

## Thermal Decomposition of Bismesitylsulphonyl- and Bis-2,4-xylylsulphonyl-diazomethanes

By William T. Flowers, Graham Heyes, and Geoffrey Holt,\* Department of Chemistry, University of Manchester Institute of Science and Technology, Sackville Street, Manchester M60 1QD

Thermal decomposition of bismesitylsulphonyldiazomethane provides 2,3-dihydro-5,7-dimethyl-2-mesitylsulphonylbenzo[*b*]thiophen 1,1-dioxide, the product of carbenic insertion into one of the *ortho*-methyl groups. An analogous product could not be isolated from bis-2,4-xylylsulphonyldiazomethane, whose decomposition was much more complex but provided small yields of 2,3-dihydro-5-methyl-2-(2,4-xylyl)benzo[*b*]thiophen 1,1-dioxide, 2,4-dimethylbenzoic acid, and di-2,4-xylyl disulphide. Small yields of the corresponding acid and disulphide were obtained from the mesityl diazo-compound and in both instances it is suggested that these arise from a Wolff-type rearrangement.

ALTHOUGH bisarylsulphonyldiazomethanes (I) have been known<sup>1</sup> for a number of years, the bisphenylsulphonyl derivative is the only one whose carbenic decomposition has received any study.<sup>2</sup> The expected reactions with alcohols and sulphides were realised, but surprisingly only tarry products resulted from experiments designed to give insertion into the C-H bond of an aromatic system. However, Abramovitch *et al.*<sup>3</sup> have recently reported an intramolecular insertion of a monosulphonylcarbene ( $\text{ArSO}_2\dot{\text{C}}\text{H}$ ) into an aromatic C-H bond.

We now report the insertion of such carbenes into the C-H bond of a methyl group. Thus the major product (44%) from heating bismesitylsulphonyldiazomethane (I; R = Me, Ar = mesityl) in boiling *o*-dichlorobenzene

was the arylsulphonylbenzothiophen 1,1-dioxide (III; R = Me, Ar = mesityl). This insertion [(II)  $\longrightarrow$  (III)] is not the only reaction taking place: during the decomposition sulphur dioxide is evolved and from the residual material were isolated small amounts of mesitoic acid (VIII; Ar = mesityl) and dimesityl disulphide (X; Ar = mesityl). A similar decomposition of bis-2,4-xylylsulphonyldiazomethane (I; R = H, Ar = 2,4-xylyl) was much more complex, but the corresponding carboxylic acid (VIII; Ar = 2,4-xylyl) and disulphide (X; Ar = 2,4-xylyl) were again isolated; the only other product identified was the benzothiophen 1,1-dioxide (VI; R = H, Ar = 2,4-xylyl). However, no products arising from direct carbenic insertion of (II) into the

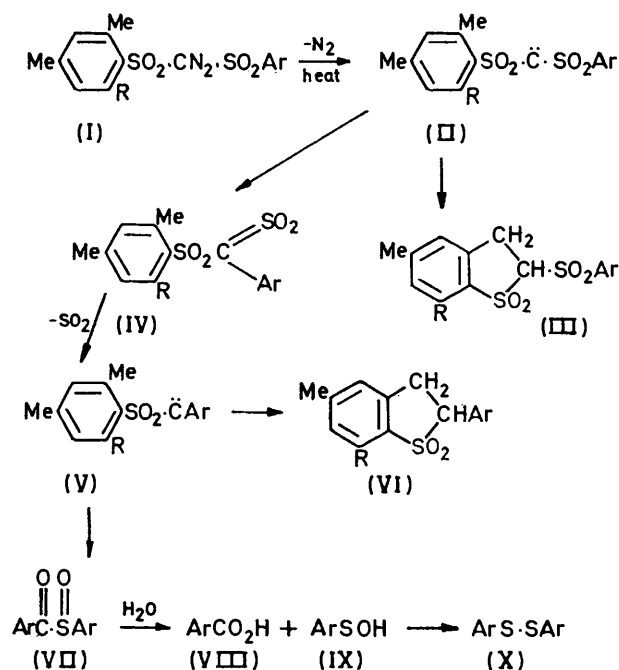
<sup>1</sup> F. Klages and K. Bott, *Chem. Ber.*, 1964, **97**, 735

<sup>2</sup> J. Diekmann, *J. Org. Chem.*, 1965, **30**, 2272.

<sup>3</sup> R. A. Abramovitch, V. Alexanian, and E. M. Smith, *J.C.S. Chem. Comm.*, 1972, 893.

*ortho*-methyl groups were isolated. Apparently such a process [(II)  $\rightarrow$  (III)] occurs to a significant degree only when, as in the mesityl derivative, steric crowding is extreme.

We tentatively rationalise formation of the products arising from the 2,4-xylyl derivative (I; R = H, Ar = 2,4-xylyl) in terms of a Wolff-type rearrangement of the



diazocompound to provide the sulphonyl thioketone dioxide (IV; R = H, Ar = 2,4-xylyl). Such a rearrangement of bisarylsulphonyldiazomethanes has not been reported previously but apparently, as with the monosulphonyl derivatives,<sup>4</sup> it constitutes only a minor pathway. At the temperature employed the intermediate (IV) might lose SO<sub>2</sub> in a manner analogous to that in which it has been reported that carbon monoxide is produced in the thermal decomposition of  $\alpha$ -diazob- $\beta$ -diketones.<sup>5</sup> The resulting monosulphonylcarbene may then stabilise itself in one of two ways. The benzothiophen apparently arises by insertion of the carbenic centre into an *ortho*-methyl group of the sulphone-bearing ring [(V)  $\rightarrow$  (VI); R = H, Ar = 2,4-xylyl]. Alternatively, oxygen transfer from sulphur to the carbenic centre would provide the species (VII). Such a reaction has not previously been reported but under much milder conditions oxygen transfer from a sulphoxide to a carbenic centre has been demonstrated.<sup>6</sup> Apparently little is known about  $\alpha$ -keto-sulphoxides (VII) but it is not unreasonable that hydrolysis during

work-up would provide a mixture of carboxylic and sulphenic acids. Decomposition of such a sulphenic acid is known<sup>7</sup> to proceed spontaneously to provide, among other products, disulphides [(IX)  $\rightarrow$  (X)]. Disulphides have also been reported<sup>3</sup> as minor products in the decomposition of monoarylsulphonyldiazomethanes.

The 100 MHz n.m.r. spectra of the substituted dihydrobenzothiophen 1,1-dioxides [(III) and (VI)] are in general accord with that for the unsubstituted compound;<sup>8</sup> for instance the coupling between the geminal protons on C-3 in (III) has the high value of 16.8 Hz. In the spectrum of (III) change of solvent from CDCl<sub>3</sub> to C<sub>6</sub>H<sub>6</sub> brings about a large downfield shift (0.34 p.p.m.) of the signal due to the 3-proton *cis* to the mesitylsulphonyl group, whereas the *gem*-proton on C-2 and the *trans*-3-proton are unaffected.<sup>9</sup> In addition, whereas variable-temperature measurements of the *cis*- and *trans*-couplings between the protons in the dihydrothiophen ring of (VI) indicate that the ring is flexible and undistorted at 30 °C, interaction between the two sulphonyl groups in (III) apparently leads to puckering of the ring to the extent of *ca.* 25°.<sup>8</sup>

#### EXPERIMENTAL

Bismesitylsulphonyldiazomethane<sup>10</sup> (4.8 g, 11.8 mmol) in *o*-dichlorobenzene (50 ml) was added to refluxing *o*-dichlorobenzene (50 ml) during 15 min. The evolved gases were passed through traps cooled to -78°, in which a small amount of liquid collected. From its smell, reduction of dichromate paper, i.r. spectrum, and molecular weight this was shown to be essentially sulphur dioxide. Concentration of the *o*-dichlorobenzene solution under reduced pressure at 40° provided a sticky solid; this was stirred with ether (100 ml) and the insoluble material (0.2 g) was filtered off. Extraction of the filtrate with sodium hydroxide (2  $\times$  25 cm) removed mesitoic acid (*ca.* 0.1 g), m.p. 151–153° (lit.<sup>11</sup> 152°), *m/e* 164 (*M*<sup>+</sup>, 78%). The ethereal solution was dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to provide a solid from which dimesityl disulphide (0.4 g, 22%), m.p. 117–120° (lit.<sup>12</sup> 125°), was removed by washing with light petroleum (b.p. 60–80°; 100 ml). The disulphide-free residue was 2,3-dihydro-5,7-dimethyl-2-mesitylsulphonylbenzo[b]thiophen 1,1-dioxide (2.0 g, 44%), m.p. 182–184° (from ethanol) (Found: C, 60.7; H, 6.1; S, 16.5. C<sub>19</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub> requires C, 60.3; H, 5.8; 16.9%),  $\lambda_{\text{max}}$  2975m, 2960m, 1602s, 1590s, 1450m, 1325s and 1314s (SO<sub>2</sub>), 1170s and 1158s (SO<sub>2</sub>), 1130m, 895m, 848s, 832s, 675s, and 648s cm<sup>-1</sup>,  $\tau$  (CDCl<sub>3</sub>) 3.0br (4H, s, aromatic), 5.08 (1H, dd, *J*<sub>*cis*</sub> 7.0, *J*<sub>*trans*</sub> 9.2 Hz, 2-H), 6.0–6.6 (2H, AB part of ABC system, *J*<sub>*gem*</sub> 16.8 Hz, CH<sub>2</sub>), 7.32 (6H, s, Me<sub>2</sub>), 7.60 (3H, s, Me), 7.71 (3H, s, Me), and 7.74 (3H, s, Me), *m/e* 314 (C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>S<sup>+</sup>, 3%), 195 (C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>S<sup>+</sup>, 10), 119 (C<sub>8</sub>H<sub>11</sub><sup>+</sup>, 86), 105 (C<sub>8</sub>H<sub>9</sub><sup>+</sup>, 22.5), 91 (C<sub>7</sub>H<sub>7</sub><sup>+</sup>, 20), 77 (Ph<sup>+</sup>, 13), and 44 (100%).

<sup>4</sup> R. J. Mulder, A. M. van Leusen, and J. Strating, *Tetrahedron Letters*, 1967, 3057.

<sup>5</sup> W. Bartz and M. Regitz, *Chem. Ber.*, 1970, **103**, 1463.

<sup>6</sup> D. Hodson and G. Holt, *J. Chem. Soc. (C)*, 1968, 1602.

<sup>7</sup> N. Karasch, 'Organic Sulphur Compounds,' vol. 1, Pergamon Press, Oxford, 1961, p. 392.

<sup>8</sup> J. B. Lambert and F. R. Koeng, *Org. Magnetic Resonance*, 1971, **3**, 389.

<sup>9</sup> D. F. Ewing and R. M. Scrowston, *Org. Magnetic Resonance*, 1971, **3**, 405.

<sup>10</sup> G. Heyes and G. Holt, *J.C.S. Perkin I*, 1973, 189.

<sup>11</sup> H. Reitter, *Ber.*, 1894, **27**, 3446.

<sup>12</sup> H. J. Backer and E. Westerhuis, *Rec. Trav. chim.*, 1952, **71**, 1078.

When bis-2,4-xylylsulphonyldiazomethane (18.0 g, 47.6 mmol) was decomposed in a similar manner the organic product of the reaction was tarry. Extraction with alkali removed 2,4-dimethylbenzoic acid (1.0 g, 14%), m.p. 121—123° (lit.,<sup>13</sup> 125—126°). The neutral residue was chromatographed on silica gel (5 × 50 cm); elution with light petroleum (b.p. 60—80°) gave di-2,4-xylyl disulphide (1.1 g, 17%). Subsequent elution with solvents of increasing polarity provided a multiplicity of fractions. The only one which yielded identifiable material was that obtained with toluene—

chloroform (4 : 1); this gave 2,3-dihydro-5-methyl-2-(2,4-xylyl)benzo[b]thiophen 1,1-dioxide (0.5 g, 4%), m.p. mainly 167—169° (from ethanol) (Found: C, 71.3; H, 6.6; S, 11.6. C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>S requires C, 71.1; H, 6.3; S, 11.2%),  $\lambda_{\max}$  2960m, 2920m, 1602m, 1505m, 1445s, 1299s (SO<sub>2</sub>), 1280m, 1160s (SO<sub>2</sub>), 1145s, 1130s, 1058m, 955w, 945, 872w, 815s, 742w, 721w, 680m, and 660m cm<sup>-1</sup>,  $\tau$  (CDCl<sub>3</sub>) 2.44 (1H, d, *J* 8.0 Hz, 7-H), 2.7—3.0 (5H, complex m, aromatic), 5.06 (1H, t, *J* 7.8 Hz, 2-H), 6.54 (2H, d, *J* 7.8 Hz, CH<sub>2</sub>), 7.58 (3H, s, Me), 7.62 (3H, s, Me), and 7.75 (3H, s, Me).

<sup>13</sup> W. H. Perkin and J. F. S. Stone, *J. Chem. Soc.*, 1925, 2283.

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