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CHEMISTRY OF α-DIAZOSULPHONES

A SULPHONYLCARBENE

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As would be anticipated α-diazosulphones[1,2,3], a new class of compounds recently prepared in our laboratory, are potential sulphonylcarbene forming agents. The most conclusive way of trapping a carbene is by reaction with an olefin to produce a cyclopropane derivative. Indeed, when p-methoxyphenylsulphonyl diazomethane (I) was irradiated[4] in refluxing isobutene 1-(p-methoxyphenylsulphonyl)-2,2-dimethylcyclopropane (III) was formed:

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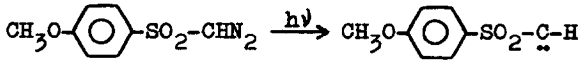
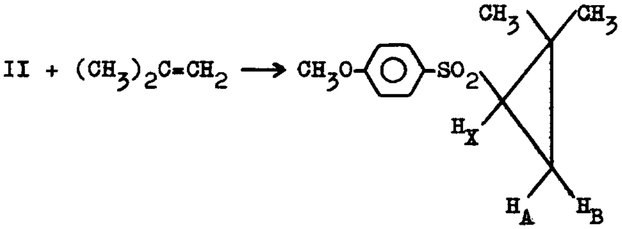
1. Part 1: J.Strating and A.M.van Leusen, Rec.trav.chim. 81, 966 (1962).
2. F.Klages, Angew.Chem. 74, 725 (1962), and K.Bott, thesis München (1962).
3. J.Diekmann, J.Org.Chem. 28, 2933 (1963).
4. Using a Hanau S 81 UV-lamp.



I II



III

The structure of III, m.p. 74-75°, is confirmed[5] by its NMR spectrum and by independent synthesis.

The NMR spectrum[6] of III (in deuteriochloroform) consists of an aromatic multiplet between τ 2-3, a single peak for the methoxy protons at τ 6.10 and two singlets for the two methyl groups at τ 8.54 and 8.89. Furthermore the three ring protons give the expected ABX system[7], with τ_X 7.76, $\tau_A \sim$ 8.6, $\tau_B \sim$ 9.0, $J_{AB} \sim$ 5.4, $J_{AX} \sim$ 5.2 and $J_{BX} \sim$ 8.6 (apart from the sign of J). The absorptions due to the A and B protons are partially masked by the methyl peaks. The replacement of deuteriochloroform by benzene does not give an essentially better resolution, although there is a considerable solvent effect.

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5. Satisfactory elemental analyses were obtained for all new compounds.
6. Recorded at 60 Mc on a Varian A 60 apparatus, with tetramethylsilane as an internal standard. The τ values are expressed in ppm, the J values in c.p.s.
7. cf. D.J.Patel, M.E.H.Howden and J.D.Roberts, <u>J.Am.Chem.Soc.</u> **85**, 3218 (1963); K.B.Wiberg and B.J.Nist, <u>ibid.</u> **85**, 2788 (1963); U.Schöllkopf, A.Lerch and J.Paust, <u>Chem.Ber.</u> **96**, 2266 (1963) and references cited therein.

Compound III is identical (mixed m.p., IR and NMR spectra) with a sample prepared according to the method of Schöllkopf and Lehmann[8]. Isobutene and p-methoxyphenylthiocarbene (from p-methoxyphenyl chloromethyl sulphide and potassium tert.butoxide) formed 1-(p-methoxyphenylthio)-2,2-dimethylcyclopropane (IV), b.p. 92-93°/0.2 mm, n_D^{20} 1.5553. This was oxidised with hydrogenperoxide (30%) to the sulphone III.

The NMR spectrum of IV (in carbon tetrachloride) gives an ABX system, with τ_X 8.01, $\tau_A \sim 9.2$, $\tau_B \sim 9.6$, J_{AB} 4.9, $J_{AX} \sim 8.3$ and $J_{BX} \sim 5.0$ (apart from the sign of J) in good agreement with the values given by Schöllkopf and Lehmann[9].

The same carbene II is possibly the intermediate in the reaction of p-methoxyphenylsulphonyl diazomethane with methanol[10]. Both under the influence of ultraviolet radiation and with a catalyst (Ag_2O) p-methoxyphenyl methoxymethyl sulphone (V), m.p. 56-57°, was formed. The structure of V is supported by its NMR spectrum (in acetone) with a singlet for the methylene group at τ 5.44.

The sulphone V was prepared by an independent route. Using the method of Fehnel and Carmack[11] p-methoxy-thiophenol and monochlorodimethylether were converted to p-methoxyphenyl methoxymethyl sulphide, b.p. 93-95°/0.1 mm, n_D^{20} 1.5612. This

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[8] U.Schöllkopf and G.J.Lehmann, Tetrahedron Letters 1962, 165.

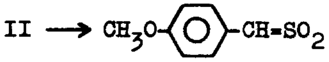
[9] cf. U.Schöllkopf and H.Küppers, ibid. 1963, 105.

[10] A similar reaction of bis-(phenylsulphonyl) diazomethane is mentioned recently by Diekmann, reference 3.

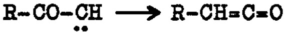
[11] E.A.Fehnel and M.Carmack, J.Am.Chem.Soc. 71, 84 (1949).

was oxidised with mono-perphthalic acid to a compound identical with V (mixed m.p. and IR spectrum).

Thusfar we have found no experimental evidence for a rearrangement of the sulphonylcarbene to a sulphene[12]:



which would be similar to the behaviour of ketocarbenes in the Wolff rearrangement[13]:



$$R{-}CO{-}\underset{\bullet\bullet}{CH} \longrightarrow R{-}CH{=}C{=}O$$

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[12] G.Opitz and H.Adolph, *Angew.Chem.* **74**, 77 (1962);W.E.Truce, J.J.Breiter, D.J.Abraham and J.R.Norell, *J.Am.Chem.Soc.* **84**, 3030 (1962).

[13] F.Weygand and H.J.Bestmann, *Angew.Chem.* **72**, 535 (1960).