

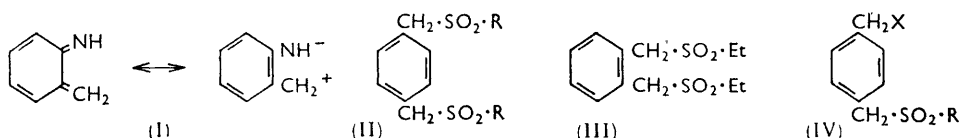
674. Elimination-Addition. Part II.¹ Quinonoid Intermediates in Reactions of $\omega\omega'$ -Dialkylsulphonylxylenes.

By A. T. KADER and C. J. M. STIRLING.

$\omega\omega'$ -Diethylsulphonyl-*p*-xylene (II; R = Et), on treatment with sodium ethoxide, gave the ethoxy-sulphone (IV; R = Et, X = OEt). The disulphone did not react with piperidine, but on the addition of sodium ethoxide gave the piperidino-sulphone (IV; R = Et, X = C₅H₁₀N). The sulphones (II; R = Ph or Bu^t) and (III) behaved similarly; the formation of quinonoid intermediates R·SO₂·CH:C₆H₄:CH₂ is suggested.

Elimination occurs more slowly in the xylenes than in the open-chain vinylogue (VIII), and deuterium-labelling experiments indicate that it is concerted.

FORMATION of *o*- and *p*-quinonoid intermediates CH₂:C₆H₄:CH₂* in eliminations has frequently been suggested to account for the products of reactions with ω -substituted xylenes.²⁻⁴ These intermediates usually dimerise³ or polymerise^{2a,5} but in a few cases monomeric products formed by addition of electrophiles have been isolated,⁴ and nucleophilic addition to the closely related *o*- and *p*-methylene-imines (I) has been observed.^{2b} In the latter case, the dipolar structure encourages the attack of the nucleophile at the methylene-carbon atom.



Elimination-addition reactions of 1,2-diarylsulphonylalkanes have been discussed in the preceding paper,¹ and it was of interest to discover whether similar reactions would occur with the vinylogous dialkylsulphonyl-*p*- and *o*-xylene (II) and (III). $\omega\omega'$ -Diethylsulphonyl-*p*-xylene (II; R = Et) was readily obtained from $\omega\omega'$ -dichloro-*p*-xylene and ethanethiol, with subsequent oxidation of the bis-sulphide to the sulphone. Treatment of the sulphone with sodium ethoxide in ethanol-pyridine at 80° gave the ethoxy-sulphone (IV; R = Et, X = OEt) in 73% yield. In a partial reaction, only recovered sulphone (61%) and ethoxy-sulphone (27%) were obtained. This sulphone was identical with the ethanolysis product of the bromide (IV; R = Et, X = Br), obtained by treatment of the sulphone (IV; R = Et, X = H) with *N*-bromosuccinimide. The position of bromine in the bromo-sulphone was shown by conversion into the disulphone (II; R = Et).

As for 1,2-diarylsulphonylalkanes,¹ these observations may be accommodated by mechanisms which involve either direct replacement of the alkylsulphonyl group by ethoxide ion, or elimination-addition, which, in the present instance, involves the quinonoid intermediate (V). Sulphonyl groups in simple monosulphones are replaced only under severe conditions⁶ and so it is improbable that direct substitution occurs. In

* Frequently termed xylenes.

¹ Part I, Paper No. 715, this issue.

² Mann and Stewart, *J.*, 1954, (a) 2826, (b) 4127.

³ Cava and Deana, *J. Amer. Chem. Soc.*, 1959, **81**, 4266; Winberg, Fawcett, Mochel, and Theobald, *ibid.*, 1960, **82**, 1428; Errede, *ibid.*, 1961, **83**, 949.

⁴ Errede, Hoyt, and Gregorian, *J. Amer. Chem. Soc.*, 1960, **82**, 5224.

⁵ Errede and Swarc, *Quart. Rev.*, 1958, **12**, 301.

⁶ Fenton and Ingold, *J.*, 1930, 705.

In order to differentiate between concerted *E2* and *E1cb* mechanisms⁹ for the eliminations, we have carried out partial reactions in deuterioethanol (EtO^2H) and have examined the recovered sulphone for contamination by deuterium which would indicate the operation of the latter mechanism. Diethylsulphonyl-*p*-xylene (II; $\text{R} = \text{Et}$) was unsuitable as it possesses hydrogen atoms, which are not concerned in elimination, adjacent to the sulphonyl groups. Diphenylsulphonyl-*p*-xylene (II; $\text{R} = \text{Ph}$) reacted too rapidly under the standard conditions for sufficient unchanged sulphone to be recoverable, but the *t*-butyl sulphone (II; $\text{R} = \text{Bu}^t$) was readily recovered from partial reactions together with the ethoxy-sulphone (IV; $\text{R} = \text{Bu}^t$, $\text{X} = \text{OEt}$). When reactions with this sulphone were carried out in deuterioethanol, no deuterium incorporation was detectable by comparison of the infrared spectra of the recovered sulphone and the starting material. We tentatively conclude, therefore, that elimination follows too rapidly after proton removal to allow exchange with the solvent.

⁹ Cf. Skell and Hauser, *J. Amer. Chem. Soc.*, 1945, **67**, 1661.

EXPERIMENTAL

For general directions see Part I.¹

$\omega\omega'$ -Diethylsulphonyl-*p*-xylene.—Ethanethiol (7.43 g.), $\omega\omega'$ -dichloro-*p*-xylene (10 g.), and sodium ethoxide (8.15 g.) in ethanol (50 ml.) were refluxed together for 30 min. The mixture was poured into water, acidified, and extracted with chloroform. Evaporation of the extracts and distillation of the residue gave $\omega\omega'$ -diethylthio-*p*-xylene (11.76 g.), b. p. 110°/0.1 mm., m. p. 31—32° (from methanol) (Found: C, 64.1; H, 7.95. $C_{12}H_{18}S_2$ requires C, 63.7; H, 8.0%). Oxidation of the sulphide gave the *disulphone* (91%), m. p. 185—186° (from ethanol) (Found: C, 49.5; H, 6.1. $C_{12}H_{18}O_4S_2$ requires C, 49.7; H, 6.3%).

Reactions of the Sulphone.—(a) *With sodium ethoxide.* The sulphone (2.9 g.) and sodium ethoxide (6.8 g.) in ethanol (75 ml.) and pyridine (25 ml.) were kept at 80° for 24 hr. Distillation gave ω -ethoxy- ω' -ethylsulphonyl-*p*-xylene (1.77 g., 73%), b. p. 150°/0.05 mm., m. p. 40—41° alone or mixed with an authentic specimen (below) (Found: C, 59.5; H, 7.5. $C_{12}H_{18}O_3S$ requires C, 59.7; H, 7.4%). When the period of heating was reduced to 15 min., recovered sulphone (61%) and ethoxy-compound (27%) were obtained.

(b) *With sodium ethoxide and piperidine.* The preceding experiment was repeated with the addition of piperidine (4.68 g.) to the reaction mixture. After the mixture had been kept at 80° for 24 hr., most of the solvent was removed and the residue was poured into water. Extraction with benzene gave a product (2.3 g.) which, on recrystallisation from benzene-light petroleum, gave ω -ethylsulphonyl- ω' -piperidino-*p*-xylene (1.83 g., 65%), m. p. 116—117° alone or mixed with an authentic specimen (below). Distillation of the mother-liquors gave the ethoxy-sulphone (0.32 g., 13%), b. p. 160°/0.2 mm., m. p. and mixed m. p. 41—42°.

The disulphone and the ethoxy-sulphone were both unaffected by treatment with piperidine in the absence of sodium ethoxide. Benzyl ethyl sulphone and ω -ethylsulphonyl-*p*-xylene¹⁰ were quantitatively recovered from reactions with sodium ethoxide.

ω -Bromo- ω' -ethylsulphonyl-*p*-xylene.— ω -Ethylsulphonyl-*p*-xylene (3 g.), *N*-bromosuccinimide (4.1 g.), benzoyl peroxide (0.1 g.), and carbon tetrachloride (70 ml.) were refluxed together for 1 hr. Removal of the solvent and extraction of the residue with benzene gave the *bromo-sulphone* (2.5 g.), m. p. 134—136° (from benzene-light petroleum) (Found: C, 43.2; H, 4.75. $C_{10}H_{13}BrO_2S$ requires C, 43.3; H, 4.7%). Treatment of the bromo-sulphone with ethanethiol (1.25 mol.) in ethanolic sodium ethoxide (1.1 mol.) gave the crude sulphide, oxidation of which afforded $\omega\omega'$ -diethylsulphonyl-*p*-xylene, m. p. and mixed m. p. 185—186°.

ω -Ethoxy- ω' -ethylsulphonyl-*p*-xylene.—The bromo-sulphone (1 g.) was refluxed for 48 hr. with a suspension of calcium carbonate (2 g.) in ethanol (30 ml.). The mixture was poured into water and extracted with chloroform. Distillation gave the ethoxy-sulphone (0.8 g.), b. p. 146°/0.01 mm., m. p. 45° (Found: C, 59.6; H, 7.55%).

ω -Ethylsulphonyl- ω' -piperidino-*p*-xylene.—The bromo-sulphone (1 g.) was refluxed with piperidine (1.53 g.) in ethanol (30 ml.) for 1 hr. Most of the solvent was removed and the residue, after treatment with aqueous sodium carbonate, was extracted with benzene. Evaporation of the extracts gave the piperidino-sulphone (0.81 g.), m. p. 105—107°, raised to 117—118° (from benzene-light petroleum) (Found: C, 64.3; H, 7.85. $C_{15}H_{23}NO_2S$ requires C, 64.1; H, 8.2%).

$\omega\omega'$ -Diethylsulphonyl-*o*-xylene.—The *bis-sulphide*, obtained from $\omega\omega'$ -dibromo-*o*-xylene by the procedure used for the *para*-isomer, had b. p. 170°/3 mm., n_D^{17} 1.5780 (Found: C, 63.8; H, 8.0%). Oxidation gave the *disulphone*, m. p. 130—131° (Found: C, 50.0; H, 6.4%). Treatment of the sulphone (2.9 g.) with sodium ethoxide in ethanol-pyridine for 24 hr. at 80° as for the *para*-isomer gave ω -ethoxy- ω' -ethylsulphonyl-*o*-xylene (1.83 g.), b. p. 160°/0.1 mm., n_D^{19} 1.5323 (Found: C, 59.6; H, 7.4%). The residue from the distillation yielded recovered sulphone (0.52 g.), m. p. and mixed m. p. 130—131°.

$\omega\omega'$ -Diphenylsulphonyl-*p*-xylene.—Treatment of $\omega\omega'$ -dichloro-*p*-xylene with thiophenol and ethanolic sodium ethoxide as before gave the *bis-sulphide* (86%), m. p. 141—142° (from ethanol) (Found: C, 74.8; H, 5.45. $C_{20}H_{18}S_2$ requires C, 74.5; H, 5.6%). Oxidation gave the *disulphone* (72%), m. p. 280° (from chloroform) (Found: C, 62.4; H, 4.9. $C_{20}H_{18}O_4S_2$ requires C, 62.2; H, 4.6%).

¹⁰ Shriner, Struck, and Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060.

Treatment of the sulphone (1.93 g.) with sodium ethoxide (13.6 g.) in ethanol (100 ml.) and pyridine (100 ml.) for 24 hr. at 80° gave *ω*-ethoxy-*ω'*-phenylsulphonyl-*p*-xylene (1.32 g., 91%), m. p. 120–125°, raised to 128° (from benzene–light petroleum) (Found: C, 66.2; H, 6.3. $C_{16}H_{18}O_3S$ requires C, 66.2; H, 6.2%). The aqueous extracts yielded benzenesulphonic acid (95%) as 4-nitrobenzyl phenyl sulphone, m. p. and mixed m. p. 208–209° (lit.,¹¹ m. p. 208–209°).

ωω'-*Di-t*-butylsulphonyl-*p*-xylene.—The *bis*-sulphide (76%), m. p. 90° (from benzene–light petroleum), was obtained from *ωω'*-dichloro-*p*-xylene and 2-methylpropane-2-thiol (Found: C, 67.9; H, 9.2. $C_{16}H_{26}S_2$ requires C, 68.1; H, 9.2%). Oxidation gave the *disulphone* (83%), m. p. 246–247° (from methanol) (Found: C, 55.5; H, 7.5. $C_{16}H_{26}O_4S_2$ requires C, 55.5; H, 7.5%).

Reactions of the Di-t-butyl Sulphone with Sodium Ethoxide.—(i) The sulphone (1 g.) and sodium ethoxide (1.36 g.) in 1,2-diethoxyethane (10 ml.) and ethanol (10 ml.) were kept at 80° for 24 hr. The usual working-up gave *ω*-ethoxy-*ω'*-*t*-butylsulphonyl-*p*-xylene (0.67 g., 86%), m. p. 83° (from benzene–light petroleum) (Found: C, 62.2; H, 8.3. $C_{14}H_{22}O_3S$ requires C, 62.2; H, 8.2%). The aqueous extracts gave 2-methylpropane-2-sulphonic acid (85%) as 4-nitrobenzyl *t*-butyl sulphone, m. p. 178° (from benzene–light petroleum) (Found: C, 51.0; H, 5.8. $C_{11}H_{15}NO_4S$ requires C, 51.4; H, 5.8%).

(ii) The sulphone (0.7 g.), in 1,2-diethoxyethane (9 ml.), was added to sodium ethoxide (0.476 g.) in [*O*-³H]ethanol¹² (5 ml.). The mixture was kept at 80° for 5 min. and then was added to a mixture of saturated brine (50 ml.) and concentrated hydrochloric acid (2 ml.). The usual working-up gave recovered sulphone (0.56 g.), m. p. 242–245°, together with the ethoxy-sulphone (0.059 g.), m. p. and mixed m. p. 81–82°, which was obtained by extraction of the mixture of neutral products with cold benzene. The recovered sulphone was recrystallised to constant m. p. from ethanol, and the infrared spectrum (10% solution in $CHCl_3$) in the range 3000–2000 cm^{-1} was compared with that of the original sulphone. The Perkin–Elmer 21 infrared spectrometer was used with 1 mm. micro-cells. Although the recovered sulphone showed a slightly reduced intensity of absorption in the 2900 cm^{-1} region, there was no detectable difference in absorption in the region near 2100 cm^{-1} (C–D stretching).

1,4-Diethylsulphonyl-trans-but-2-ene.—1,4-Dibromo-*trans*-but-2-ene was converted by treatment with ethanethiol and sodium ethoxide into the *bis*-sulphide (89%), b. p. 118°/1 mm., n_D^{20} 1.5256 (Found: C, 54.3; H, 8.9. $C_8H_{16}S_2$ requires C, 54.5; H, 9.1%). Oxidation gave the *disulphone* (67%), m. p. 104° (from ethanol) (Found: C, 40.4; H, 6.9. $C_8H_{16}O_4S_2$ requires C, 40.1; H, 6.7%). The disulphone (1.6 g.), in *N*-ethanolic sodium ethoxide (67 ml.), was kept at 20° for 15 min. The usual working-up gave 1,3-diethoxy-4-ethylsulphonylbutane (1.38 g., 89%), b. p. 170°/10 mm., n_D^{17} 1.4612 (Found: C, 50.2; H, 9.0. $C_{10}H_{22}O_4S$ requires C, 50.4; H, 9.2%).

We are grateful to Dr. A. D. E. Pullin for advice and help with infrared measurements, and to Professor H. B. Henbest for his interest. One of us (A. T. K.) thanks the Ministry of Education, The Republic of Iraq, for a scholarship.

THE QUEEN'S UNIVERSITY OF BELFAST.

[Received, March 7th, 1962.]

¹¹ Troger and Nolte, *J. prakt. Chem.*, 1920, **101**, 136.

¹² Cristol and Fix, *J. Amer. Chem. Soc.*, 1953, **75**, 2647.