounds in 3.00 ml. pyridine (with pyridine as blank) using The Perkin-Elmer Corporation, Recording Infrared Spectrophotometer, however, had sufficient differences in the amplitude and width of the absorption peaks to exclude this possibility of polymorphism.
I, Edward George Cafilisch, Jr., was born in Union City, Pennsylvania, December 6, 1925. All but the first year of my elementary and secondary education was obtained in the public schools of that city. My undergraduate training, which was taken at Allegheny College, Meadville, Pennsylvania, was temporarily interrupted by a period of military service. I graduated from a United States Navy electronics school in 1945. After returning to Allegheny College, I received the degree Bachelor of Science in 1948. I was married to Dorothy Gail Barrett in 1949 and a son, George Barrett, was born in 1952. While in residence at The Ohio State University, where I specialized in Organic Chemistry, I received an appointment as the Union Carbide and Carbon Fellow for the year 1952-53. I also acted as Assistant and Research Assistant in the Department of Chemistry during the year 1951-52 and the year 1953-54 up to the time of completion of the requirements for the degree, Doctor of Philosophy.