

**Chemistry of Sulfoacetic Acid Derivatives. III.<sup>1</sup>**  
**Reactions of Derivatives of Sulfoacetic Acid, Benzoylmethanesulfonic Acid,**  
**and *p*-Nitrophenylmethanesulfonic Acid with Salicylaldehydes**

Bernard E. Hoogenboom,\* Muhammed S. El-Faghi, Steven C. Fink, Philip J. Ihrig,  
 Arne N. Langsjoen, Carol J. Linn, and Kevin L. Maehling

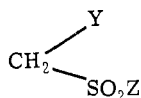
*Department of Chemistry, Gustavus Adolphus College, St. Peter, Minnesota 56082*

Received October 3, 1974

Diphenyl sulfoacetate (1a), sulfoacetic acid dianilide (1b), and carbophenoxymethanesulfonanilide (1c) react with salicylaldehydes under the conditions of the Knoevenagel reaction to form products characterized as coumarins (2). Phenyl *N*-phenylcarbonylmethanesulfonate (1d), phenyl benzoylmethanesulfonate (1e), and phenyl *p*-nitrophenylmethanesulfonate (1f) condense with salicylaldehydes to form sultones (4) by mechanisms involving nucleophilic transesterification at a sulfophenoxy sulfonyl group. The transesterification, hydrolysis, and anilino-lysis reactions of 1f and the conversion of 1d, 1e, and 1f to sultones appear to proceed analogously via sulfene intermediates.

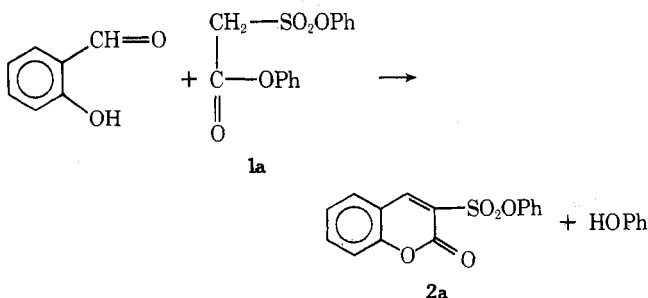
In a previous communication,<sup>1a</sup> we have demonstrated that diphenyl sulfoacetate (1a) undergoes a number of classical reactions at its central methylene group (in its anionic form) and nucleophilic substitution reactions at both the carbophenoxy and the sulfophenoxy groups. The unusual reactivity of the sulfophenoxy group toward nucleophiles was noted and was attributed to its proximity to the electron-withdrawing carbophenoxy group and its ability to form a sulfene intermediate ( $>C=SO_2$ )<sup>2</sup> under the basic conditions of the reactions studied.

We now wish to summarize another series of related reactions performed with 1a, with the dianilide (1b) and phenyl ester anilide (1c, 1d) derivatives of sulfoacetic acid, and with phenyl esters (1e, 1f) of other similar negatively substituted methanesulfonic acids indicated generally by structure 1.



- 1a, Y = CO<sub>2</sub>Ph; Z = OPh  
 b, Y = CONHPh; Z = NHPh  
 c, Y = CO<sub>2</sub>Ph; Z = NHPh  
 d, Y = CONHPh; Z = OPh  
 e, Y = COPh; Z = OPh  
 f, Y = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; Z = OPh

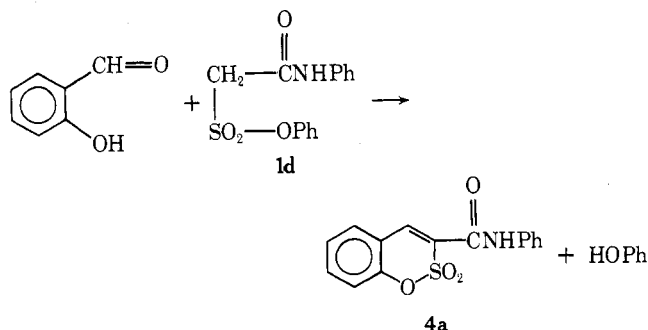
The members of this series of compounds react rapidly and in high yields with salicylaldehydes to form cyclic condensation products. For example, 1a condenses with salicylaldehyde to produce a material that has been characterized as phenyl 3-coumarinsulfonate (2a).<sup>3</sup> A number of



such coumarins (Table I) have been derived from variously substituted salicylaldehydes and 1a, 1b, and 1c. In a parallel study, it was found that diphenyl malonate could be converted with the same salicylaldehydes to a series of previously unknown 3-carbophenoxy coumarins (3) (see Table II).

The formation of coumarin derivatives from 1a, 1b, 1c, and diphenyl malonate is catalyzed by piperidine, the usual Knoevenagel reaction catalyst.<sup>4</sup> A variety of other basic agents, such as pyridine, potassium carbonate, sodium acetate, potassium fluoride, and the hydroxy, carbonate, and acetate forms of Dowex 1X4 anionic exchange resin,<sup>4,5</sup> all proved to be as effective as piperidine in promoting the reaction. Diphenyl malonate is generally more reactive with salicylaldehyde than 1a under the same experimental conditions.<sup>6</sup> Both diphenyl malonate and 1a failed to react with *o*-hydroxyacetophenone under all conditions attempted.

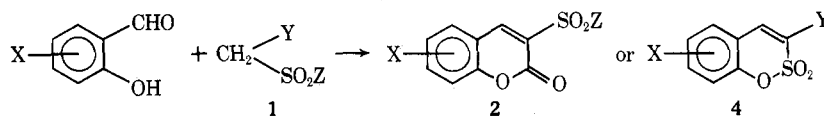
1a fails to react with benzaldehyde or *p*-nitrobenzaldehyde under the usual conditions of the Knoevenagel reaction.<sup>4</sup> Its facile condensation with salicylaldehydes is apparently dependent upon the formation of the stable lactone structure of the coumarin (2) by a transesterification occurring, as a crucial step, at the carbonyl portion of the carbophenoxy group in 1a. A nucleophilic displacement of the phenoxide ion at the sulfonyl portion of the sulfophenoxy group is apparently not favored in this case and therefore no sultone (4) is formed. Similarly, the dianilide (1b) and carbophenoxymethanesulfonanilide (1c), in condensing with salicylaldehyde, both form *N*-phenyl-3-coumarinsulfonamide (2i) by mechanisms involving nucleophilic attack at the carbonyl groups in 1b and 1c. In contrast, the isomer of 1c, phenyl *N*-phenylcarbonylmethanesulfonate (1d), forms sultones 4a and 4b (see Table I) when treated



with salicylaldehyde and 3-nitrosalicylaldehyde by mechanisms which must involve nucleophilic transesterification at the sulfonyl group in 1d. In an analogous manner, phenyl benzoylmethanesulfonate (1e) and phenyl *p*-nitrophenylmethanesulfonate (1f) both form the corresponding sultones (4c-f and 4g-j).<sup>7</sup>

As reported previously for 1a,<sup>1a</sup> compounds 1e and 1f both react in refluxing pyridine with aniline to form the

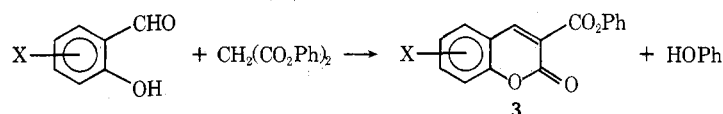
**Table I**  
Cyclization Reactions of Compounds 1a-f with Salicylaldehydes



| Salicylaldehyde |   | Substituent |   |      | Condi-<br>tions <sup>a</sup> | Product | Formula <sup>b</sup>  | Yield, % | Mp, °C <sup>c</sup> |
|-----------------|---|-------------|---|------|------------------------------|---------|---|----------|---------------------|
| Registry no.    | Substituent, X                          | Compd       | Y   | Z    |                              |         |   |          |                     |
| 90-02-8         | H                                       | 1a          | CO <sub>2</sub> Ph                                      | OPh  | B                            | 2a      | C <sub>15</sub> H <sub>10</sub> O <sub>5</sub> S                | 77       | 138-139             |
| 89-55-4         | 5-Br                                    | 1a          | CO <sub>2</sub> Ph                                      | OPh  | B <sup>d</sup>               | 2b      | C <sub>15</sub> H <sub>9</sub> BrO <sub>5</sub> S               | 100      | 182-183             |
| 321-14-2        | 5-Cl                                    | 1a          | CO <sub>2</sub> Ph                                      | OPh  | B                            | 2c      | C <sub>15</sub> H <sub>9</sub> ClO <sub>5</sub> S               | 98       | 174-175             |
| 85-38-1         | 3-NO <sub>2</sub>                       | 1a          | CO <sub>2</sub> Ph                                      | OPh  | B                            | 2d      | C <sub>15</sub> H <sub>9</sub> NO <sub>7</sub> S                | 40       | 138-139             |
| 96-97-9         | 5-NO <sub>2</sub>                       | 1a          | CO <sub>2</sub> Ph                                      | OPh  | B                            | 2e      | C <sub>15</sub> H <sub>9</sub> NO <sub>7</sub> S                | 93       | 201-202             |
| 95-01-2         | 4-OH                                    | 1a          | CO <sub>2</sub> Ph                                      | OPh  | C                            | 2f      | C <sub>15</sub> H <sub>10</sub> O <sub>6</sub> S                | 58       | 173-174             |
| 148-53-8        | 3-OCH <sub>3</sub>                      | 1a          | CO <sub>2</sub> Ph                                      | OPh  | B                            | 2g      | C <sub>16</sub> H <sub>12</sub> O <sub>6</sub> S                | 91       | 185-186             |
| 708-06-5        | 2-Hydroxy-1-naphthaldehyde <sup>e</sup> | 1a          | CO <sub>2</sub> Ph                                      | OPh  | B                            | 2h      | C <sub>19</sub> H <sub>12</sub> O <sub>5</sub> S                | 93       | 186-187             |
|                 | H                                       | 1b          | CONHPh  | NHPh | A                            | 2i      | C <sub>15</sub> H <sub>11</sub> NO <sub>4</sub> S               | 42       | 200-200.5           |
|                 | H                                       | 1c          | CO <sub>2</sub> Ph                                      | NHPh | A                            | 2i      | C <sub>15</sub> H <sub>11</sub> NO <sub>4</sub> S               | 48       | 200-200.5           |
|                 | H                                       | 1d          | CONHPh  | OPh  | B                            | 4a      | C <sub>15</sub> H <sub>11</sub> NO <sub>4</sub> S               | 35       | 173-174             |
|                 | 3-NO <sub>2</sub>                       | 1d          | CONHPh  | OPh  | A                            | 4b      | C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>6</sub> S | 57       | 212-214             |
|                 | H                                       | 1e          | COPh  | OPh  | A                            | 4c      | C <sub>15</sub> H <sub>10</sub> O <sub>4</sub> S                | 65       | 142-143             |
|                 | 5-Br                                    | 1e          | COPh  | OPh  | D                            | 4d      | C <sub>15</sub> H <sub>9</sub> BrO <sub>4</sub> S               | 58       | 159-160             |
|                 | 5-NO <sub>2</sub>                       | 1e          | COPh  | OPh  | A <sup>f</sup>               | 4e      | C <sub>15</sub> H <sub>9</sub> NO <sub>6</sub> S                | 30       | 139-140             |
|                 | 2-Hydroxy-1-naphthaldehyde <sup>e</sup> | 1e          | COPh  | OPh  | A <sup>f</sup>               | 4f      | C <sub>19</sub> H <sub>12</sub> O <sub>4</sub> S                | 69       | 208-209             |
|                 | H                                       | 1f          | <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | OPh  | A                            | 4g      | C <sub>14</sub> H <sub>9</sub> NO <sub>5</sub> S                | 54       | 220-221             |
|                 | 5-Br                                    | 1f          | <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | OPh  | D                            | 4h      | C <sub>14</sub> H <sub>9</sub> BrNO <sub>5</sub> S              | 82       | 238-239             |
|                 | 5-Cl                                    | 1f          | <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | OPh  | D                            | 4i      | C <sub>14</sub> H <sub>9</sub> ClNO <sub>5</sub> S              | 50       | 220-221             |
|                 | 5-NO <sub>2</sub>                       | 1f          | <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | OPh  | D                            | 4j      | C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>7</sub> S  | 60       | 213-214             |

<sup>a</sup> See Experimental Section. <sup>b</sup> Satisfactory analytical data ( $\pm 0.3\%$  for C, H, N) were reported for all new compounds listed in the table. <sup>c</sup> Determined (uncorrected) on a Fisher-Johns apparatus. <sup>d</sup> Conditions C gave 67% yield. <sup>e</sup> A. Russell and L. B. Lockhart, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 463. <sup>f</sup> Room temperature.

**Table II**  
Reactions of Diphenyl Malonate with Salicylaldehydes



| Salicylaldehyde Substituent, X          | Compd | Formula <sup>a</sup>                            | Yield, %        | Mp, °C <sup>b</sup>  | Registry no. |
|---|-------|---|-----------------|----------------------|--------------|
| H                                       | 3a    | C <sub>16</sub> H <sub>10</sub> O <sub>4</sub>  | 51              | 158-159 <sup>c</sup> | 53992-24-8   |
| 5-Br                                    | 3b    | C <sub>16</sub> H <sub>9</sub> BrO <sub>4</sub> | 91 <sup>d</sup> | 233-234              | 53992-25-9   |
| 5-Cl                                    | 3c    | C <sub>16</sub> H <sub>9</sub> ClO <sub>4</sub> | 80              | 228-229              | 53992-26-0   |
| 3-NO <sub>2</sub>                       | 3d    | C <sub>16</sub> H <sub>9</sub> NO <sub>6</sub>  | 21              | 235-236              | 53992-27-1   |
| 5-NO <sub>2</sub>                       | 3e    | C <sub>16</sub> H <sub>9</sub> NO <sub>6</sub>  | 67              | 250-251              | 53992-28-2   |
| 3-OCH <sub>3</sub>                      | 3g    | C <sub>17</sub> H <sub>12</sub> O <sub>5</sub>  | 76              | 148-149              | 53992-29-3   |
| 2-Hydroxy-1-naphthaldehyde <sup>e</sup> | 3h    | C <sub>20</sub> H <sub>12</sub> O <sub>4</sub>  | 69              | 193-194              | 53992-30-6   |

<sup>a</sup> Satisfactory analytical data ( $\pm 0.3\%$  for C, H) were reported for all new compounds listed in the table. <sup>b</sup> Determined (uncorrected) on a Fisher-Johns apparatus. <sup>c</sup> Mp 156° reported by P. M. Bhargava and S. H. Zaheer, *J. Chem. Soc.*, 311 (1952). <sup>d</sup> See ref 6. <sup>e</sup> See footnote e, Table I.

corresponding anilides (5 and 6) and with water to form with corresponding sulfonic acids, isolated as their pyridine salts (7 and 8) (see Table III). It seems quite likely that these reactions occur by way of a sulfene intermediate (9) generated in the basic medium by the elimination of phenol, followed by the addition of aniline or water to the sulfene.<sup>1a,2</sup>

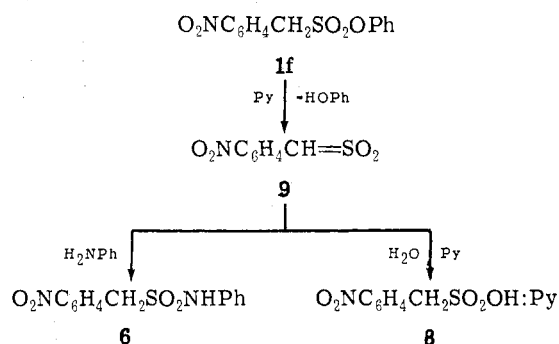
It is tempting to rationalize the cyclization of 1d, 1e, and 1f with salicylaldehydes to form sultones in terms of a reaction mechanism involving a sulfene intermediate. If a sul-

fene is involved, structure 10, which would result from a simple Knoevenagel reaction of salicylaldehyde with 1f and which, like phenyl benzenesulfonate, is incapable of forming a sulfene, cannot be an intermediate in the cyclization reaction. In support of this conclusion, it was found that under the conditions (piperidine in refluxing benzene or hot pyridine) used for the reactions of 1f with salicylaldehydes to form sultones (4g-j), 1f, like 1a, does not react with benzaldehyde or *p*-nitrobenzaldehyde.<sup>8</sup> When heated under the same conditions (hot pyridine) with a 3-molar

**Table III**  
Products of the Anilinolysis and Hydrolysis of 1e and 1f

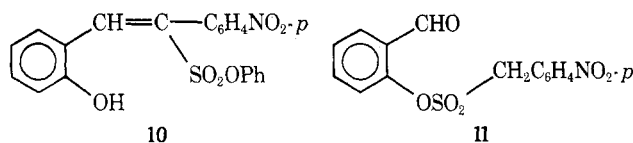
| Compd | Structure <sup>a</sup>  | Yield, % | Mp, °C <sup>b</sup> | Registry no. |
|-------|---|----------|---------------------|--------------|
| 5     | PhCOCH <sub>2</sub> SO <sub>2</sub> NHPh  | 74       | 109–110             | 7117-22-8    |
| 6     | O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> SO <sub>2</sub> NHPh  | 83       | 125–126             | 53992-31-7   |
| 7     | PhCOCH <sub>2</sub> SO <sub>2</sub> OH:Py   | 56       | 109–110             | 53992-32-8   |
| 8     | O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> SO <sub>2</sub> OH:Py | 80       | 157–161             | 53992-34-0   |

<sup>a</sup> Satisfactory analytical data ( $\pm 0.2\%$  for C, H, N) were reported for all new compounds listed in the table, with the exception of 7 ( $\pm 0.4\%$  for C). <sup>b</sup> Determined (uncorrected) on a Fisher-Johns apparatus.

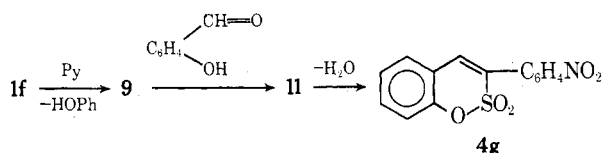


excess of *p*-chlorophenol, 1f is converted by transesterification to the corresponding *p*-chlorophenyl ester in approximately 35% yield (by NMR analysis of the resulting ester mixture), a reaction which is analogous to the anilinolysis and hydrolysis of 1f described above.

These results provide compelling support for structure 11, rather than 10, as the initially formed intermediate in



the cyclization of 1f with salicylaldehyde to form the sultone 4g and for the possibility that in the overall cyclization reactions of 1d, 1e, and 1f with salicylaldehydes, transesterification, via a sulfene, precedes the Knoevenagel elimination of water.



In the general formation of sultones (4) under the rather mild conditions of the reactions that we have described, the facile replacement of a phenoxide ion at a sulfonyl group is remarkable in view of the well-known inertness of other phenyl sulfonate esters, such as phenyl methanesulfonate and phenyl benzenesulfonate, toward nucleophilic agents under considerably more strenuous conditions.<sup>1a</sup> The present work suggests that reactions of this type may eventually have greater synthetic utility than is now generally recognized.

### Experimental Section

**Reactions of 1 and Diphenyl Malonate with Salicylaldehydes.** The phenyl ester or anilide represented by structure 1 or diphenyl malonate and an equimolar quantity of a salicylaldehyde were dissolved in a reagent-grade solvent, approximately a 0.1 molar equiv quantity of the basic agent was added, and the resulting mixture was stirred and/or heated. The various conditions em-

ployed may be summarized as follows: A, benzene, piperidine, reflux 4–8 hr; B, acetone, K<sub>2</sub>CO<sub>3</sub>, or the carbonate form of Dowex 1X4 (J. T. Baker Chemical Co.) anionic exchange resin at room temperature; C, acetone, KF, or NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> at room temperature; D, pyridine, steam heat 24 hr. Completeness of the reaction was determined by TLC. The product was isolated by evaporation of the solvent, rinsing with water or with dilute HCl when necessary, and recrystallization from acetone–water or methanol–water mixtures. Products were characterized by melting point, ir, NMR, and by elementary analyses, which were performed by Galbraith Laboratories, Knoxville, Tenn. The reactions, conditions, and the products derived from compounds 1a–f are summarized in Table I. The new products derived from diphenyl malonate are summarized in Table II.

**Preparation of Materials. A.** Compounds 1a–d were prepared by methods described previously in part II of this series.<sup>1a</sup>

**B. Phenyl Benzoylmethanesulfonate (1e).** PhOSO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H (5 g, 23.1 mmol), obtained by the acidic hydrolysis of 1a,<sup>1a</sup> was treated with 20 ml of refluxing SOCl<sub>2</sub> for 45 min. Excess SOCl<sub>2</sub> was removed by evaporation under reduced pressure, last traces being removed by evaporation with a small quantity of anhydrous ethyl ether added to the crude mixture. The residual sulfonyl chloride was taken up in 10 ml of anhydrous benzene, 10 g of anhydrous AlCl<sub>3</sub> was added, and the resulting mixture was stirred and warmed at gentle reflux for 45 min. Excess benzene was removed by evaporation and ice and dilute HCl was added to the residual mixture. The crude solid was removed by filtration and was recrystallized from a methanol–water mixture to afford 4.1 g (64%) of product, mp 57–58°.

Anal. Calcd for C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>S: C, 60.85; H, 4.38. Found: C, 61.30; H, 4.29.

**C. Phenyl *p*-Nitrophenylmethanesulfonate (1f).** A solution of 5.0 g (26.8 mmol) of *p*-nitrobenzyl chloride and 3.69 g (29.3 mmol) of Na<sub>2</sub>SO<sub>3</sub> in 150 ml of 50% aqueous acetone was heated at gentle reflux for a period of 10 hr. The resulting clear solution was evaporated to about 35 ml, chilled, and filtered to remove unchanged *p*-nitrobenzyl chloride, rinsing with a small portion of cold water. The clear filtrate was passed through a column of Dowex 50W-X4 cation exchange resin (J. T. Baker Chemical Co.). The strongly acidic eluent was evaporated to a syrupy liquid form of the intermediate *p*-nitrophenylmethanesulfonic acid, which partially crystallized on cooling. To the crude sulfonic acid was added 3.5 g (37.1 mmol) of phenol and 10 ml of POCl<sub>3</sub> and the resulting mixture was heated at 75–85° for a period of 8 hr, when evolution of HCl seemed to be complete. The reaction mixture was poured onto ice with stirring. After hydrolysis of excess POCl<sub>3</sub> was complete, excess acid was neutralized by adding solid Na<sub>2</sub>CO<sub>3</sub>. The resulting crude solid was removed by filtration and washed with large volumes of cold water. The wet solid was recrystallized several times from methanol–water mixtures to afford 4.2 g (49% overall) of a flaky, light-gold material: mp 135–136°; NMR (Hitachi Perkin-Elmer R-24) (acetone)  $\delta$  4.45 (s, 2 H), 6.65 (br s, 5 H), 7.20, 7.65 (2 d, 4 H,  $J = 1.5$  Hz).

Anal. Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>5</sub>S: C, 53.23; H, 3.78; N, 4.78. Found: C, 53.40; H, 4.07; N, 4.96.

**D.** Diphenyl malonate was prepared by an adaption of the method of Auger.<sup>9</sup>

**E.** The various salicylaldehydes were used as obtained from Eastman Chemicals Co., Rochester, N.Y.

**Hydrolysis and Anilinolysis of 1e and 1f.** The reactions of 1e and 1f with water and aniline were carried out in refluxing pyridine as described in part II of this series.<sup>1a</sup> The products of these reactions are summarized in Table III.

**Transesterification of 1f.** A solution of 0.5 g (1.7 mmol) of 1f and 0.66 g (5.1 mmol) of *p*-chlorophenol in pyridine was heated on a steam bath for 24 hr. The mixture was then poured into ice-water and the resulting solid material was removed by filtration. The crude solid was washed repeatedly by stirring with water until the supernatant, according to a FeCl<sub>3</sub> test, was free of phenols. After a single recrystallization, TLC indicated the solid to be a mixture. A comparison of the NMR spectrum of the mixture dissolved in acetone with that of 1f indicated the presence of a new pair of doublets ( $J = 1.5$  Hz) for the *p*-chlorophenoxy group centered at  $\delta$  6.65 and superimposed on the aromatic singlet for the original phenyl ester 1f. Using the CH<sub>2</sub> singlet ( $\delta$  4.45) as a reference, the integration of the  $\delta$  6.65 signals indicated the mixture to contain approximately 35% of the *p*-chlorophenyl ester and 65% of 1f. The equilibrium composition of the transesterification mixture was not determined.

**Registry No.**—**1a**, 53973-62-9; **1b**, 7117-27-3; **1c**, 16753-80-3; **1d**, 16753-81-4; **1e**, 53992-03-3; **1f**, 53992-04-4; **2a**, 53992-05-5; **2b**, 53992-06-6; **1f**, 53992-04-4; **2a**, 53992-05-5; **2b**, 53992-06-6; **2c**, 53992-07-7; **2d**, 53992-08-8; **2e**, 53992-09-9; **2f**, 53992-10-2; **2g**, 53992-11-3; **2h**, 53992-12-4; **2i**, 53992-13-5; **4a**, 53992-14-6; **4b**, 53992-15-7; **4c**, 53992-16-8; **4d**, 53992-17-9; **4e**, 53992-18-0; **4f**, 53992-19-1; **4g**, 53992-20-4; **4h**, 53992-21-5; **4i**, 53992-22-6; **4j**, 53992-23-7; diphenyl malonate, 1969-44-4.

### References and Notes

- (1) (a) Part II: B. E. Hoogenboom, M. S. El-Faghi, S. C. Fink, E. D. Hoganson, S. E. Lindberg, T. J. Lindell, C. J. Linn, D. J. Nelson, J. O. Olson, L. Rennerfeldt, and K. A. Wellington, *J. Org. Chem.*, **34**, 3414 (1969). (b) Supported by a F. G. Cottrell grant from Research Corporation, Public Health Service Grant GM12153, National Science Foundation Undergraduate Research Participation Grant No. GE-9467, and the Gustavus Adolphus College Research Fund.
- (2) G. Oplitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967).
- (3) Phenyl carboxymethanesulfonate, PhOSO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, derived from

- CISO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub> [R. Vieillefosse, *Bull. Soc. Chim. Fr.*, 351 (1947)], reacts with salicylaldehyde under the same conditions to produce the same product, **2a**. Phenyl carboxymethanesulfonate, PhOSO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, is not cyclized to **2a** under the same conditions (piperidine in refluxing benzene) but is instead decarboxylated to form PhOSO<sub>2</sub>CH<sub>3</sub> in 98% yield.<sup>1a</sup> *N*-Phenylsulfamylacetic acid, PhNHSO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H,<sup>1a</sup> is less readily decarboxylated, however, and is cyclized under the same conditions or in refluxing pyridine to form the coumarin (**2i**) in 83% yield.
- (4) G. Jones, *Org. React.*, **15**, 204 (1967).
  - (5) R. W. Hein, M. J. Astle, and J. R. Shelton, *J. Org. Chem.*, **26**, 4874 (1961).
  - (6) Diphenyl malonate reacts with 5-bromosalicylaldehyde in an acetone solvent without the benefit of an added basic agent to form a high yield (91%) of 6-bromo-3-carbophenoxycoumarin (**3b**, Table II).
  - (7) The parent sulfone is referred to in *Chemical Abstracts* as 1,2-benzoxathin 2,2-dioxide.
  - (8) In fact, when water is not carefully excluded from the reaction mixture, the product isolated is the hydrolysis product (**8**). Apparently, once the anion of **1f** is formed, the unimolecular dissociation to form a sulfene (**9**) is faster than the bimolecular reaction with an aldehyde to form the Knoevenagel intermediate addition product, ArCHOHCHAr'SO<sub>2</sub>O<sup>-</sup>.
  - (9) V. Auger, *C. R. Acad. Sci.*, **136**, 556 (1903).

## Thermal Decomposition of *o*- and *p*-Benzenedisulfonyl Azides in Benzene, Cyclohexane, Cyclohexene, and Tetracyclone<sup>1</sup>

R. A. Abramovitch\* and G. N. Knaus

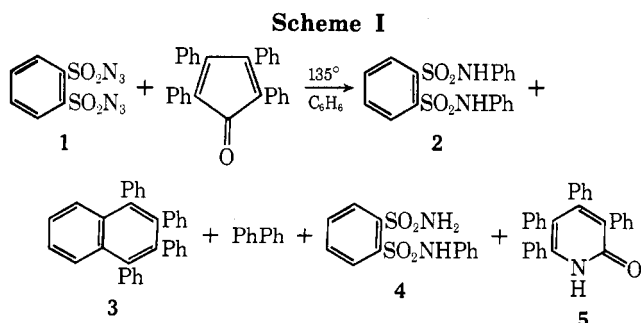
Department of Chemistry, University of Alabama, University, Alabama 35486

Received October 29, 1974

The thermolysis of *o*-benzenedisulfonyl azide in benzene and cyclohexane gives products which can be rationalized as arising from both benzyne and a singlet sulfonyl nitrene. The former can be trapped with tetracyclone whereas the sulfonyl nitrene undergoes aromatic substitution with benzene, C-H insertion into cyclohexane, and addition to tetracyclone. The thermolysis of *p*-benzenedisulfonyl azide in benzene, toluene, and cyclohexane leads only to singlet sulfonyl nitrene. Both *o*- and *p*-benzenedisulfonyl azide react readily with cyclohexene to give a diimine or dienamine as the primary product. In the case of the *o*-diazide, an interesting secondary product was isolated. Formation of the primary product is best explained in terms of a 1,3-dipolar addition mechanism.

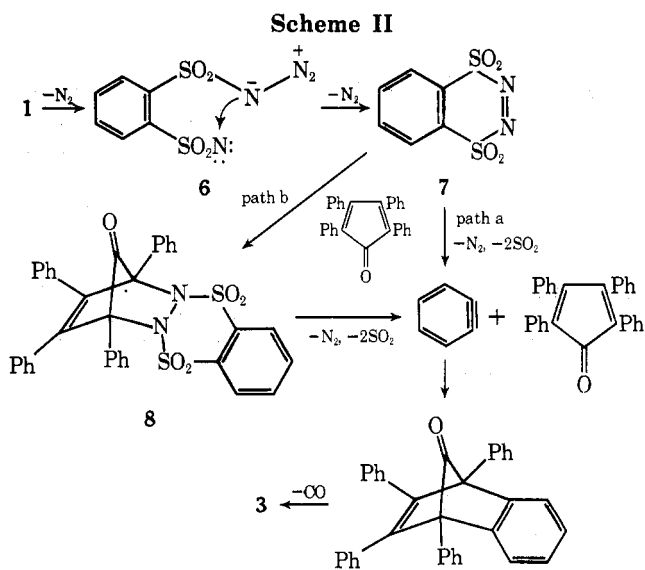
The thermal decomposition of monosulfonyl azides in benzene and cyclohexane is known<sup>2</sup> to give singlet sulfonyl nitrene. While disulfonyl azides have been used for the cross-linking of hydrocarbon polymers,<sup>2b</sup> their reactions with aromatic hydrocarbons have not been reported. In this paper we report the thermal decompositions of *o*- and *p*-benzenedisulfonyl azide in benzene, cyclohexane, tetracyclone, and cyclohexene.

Thermolysis of the *o*-diazide (**1**) in a large excess of benzene at 135° gave the expected nitrene product, *o*-benzenedisulfonylanilide (**2**, 21%) as the only isolable product. When the same reaction was carried out in the presence of tetracyclone (1.1 molar equiv), an interesting array of products was isolated and these are illustrated in Scheme I.



From the nature of the products, it is evident that two different reactive intermediates, likely a benzyne and a sulfonyl nitrene, are being generated from **1** and that at least three mechanisms must be invoked in order to explain the

formation of all products. The tetraphenyl naphthalene (**3**, 6%) probably results from the cycloaddition of benzyne to tetracyclone. Possible mechanisms leading to benzyne from **1** are depicted in Scheme II. The electrophilic singlet ni-



rene (**6**) could cyclize to the unstable cyclic azodisulfone (**7**), which could either eliminate nitrogen and two molecules of sulfur dioxide (path a) or undergo cycloaddition (path b) to tetracyclone to give adduct **8**, and then eliminate nitrogen and sulfur dioxide to give benzyne. Although