Addition of Arylsulphonylcarbenes to Benzene

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Arylsulphonylcarbenes have been generated in benzene by thermolysis of arylsulphonyldiazomethanes. Contrary to previous findings arylsulphonylcarbenes add to benzene giving the corresponding arylsulphonylcycloheptatrienes

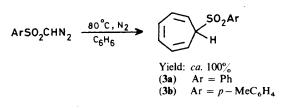
In 1977 Abramovitch, Alexanian and Roy¹ described the generation of phenylsulphonylcarbene by thermolysis and photolysis of phenylsulphonyldiazomethane in cyclohexene, cyclohexane, and benzene. As a result of the reaction in cyclohexene they obtained the corresponding norcarane which is the normal addition product of carbene. With cyclohexane the product was a compound formed by insertion of carbene into a C-H bond. However, with benzene the authors found no addition product and only 1-2% of a product formed probably by insertion. On analysis of the reaction mixture by g.l.c. (column temp. > 180 °C) they found that the reaction proceeded according to Scheme 1. This result is surprising because phenylsulphonyl-

$$\begin{array}{c} PhSO_{2}CHN_{2} \\ Heat \\ \hline \\ PhSO_{2}CH_{2}Ph + (PhSO_{2}CH_{2}+ PhSO_{3}CH_{2}SO_{2}Ph \\ (1) \\ \end{array}$$



carbene should be sufficiently electrophilic to add to benzene to give cycloheptatriene.²

We have repeated the experiment described by Abramovitch and co-workers. The thermolysis of phenylsulphonyldiazomethane³ was performed in dry benzene at 80 °C. After evaporation of the solvent the residue was identified as almost pure phenylsulphonylcycloheptatriene (**3a**). Starting from tosyldiazomethane⁴ we obtained a similar product (**3b**) (Scheme 2).



Scheme 2.

Spectral properties of the arylsulphonylcycloheptatrienes (3a,b) are given in the Experimental section. M.p.s are consistent with those described for (3a) and (3b) prepared by a different method.⁵

The products decomposed at < 150 °C and were sensitive to even weak acids. This is probably why Abramovitch and coworkers did not separate the primary product from the reaction mixture (as it was directly analysed by g.l.c.). When we passed (3a) in benzene through a column of SiO_2 we obtained a mixture similar to that described by Abramovitch.

$$(3a) \xrightarrow{\text{SiO}_2} (1) + (2) + \text{PhSO}_2\text{SPh}$$
(4)

Experimental

Thermolysis of Arylsulphonyldiazomethanes in Benzene.— Arylsulphonyldiazomethane (5 mmol) in dry benzene (100 ml) was gently refluxed under N₂ until disappearance of the diazo compound signals in the ¹H n.m.r. spectrum (*ca.* 10 h). The solvent was evaporated and the residue was identified as almost pure arylsulphonylcycloheptatriene (**3a**) or (**3b**). (**3a**), M.p. 90—91 °C (from MeOH) (lit.,⁵ 93—94 °C); v_{max} .(KBr) 1 302 and 1 143 cm⁻¹ (SO₂); $\delta_{\rm H}$ (60 MHz; CDCl₃) 3.6 (1 H, t, J 6.5 Hz, 7-H), 5.3—5.7 (2 H, m, 1,6-H), 6.1—6.4 (4 H, m, 2,3,4,5,-H), 7.3—8.0 (5 H, m, ArH); *m/z* 232 (*M*⁺, 2.3%), and 91 (C₇H₇⁺, 100%). (**3b**), M.p. 129.5—131 °C (from MeOH) (lit.,⁵ 128—129 °C); v_{max} .(KBr) 1 302 and 1 147 cm⁻¹ (SO₂); $\delta_{\rm H}$ (60 MHz; CDCl₃) 2.4 (3 H, s, CH₃), 3.6 (1 H, t, J 6.5 Hz, 7-H), 5.3—5.7 (2 H, m, 1,6-H), 6.2—6.4 (4 H, m, 2,3,4,5-H), 7.2—7.9 (4 H, AA'BB', C₆H₄); *m/z* 246 (*M*⁺, 2.6%) and 91 (C₇H₇⁺, 100%).

Decomposition of (3a).—A solution of (3a) and (3b) in benzene was passed through a column (60 cm) of silica gel (50-100 mesh) to yield compounds $(1)^{6}(160 \text{ mg}), (2)^{1.8}(200 \text{ mg})$, and $(4)^{7}$ (120 mg). Products were identified by comparison of m.p.s and i.r. and n.m.r. spectra with those of authentic samples.

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