

Reactions of Benzenesulphonylcarbene

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THE preparation of *p*-methoxyphenylsulphonylcarbene and its addition to isobutene has recently been reported.¹ We describe the composition of some of the more complex products resulting

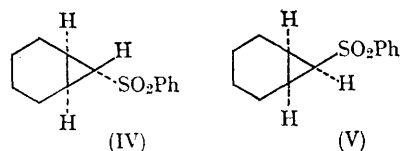
¹ A. M. van Leusen, R. J. Mulder, and J. Strating, *Tetrahedron Letters*, 1964, 543.

from the photolysis or thermolysis of benzenesulphonyldiazomethane² $\text{PhSO}_2\cdot\text{CH}\cdot\text{N}_2$ (I) in various solvents.

The thermal decomposition of (I) in benzene gave an appreciable quantity of low-boiling material together with *trans*-1,2-dibenzesulphonylethylene (II) $\text{Ph}\cdot\text{SO}_2\cdot\text{CH}=\text{CH}\cdot\text{SO}_2\cdot\text{Ph}$ (23%),³ benzyl phenyl sulphone⁴ (1.2%), and a compound (III), $\text{C}_{13}\text{H}_{12}\text{O}_5\text{S}_2$, m.p. 96–96.5° (3.0%). Compound (III) exhibited a 10H-multiplet centred at τ 2.41 and a 2H-singlet at τ 5.06. The n.m.r., infrared, and mass spectra of (III) establish its structure as $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$. This ester must be formed by an abstraction of oxygen by $\text{C}_6\text{H}_5\text{SO}_2\cdot$ from a benzenesulphonyl derivative to give $\text{C}_6\text{H}_5\cdot\text{SO}_3$, followed by coupling with $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{CH}_2\cdot$ (arising, presumably from $\text{C}_6\text{H}_5\cdot\text{SO}_2\text{CH}:\text{ + RH} \rightarrow \text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{ + R}^{\cdot}$). Thus, (III) is also formed (3.1%), together with (II) (28%) and the phenyl sulphone (1.2%), when the thermolysis is carried out in degassed solvent in the absence of atmospheric oxygen. Almost no (II) is obtained in the photolysis of (I) in benzene; benzyl phenyl sulphone is again formed (1.1%) but the yield of (III) increases markedly (23.0%).

That (II) and (III) probably arise from a carbene precursor was confirmed by trapping the latter before it could undergo the slower reactions leading to these compounds. Photolysis of (I) in cyclohexene gave the 7-benzesulphonylnorcaranes⁵ (48.2%); no (II) or (III) could be

detected by gas chromatography. The *exo*- (IV) to *endo*- (V) ratio was 68:32, which is to be contrasted with an *exo*-/*endo*- ratio of 1:1.3 reported⁵ (and confirmed here) for the addition of benzenesulphonylcarbene to cyclohexene. The same ratio (IV)/(V) was obtained on thermolysis of (I) in cyclohexene but the yield of product was slightly higher (53.1%); again, no (II) or (III) was detected.



Thermal decomposition of (I) in cyclohexane in the presence of air gave the insertion product, cyclohexylmethyl phenyl sulphone (VI), m.p. 53–54° (28.9%), together with (III) (5.8%). In the absence of oxygen, (VI) (43.5%) and (III) (6.9%) were again obtained, while photolysis gave only 12.1% of (VI) and, as with benzene, the yield of (III) increased greatly (34.6%). It appears, therefore, that while sulphonylimido-intermediates⁶ and sulphonylcarbenes undergo C–H insertions readily, only the former⁷ give appreciable quantities of aromatic substitution products.

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⁶ M. F. Sloan, D. S. Breslow, and W. B. Renfrow, *Tetrahedron Letters*, 1964, 2905.

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