An organometallic route to 2,7-dihydrothiepin-1,1-dioxides[*]

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Reaction of divinylsulphone with alkyne-cobalt complexes $(RC{\equiv}CR')Co_2(CO)_6$ is shown to yield 2,7-dihydrothiepin-1,1-dioxides with the alkyne substituents (R=Ph; R'=H or Ph) in the 4 and 5 positions.

[*] Dedication: to Prof. Tetsuo Nozoe, whose work on seven-membered ring compounds has been an inspiration to organic chemists, on the occasion of his 77th birthday.

We have shown[1] that alkenes bearing such electron withdrawing groups (Y) as cyano or carbonyl give dienes (2) on treatment with the alkyne-cobalt-carbonyl complexes (1):

$$(RC{\equiv}CR')Co_2(CO)_6 + R''CH{=}CHY \rightarrow RCH{=}CR'{-}CR''{=}CHY$$

1 2

In attempting to extend this reaction we have now examined the reaction of divinylsulphone with the phenyl- and diphenylacetylene complexes (1; R = Ph; R' = H or Ph). Although the analyses and mass spectra of the products corresponded to the expected formulae of 1:1 adducts of the alkyne moiety, $RC{\equiv}CR'$, and the alkene, $(CH_2{=}CH)_2SO_2$, their ^1H n.m.r. spectra immediately ruled out formulations as dienes of the type (2). The ready loss of SO_2 from the weak parent ions in the mass spectra, leading to the base peaks without loss of carbon would also be difficult to reconcile with such structures (2) and is suggestive of cyclic formulations. Specifically the ^1H n.m.r. spectrum of the phenylacetylene derived product consisted of 'aromatic', 'alkene' and higher field signals (Fig. 1a) in the ratio, 5:3:4. The position of the last of these signals is intelligible only if they belong to saturated hydrogens alpha to the SO_2 group. This consideration leads to the 2,7-dihydrothiepin-1,1-dioxide formulation (3a) as the only readily compatible

structure, although the mechanism for its formation must be complex.

If correctly formulated, then a symmetrically substituted alkyne complex (1; R = R') would give a symmetrical product. The ^{1}H n.m.r. spectrum of the tolane derived product (3b) showed the expected simplification, consisting (in $CDCl_3$ at 100 MHz) of a broad singlet at τ 2.90 (10H, aromatic), a triplet at τ 3.57 (2H, -CH=, J 8Hz) and a doublet at τ 6.24 (4H, CH_2). The ^{13}C n.m.r. spectrum similarly reflected the expected increase in symmetry in the case of the diphenyl-(3b) compared to the monosubstituted dihydrothiepin dioxide (3a). Notably C_2 and C_7 which give rise to a closely spaced doublet (at 54.18, 54.36 ppm from $SiMe_4$) in the proton decoupled spectrum of compound (3a)[and a double triplet in the undecoupled spectrum] give rise to a singlet (at 54.12 ppm) in the proton decoupled spectrum of compound (3b).

The apparent triplet splitting (Fig. 1a) of the methylene protons at positions 2 and 7 is the result of accidental overlap of the two expected doublets. This becomes evident when changing from 100 to 60 MHz or when the solvent is changed to benzene-d_6 (Fig. 1b). The other signals are also much more clearly resolved in the latter solvent. The extent of the upfield shift produced by benzene seems exceptionally large and suggests strong solute-solvent interactions between the dihydrothiepin dioxides and aromatic solvents.

The ^{1}H n.m.r. data in deuteriochloroform quoted above are in good agreement with the ranges previously observed in (alkyl substituted) 2,7-dihydrothiepin-1,1-dioxides,[2,3] quoted values being H-4,5: $\tau \sim 3.5$, H-3,6: $\tau \sim 4.0$ and H-2,7: $\tau \sim 6.0$–6.5 ppm with $J_{2,3} \sim 7$Hz, $J_{3,4} \sim 10$Hz. This may be regarded as further confirmation of the structure of our products. Previous synthetic methods required numerous steps[2–5] except for those which can be effected by photolysis of cyclohexa-1,3-dienes with sulphur dioxide,[3] a reaction proceeding via hexa-1,3,5-trienes to which the dihydrothiepin dioxides may in turn be decomposed thermally. The present route is likely to prove sufficiently flexible and is simple enough to be a useful additional method for obtaining variously substituted dihydrothiepin dioxides and hence hexatrienes.

Speculatively it may be postulated that the reaction proceeds via the expected product (4) [i.e., (2; where Y = $SO_2CH{=}CH_2$)] as an intermediate, followed by intramolecular Diels–Alder addition yielding the bicyclic sulphone (5). Opening of the three-membered ring accompanied by a hydrogen shift may then yield e.g. the 2,5-dihydrothiepin dioxide (6) which would isomerize to the observed product. Paquette and Maiorana's work[5] implies that the latter would be the thermodynamically most stable isomer and provides some analogy for the last two steps. Moreover, previous observations[6] suggest a possible catalytic role of the cobalt complex (1) in both the Diels–Alder and the isomerization steps.

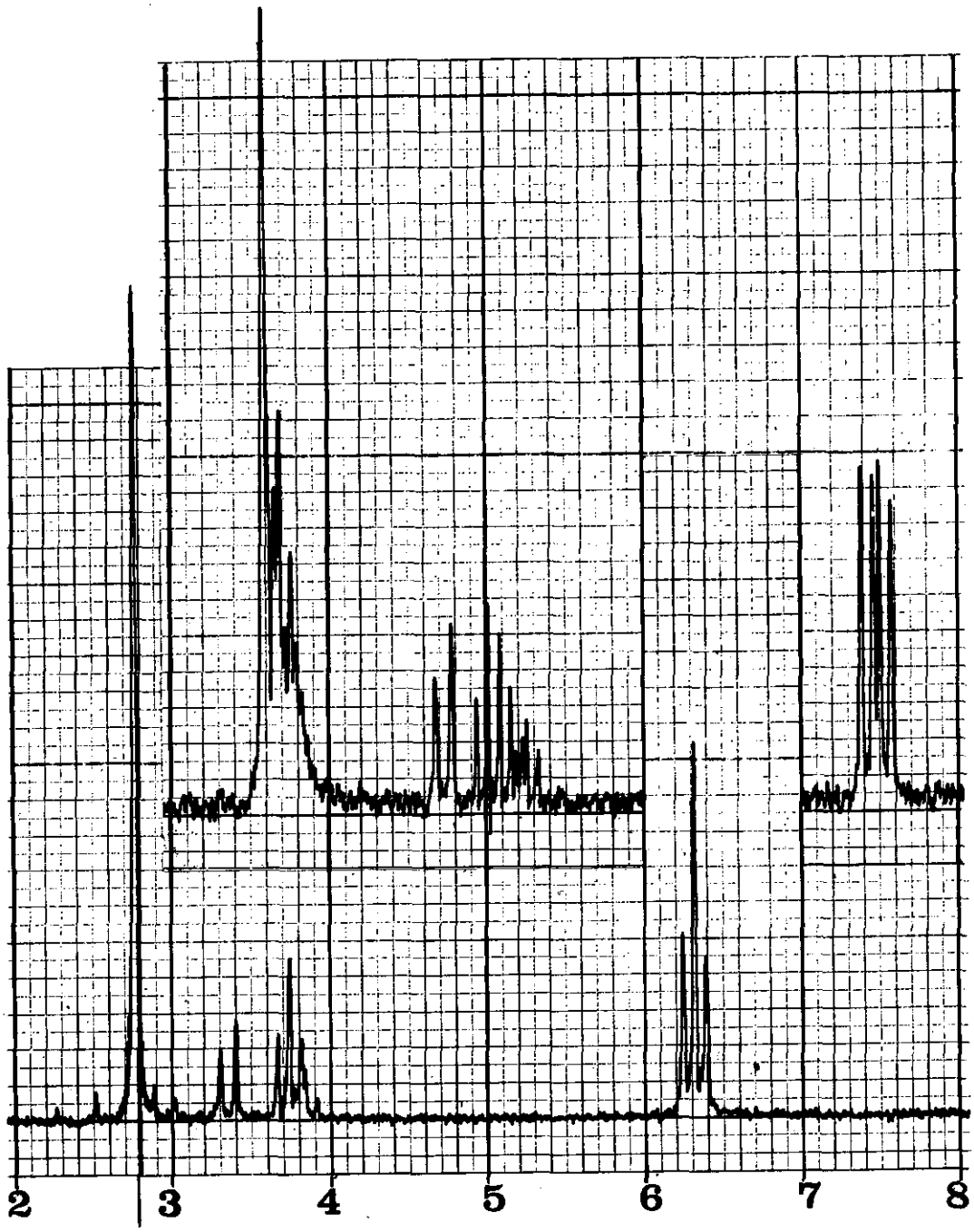
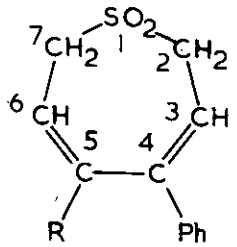
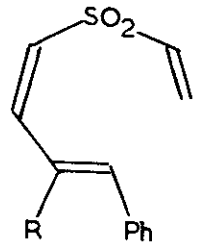


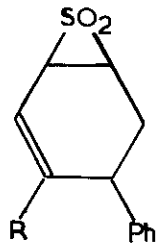
Fig. 1. ^{1}H n.m.r. Spectrum of 4-Phenyl-2,7-dihydrothiepin-1,1-dioxide in (a) $CDCl_3$ and (b) C_6D_6



3
a: R = H
b: R = Ph



4



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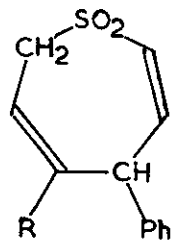

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Experimental

4-Phenyl-2,7-dihydrothiepin-1,1-dioxide (3; R=H). - A mixture of phenylacetylenehexacarbonyldicobalt (1; R=Ph; R'=H) (2.0 g, 5 mmol) and divinyl sulphone (0.75 g, 6.3 mmol) were heated in dry toluene (150 cm^3) under nitrogen for 4 hr at 80-90°C. During this time some carbon monoxide is evolved, the colour of the reaction mixture changes gradually from red to dark brown and solid decomposition products separate. The cooled mixture was filtered and the filtrate evaporated using a rotary evaporator. The residual gum was extracted by boiling with a mixture of benzene and light petroleum with addition of a little charcoal. After filtration the extract was concentrated and then refrigerated. 4-Phenyl-2,7-dihydrothiepin-1,1-dioxide (3; R=H) (325 mg; 29% yield) separated as white crystals which were further purified by dissolution in light petroleum (b.p. 40-60°C) with a few drops of benzene and cooling. M.p. 108-109°C (Found: C,65.15; H,5.45%; M,220.0560. $C_{12}H_{12}O_2S$ requires C,65.4; H,5.4%; M,220.0558). Principal ions in the mass spectrum (all accurately mass measured; relative intensities are given in parentheses) corresponded to: $C_{12}H_{12}O_2S$ (13); $^{12}C_{11}{}^{13}CH_{12}$ (16); $C_{12}H_{12}$ (100); $C_{12}H_{11}$ (60); $C_{12}H_{10}$ (9); $C_{12}H_9$ (13); $C_{11}H_9$ (71); $C_{10}H_9$ (36); $C_{10}H_8$ (58); $C_{10}H_7$ (18). C_9H_7 (60); C_8H_6 (15); C_7H_7 (48).

4,5-Diphenyl-2,7-dihydrothiepin-1,1-dioxide (3; R=Ph). - By the same method the tolane complex (1; R=R'=Ph) (2.0 g, 4.3 mmol) after 5 hr reaction time yielded 4,5-diphenyl-2,7-dihydrothiepin-1,1-dioxide (3; R=Ph) (384 mg; 30% yield) which crystallised from benzene solution on addition of pentane. M.p. 188-189°C (Found: C,72.8; H,5.3%; M,296.0869. $C_{18}H_{16}O_2S$ requires C,72.9; H,5.4%; M,296.0871). Principal mass spectral ions (as above) corresponded to $C_{18}H_{16}O_2S$ (2); $^{12}C_{17}{}^{13}CH_{16}$ (22); $C_{18}H_{16}$ (100); $C_{18}H_{15}$ (17); $C_{17}H_{13}$ (33); $C_{17}H_{12}$ (14); $C_{17}H_{11}$ (24); $C_{16}H_{13}$ (12); $C_{16}H_{12}$ (16); $C_{16}H_{11}$ (14); $C_{16}H_{10}$ (22); $C_{15}H_{11}$ (13); $C_{12}H_{11}$ (11); $C_{12}H_{10}$ (10); $C_{12}H_9$ (11); $C_{11}H_9$ (28); $C_{10}H_9$ (11); $C_{10}H_8$ (31); C_9H_9 (22); C_9H_7 (31); C_8H_5 (14) and C_7H_7 (38).

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References

1. I.U. Khand and P.L. Pauson, JCS Chem.Comm., 1974, 379.
2. W.L. Mock, J.Amer.Chem.Soc., 1967, 89, 1281.
3. W.L. Mock and J.H. McCausland, J.Org.Chem., 1976, 41, 242.
4. W.L. Mock, J.Amer.Chem.Soc., 1975, 97, 3666.
5. L.A. Paquette and S. Maiorana, Chem.Comm., 1971, 313.
6. I.U. Khand, P.L. Pauson and M.J.A. Habib, J.Chem.Research, 1978, in press.

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