## Generation and Some Reactions of Phenylsulphonylcarbene

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Phenylsulphonylcarbene has been generated in benzene, in cyclohexene, and in cyclohexane by thermolysis and photolysis of diazo(phenylsulphonyl)methane. Phenylsulphonyl radicals are also formed from the photolyses in benzene and cyclohexane. In benzene, benzyl phenyl sulphone (3) is formed in minor amounts, by substitution and not by ring contraction of 7-phenylsulphonylcyclohepta-1,3,5-triene. In cyclohexene, cyclopropane adducts are formed in an exo: endo ratio of 2.2:1.

THERE has been much interest in recent years in the generation 1-4 and chemistry of sulphonylcarbenes 1,3-7 since the first general synthesis of sulphonyldiazomethanes was developed.<sup>8</sup> We now report the results of thermal and photochemical generation of phenylsulphonylcarbene in benzene, in cyclohexene, and in

benzene substitution product (3),<sup>9</sup> the trans-dimer (4),<sup>10</sup> and the sulphonate ester (5). The yields (Table) were unaffected by the use of degassed solvents, so that the source of the additional oxygen in (5) must be a sulphonyl group. Photolysis gave much higher yields of (5) but almost no dimer (4) was formed. A possible mechanism

Products of decomposition of diazo(phenylsulphonyl)methane (1) in various solvents

Conditions	Solvent	Products (%)						
		(2)	(3)	(4)	(5) *	(9)	(10)	(11)
Heat, presence of air	Benzene	4.2	1.2	23	3.0			
Heat, degassed	Benzene	†	1.2	28	3.1			
hv	Benzene	ŧ	1.1	Trace	23			
Heat, presence of air	Cyclohexane	÷			6.9	28.9		
Heat, degassed	Cyclohexane	Ť			6.9	43.5		
hv	Cyclohexane	÷			34.6	12.1		
Heat, under N.	Cyclohexene	•					36.4	16.7
hv	Cyclohexene						33.0	15.2

† Not determined.

<sup>a</sup> M.p. 96-96.5° (Found: C, 50.2; H, 4.1; S, 20.5. C<sub>13</sub>H<sub>12</sub>S<sub>2</sub>O<sub>5</sub> requires C, 49.8; H, 4.2; S, 20.5%), δ (CDCl<sub>3</sub>) 7.59 (10 H, m and 4.94 (2 H, s); m/e 312 ( $M^{+\cdot}$ ).<sup>12</sup>

cyclohexane. Thermolysis of diazo(phenylsulphonyl)methane gives predominantly carbene-derived products, whereas photodecomposition gives mainly products derived from phenylsulphonylcarbene and phenylsulphonyl radicals.

$$\begin{array}{c} \operatorname{PhSO_2CHN_2} \xrightarrow{\text{heat}} \\ (1) & \xrightarrow{} \\ (\operatorname{PhS})_2 + \operatorname{PhSO_2} \cdot \operatorname{CH_2Ph} + \operatorname{PhSO_2} \cdot \operatorname{CH:CH} \cdot \operatorname{SO_2Ph} + \\ (2) & (3) & (4) \\ & \operatorname{PhSO_2} \cdot \operatorname{CH_2} \cdot \operatorname{O} \cdot \operatorname{SO_2Ph} \\ & (5) \end{array}$$

Thermolysis of phenylsulphonyldiazomethane (1) in dry benzene at 80 °C gave diphenyl disulphide (2), the

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<sup>‡</sup> We have observed the formation of ArS·SO<sub>2</sub>Ar in the reactions of 2-biphenylsulphonyldiazomethane.<sup>13</sup> This further implicates the intermediacy of ArSO2 and ArS. radicals.13

<sup>1</sup> A. M. van Leusen and J. Strating, Quart. Reports Sulfur Chem., 1970, 5, 67.

<sup>2</sup> K. Schank, F. Schroeder, and A. Weber, Annalen, 1973, 553.

<sup>3</sup> R. A. Abramovitch and V. Alexanian, Heterocycles, 1974, 2, 595.

<sup>4</sup> B. E. Sarver, M. Jones, jun., and A. M. van Leusen, J. Amer. Chem. Soc., 1975, 97, 4771.

<sup>5</sup> Preliminary communication, R. A. Abramovitch and J. Roy, Chem. Comm., 1965, 542. <sup>6</sup> R. A. Abramovitch, V. Alexanian, and E. M. Smith, J.C.S.

Chem. Comm., 1972, 893.

for the formation of the ester (5) involves initial cleavage to give benzenesulphonyl radicals, followed by disproportionation<sup>11</sup> to give PhSO<sub>3</sub> and PhS. The former could abstract hydrogen to give the sulphonic acid which, with unchanged diazo(phenylsulphonyl)methane, would give the ester. Indeed, we<sup>6</sup> and others <sup>12</sup> have shown that sulphonic acids react with sulphonyldiazomethanes to give esters of the type (5). Isolation of the disulphide (2) (conceivably arising from the dimerisation of PhS·) supports this scheme.<sup>7,‡</sup> There is precedent for the direct photochemical

<sup>7</sup> In a related system (W. T. Flowers, G. Heyes, and G. Holt, J.C.S. Perkin I, 1973, 2438) disulphides were proposed to arise from a complex series of steps involving Wolff rearrangement, 1,2-oxygen migration, and subsequent hydrolysis. Our data 4,6 do not require such a course of events.

<sup>8</sup> A. M. van Leusen and J. Strating, Rec. Trav. chim., 1965, 84, 151. <sup>9</sup> R. Adams and A. Ferretti, J. Amer. Chem. Soc., 1959, 81,

4927.

<sup>10</sup> R. L. Shriner, H. C. Struck, and W. J. Jorison, J. Amer. Chem. Soc., 1930, 52, 2060.

<sup>11</sup> See, for examples, M. Kobayashi, K. Tanaka, and H. Minato, Bull. Chem. Soc. Japan, 1972, 45, 2906; C. M. M. da Silva Correa and W. A. Waters, J. Chem. Soc. (C), 1968, 1872; J. L. Kice and N. A. Favstritsky, J. Org. Chem., 1970, 35, 116; A. J. Rosenthal and C. G. Overberger, J. Amer. Chem. Soc., 1960, 32, 117; J. E. Leffler and Y. Tsuno, J. Org. Chem., 1963, 09, 100

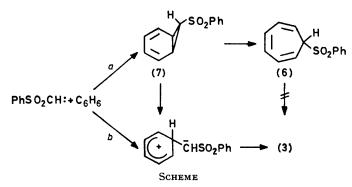
28 190. <sup>12</sup> A. Bruggink, B. Zwanenburg, and J. B. F. N. Engberts, <sup>13</sup> A. Bruggink, B. Zwanenburg, and J. B. F. N. Engberts, Tetrahedron, 1970, 26, 4995 (no physical properties were given for this compound). <sup>13</sup> R. A. Abramovitch and V. Alexanian, unpublished results.

cleavage of C-S bonds in sulphones.14 Sulphonyl azides are also known to undergo thermal radical-induced decomposition to give RSO<sub>2</sub>.<sup>15</sup> By analogy with the

(1) 
$$\xrightarrow{\text{homolysis}} \text{PhSO}_{2} \cdot \xrightarrow{\text{disproportionation}} PhSO_{3} \cdot \xrightarrow{\text{RH}} PhSO_{3}H \xrightarrow{(1)} (5)$$
  
 $\downarrow$   
 $(2)$ 

chemistry of sulphonyl azides,<sup>15</sup> the source of the radical responsible for initiation of this decomposition in our case could be triplet sulphonylcarbene.

Both thermal and photochemical reactions gave benzyl phenyl sulphone (3) in very low yield, in sharp contrast to the appreciable yields of aromatic substitution products from aryl- and alkyl-sulphonylnitrenes.<sup>16</sup> This could be related to the expectation that sulphonylnitrenes would be more electronegative than the corresponding sulphonylcarbenes, or to much of the carbene reacting in the triplet state in benzene. It has been shown that electronegativity influences considerably the ability of arylnitrenes to undergo intermolecular aromatic substitution.<sup>17</sup> It was also of interest that no 7-phenylsulphonylcyclohepta-1,3,5-triene (6) was isolated from either the thermolysis (80 °C) or the photolysis of (1) in benzene, again in contrast to the corresponding sulphonylnitrenes.<sup>17,18</sup> The possibility was considered that the sulphone (3) was the product of thermodynamic control formed under the reaction conditions from (6), the expected <sup>17</sup> product of kinetic control (path a, Scheme). Indeed, carbenes are well known to add to benzene to give cycloheptatriene



derivatives.<sup>19</sup> To test this possibility, authentic (6) was subjected to the thermolysis conditions and was

14 A. M. van Leusen, P. M. Smid, and J. Strating, Tetrahedron Letters, 1967, 1165.

<sup>15</sup> D. S. Breslow, M. F. Sloan, N. R. Newburg, and W. B. Renfrow, J. Amer. Chem. Soc., 1969, 91, 2273; R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *ibid.*, p. 1219.
 <sup>16</sup> R. A. Abramovitch, T. D. Bailey, T. Takaya, and V. Uma,

J. Org. Chem., 1974, 39, 340, and references cited therein. <sup>17</sup> R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, J. Org. Chem., 1972, 37, 2705; J. Amer. Chem. Soc., 1972, 94, 1374.

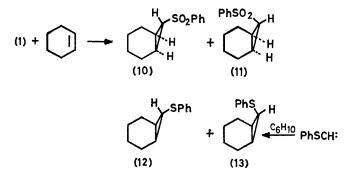
18 R. A. Abramovitch and W. D. Holcomb, J. Org. Chem., 1976, 41, 491.

recovered unchanged. Either the norcaradiene (7) is formed first (path a, Scheme) and prefers to undergo ring opening to give the  $\sigma$ -complex (8) rather than electrocyclic ring expansion to give (6) <sup>3,6</sup> [the ability of the sulphonyl group in (8) to delocalise the developing negative charge could be important here], or the  $\sigma$ complex (8) is formed directly (path b, Scheme). The failure of atmospheric oxygen to suppress the formation of phenyl benzyl sulphone (see Table 1) suggests that singlet, rather than triplet, sulphonylcarbene is the precursor of (3).

Thermolysis of (1) in cyclohexane gave the insertion product (9) together with the ester (5). Again, exclusion of atmospheric oxygen had no influence upon the yield of (5). Photolysis of (1) in cyclohexane gave mainly (5) (as was the case in benzene) and much less (9).

$$(1) + C_6H_{12} \longrightarrow PhSO_2CH_2C_6H_{11} + (5)$$
(9)

Decomposition (thermal or photochemical) of (1) in cyclohexene gave a mixture of exo- and endo-norcaranes



(10) and (11) in the ratio 2.2:1 in both cases. This contrasts with the exo: endo ratio of 0.77:1 reported <sup>20</sup> for the addition of phenylthiocarbene to cyclohexene. We have confirmed this ratio. Thus the attractive interactions<sup>21</sup> that favour formation of the endoisomer (13) in the reaction with phenylthiocarbene are mostly overcome in the reactions of (1), either because of an increase in the electronegativity of the  $\alpha$ -substituent on the carbene or, more likely, as a result of the increased steric effect of the sulphonyl substituent.<sup>22</sup>

## EXPERIMENTAL

Solvents were reagent grade and were dried and distilled before use. Dry, oxygen-free nitrogen was used to degas the solvents. Quantitative analyses were carried out by g.l.c. (helium flow rate 75 ml min<sup>-1</sup>; o-chlorobenzyl phenyl sulphone<sup>23</sup> as internal standard); retention times (min), column temperatures (°C) and types of columns used for the

<sup>19</sup> D. Bethell, in 'Organic Reactive Intermediates,' ed. S. McManus, Academic Press, London, 1973, p. 113.
 <sup>20</sup> U. Schöllkopf, G. J. Lehmann, J. Paust, and H. D. Härtl,

Chem. Ber., 1964, 97, 1527. <sup>21</sup> W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic

<sup>21</sup> W. Kirmse, 'Carbene C Press, New York, 1971, p. 286.

22 F. G. Bordwell and G. D. Cooper, J. Amer. Chem. Soc., 1951, 73, 5187.

23 R. S. Asthana and G. S. Misra, J. Indian Chem. Soc., 1954, 31, 459.

various components were: methyl phenyl sulphone,24 5.5 min at 180°, col. A; o-chlorobenzyl phenyl sulphone,<sup>23</sup> 28.0 min at 265°, col. A; benzyl phenyl sulphone,<sup>10</sup> 18.0 min at 265°, col. A and 11.3 min at 225°, col. B; phenylsulphonylmethyl benzenesulphonate, 55.0 min at 265°, col. A; cyclohexylmethyl phenyl sulphone,<sup>25</sup> 19.5 min at 265°, col. A; exo-7-phenylsulphonylnorcarane, 20 31.0 min at 240°, col. A; endo-7-phenylsulphonylnorcarane,<sup>20</sup> 34.0 min at 240°, col. A; diphenyl disulphide, 26 3.5 min at 225°, col. B [column A (9 ft  $\times$  1/4 in) was 25% Apiezon N on Chromosorb W (60—80 mesh); column B (9 ft  $\times$  1/4 in) was 25% SE-30 on GasChrom Q]. Products were identified by comparison of retention times, m.p.s, and i.r. and n.m.r. spectra with those of authentic samples.

Thermolysis of Diazo(phenylsulphonyl)methane. General Procedure.-Diazo(phenylsulphonyl)methane \* in the dry solvent in large excess (at least 100 molar) was boiled under reflux for 18 h. The mixture was concentrated to ca. 10 ml; any trans-1,2-bisphenylsulphonylethylene (4) 9 formed separated as a brown solid which was purified by sublimation. The remaining mixture was analysed quantitatively by g.l.c. as described above. The results are summarised in the Table.

\* The procedure given in ref. 2 was modified: the N-nitrosocarbamate was stirred with neutral alumina in methylene chloride in the absence of light for ca. 2 days,<sup>27</sup> rather than passed through a column of neutral alumina. This led to improved yields.

Photolysis of Diazo(phenylsulphonyl)methane. General Procedure.—Diazo(phenylsulphonyl)methane (1.5 g) in dry solvent (75 ml) was irradiated in a Rayonet reactor with 253.7-nm light for 18 h at room temperature. The mixtures were then worked up as in the case of the thermolyses.

Attempted Thermal Rearrangement of 7-Phenylsulphonylhepta-1,3,5-triene.—(a) The compound <sup>28</sup> (0.81 g) was heated in dry benzene (25 ml) at 80 °C for 16 h. Starting material was recovered quantitatively.

(b) A solution of phenylsulphonylcycloheptatriene (0.08 g) in methylene chloride (1 ml) was injected onto column B at 225 °C. The only product isolated was diphenyl disulphide. Under identical conditions an authentic sample of benzyl methyl sulphone gave a sharp peak with retention time 11.3 min.

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