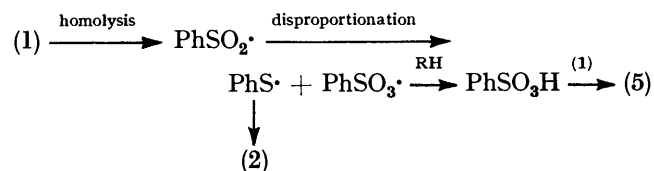


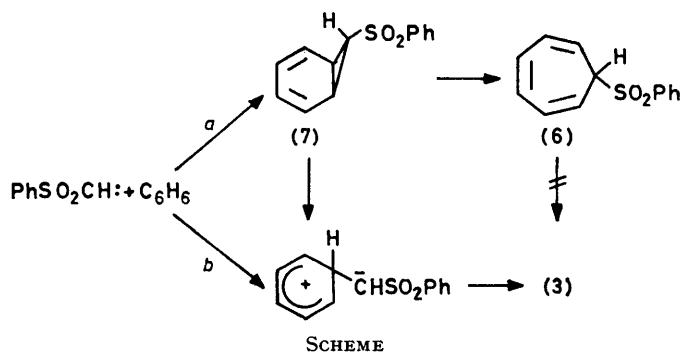


cleavage of C-S bonds in sulphones.<sup>14</sup> Sulphonyl azides are also known to undergo thermal radical-induced decomposition to give  $\text{RSO}_2\cdot$ .<sup>15</sup> By analogy with the



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 aryl nitrenes 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

<sup>14</sup> 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.

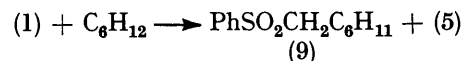
<sup>16</sup> R. A. Abramovitch, T. D. Bailey, T. Takaya, and V. Uma, *J. Org. Chem.*, 1974, **39**, 340, and references cited therein.

<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.

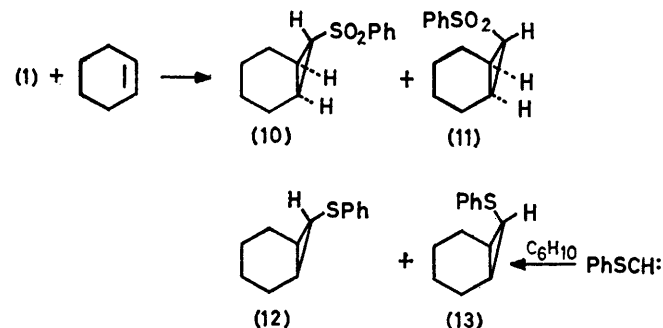
<sup>18</sup> R. A. Abramovitch and W. D. Holcomb, *J. Org. Chem.*, 1976, **41**, 491.

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).



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 *endo*-isomer (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 Press, New York, 1971, p. 286.

<sup>22</sup> F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, 1951, **73**, 5187.

<sup>23</sup> R. S. Asthana and G. S. Misra, *J. Indian Chem. Soc.*, 1954, **31**, 459.

various components were: methyl phenyl sulphone,<sup>24</sup> 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,<sup>20</sup> 31.0 min at 240°, col. A; *endo*-7-phenylsulphonylnorcarane,<sup>20</sup> 34.0 min at 240°, col. A; diphenyl disulphide,<sup>26</sup> 3.5 min at 225°, col. B [column A (9 ft × 1/4 in) was 25% Apiezon N on Chromosorb W (60–80 mesh); column B (9 ft × 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) \* 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*-nitroso-carbamate 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-Phenylsulphonyl-hepta-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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<sup>24</sup> L. Field and R. D. Clark, *J. Org. Chem.*, 1957, **22**, 1129.

<sup>25</sup> E. E. Royals and A. H. Neal, *J. Org. Chem.*, 1956, **21**, 1448.

<sup>26</sup> K. W. Rosenmund and H. Harms, *Ber.*, 1920, **53B**, 2226.

<sup>27</sup> J. M. Muchowski, *Tetrahedron Letters*, 1966, 1773.

<sup>28</sup> J. Dejana and R. Fochi, *Boll. sci. Fac. Chim. ind. Bologna*, 1964, **22**, 81 (*Chem. Abs.*, 1965, **62**, 13 083h).