Tetrahedron Letters No. 7, pp 691 - 694, 1978. Pergamon Press. Printed in Great Britain.

REACTIONS OF BISPROPADIENYL SULPHIDES. THE 3,4-DIMETHYLENETHIOPHENE DIRADICAL

Y.S. Patrick Cheng, Esther Dominguez, Peter J. Garratt, and Soon Bin Neoh
Department of Chemistry, University College London
London WC1H OAJ

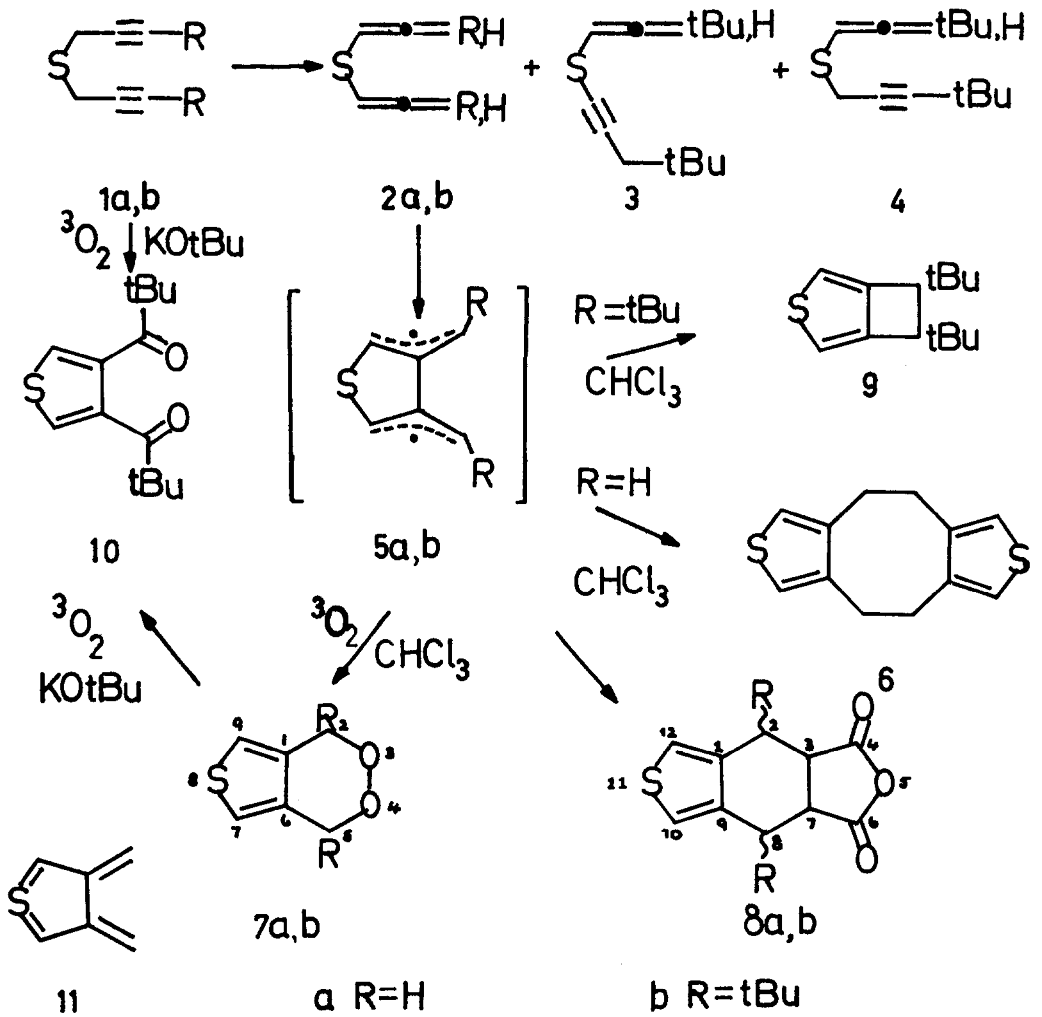
(Received in UK 20 December 1977; accepted for publication 29 December 1977)

The 3,4-dimethylenethiophene diradical 5 has been postulated as an intermediate in the base catalysed rearrangement of bispropargyl sulphides,[1] and in the thermolysis of 2,4,6,7-tetraphenyl-3-thiabicyclo[3.2.0.]hepta-1,4-diene,[2] and the analogous sulphone[3] and furan[4] diradicals have also been evoked in related reactions. We would now like to report some reactions of bispropadienyl sulphides, prepared from the base catalysed rearrangement of the corresponding bispropargyl sulphides, which are most readily explained by the intervention of the 3,4-dimethylenethiophene diradical.

Bispropadienyl sulphide (2a)[5] was prepared as an air sensitive, colourless liquid by treatment of bispropargyl sulphide (1a) with KOtBu in THF under N_2 at -65 °C for 1 min.[7] The ^{1}H NMR spectrum showed a triplet at δ5.80 (2H, J=6.0Hz) and a doublet at δ5.06 (4H, J=6.0Hz),[5] and the structure was confirmed by the ^{13}C NMR spectrum which had three absorptions at 206.5, 85.6 and 80.7 ppm.[8,9]

A solution of 2a in degassed $CHCl_3$ was warmed to 50 °C under N_2 when the dimer 6,[1,5] was obtained in virtually quantitative yield. A $^3O_2$ saturated $CHCl_3$ solution of 2a at 20-22 °C gave, after standing in the dark for 2 h, the peroxide 7a, white crystals, mp 56-58 °C.[10-12] Reaction of 2a in ether with maleic anhydride gave 8a, 20 %, mp 177-178 °C.[10,11]

Elution of 1b through a column of KOH impregnated Al_2O_3[13] gave a mixture of 2b, 3 and 4 in the ratio 3:2:1 (ca 70 % yield). Compound 4 could be separated from the mixture by tlc and was fully characterised.[10,11] Attempts to separate 2b and 3 were unsuccessful, but 3 could be obtained pure by allowing 2b to decompose, and was fully characterised.[10,11] The ^{1}H NMR spectrum of 2b, adduced by subtraction of the spectrum of 3, consists of AB doublets at δ5.28 (2H, 6.0Hz), 5.35(2H, 6.0Hz) and a singlet at 8.97 (18H).[13] Compound 2b is thermally unstable, and when a 1:1 mixture of 2b and 3 was kept at 22 °C in degassed $CHCl_3$ for 18 h, a mixture of unchanged 3 and 9 (50 %)[1] was obtained. In $CHCl_3$ saturated with $^3O_2$ a 2:1 mixture of 2b, 3, after 24 h gave, besides unchanged 3, the peroxide 7b, mp 83-84 °C,



64 %.[10-12] Treatment of 7b with $^3O_2$, KOtBu in tBuOH gave the diketone 10, mp 88-89 °C, 98 %.[10-12] The same diketone could be prepared in 53 % yield by direct treatment of 1b under the same conditions ($^3O_2$, KOtBu, tBuOH). Thermolysis of a 1 : 1 mixture of 2b, 3 in benzene in the presence of maleic anhydride gave, besides recovered 3, the adduct 8b, mp 197-199 °C, 35 %.[10-12] The ^{13}C NMR spectrum of 8b shows the presence of only 7 types of carbon atoms, which eliminates structures in which the *t*-butyl groups are differently stereochemically related to C-3,7.

The conversion of 2a into 6 and 2b into 9 provides strong support for the intermediacy of the bisallene in the base catalysed rearrangements of 1a, b. This sequence is further substantiated by the conversion of 2b in 10 via 7b, which duplicates the direct conversion of 1b into 10. The recovery of 3 from the reactions excludes it as a possible intermediate in these reactions of 1b, and compound 4 can also be excluded as an immediate precursor of 9 since it is not thermally rearranged into that compound.[14] The reactions of 2a, b with $^{3}O_2$ find precedent in the reactions of o-dipropadienylbenzene and o-dipropadienyl naphthalene,[15] both of which give cyclic peroxides. In these cases the intermediates could be intercepted with dimethylfumarate or maleate to give the corresponding adduct with a high degree of stereospecificity.[15,16] In contrast to these observations, the rearrangement of octa-4-ene-1,7-diyne in the presence of $^{3}O_2$ did not give a peroxide, though it did give an adduct with di-t-butylfumarate.[15] In none of these cases was a product with a 4-membered ring observed, although such a product was obtained when o-di(phenylpropargyl)benzene was rearranged on KOH impregnated Al_2O_3.[17] 2b appears to be the first compound in which ring closure, reaction with $^{3}O_2$ and addition of a dienophile have all been observed in solution. Roth and co-workers[18] have shown that the fate of 2,3-dimethylene-1,4-cyclohexadiyl in the gas phase is different to its fate in solution, and they attributed this difference to a singlet-triplet transition assuming importance in the solvent phase. The present results are most simply explained by assuming that the triplet and singlet states are close in energy so that intramolecular ring closure to 9 occurs via the singlet state in the absence of $^{3}O_2$, but that the peroxide 7b is formed via the triplet state in its presence. Whether the singlet state for 5 is best represented by diradical or whether it involves the bis-methylene intermediate 11, in which expansion of the sulphur octet has occurred, is not known,[17] and a more precise definition of the structure of 5 is presently being sought.

Acknowledgement. SBN thanks University College London for the award of a Thomas Witherden Batt Scholarship.

References and Notes

1. P.J. Garratt and S.B. Neoh, *J. Amer. Chem. Soc.*, **97**, 3255 (1975).
2. M.P. Cava, M.V. Lakshmikantham, and M. Behforouz, *J. Org. Chem.*, **39**, 206 (1974).
3. S. Braverman and D. Segev, *J. Amer. Chem. Soc.*, **96**, 1245 (1974).
4. P. Vogel and M. Hardy, *Helv. Chim. Acta*, **57**, 196 (1974).
5. The synthesis of bispropadienyl sulphide has been claimed by Braveman et al.[6] The conditions of formation described by these authors are unclear (KOtBu, tBuOH, 0 °C), but our ^{1}H NMR spectra are in reasonable agreement.
6. S. Braverman, Y. Duar, and D. Segev, *Tetrahedron Letters*, 3181 (1976).
7. All solvents, including those used for extraction, were degassed.

8. These values are in excellent agreement with those expected for an allene substituted by sulphur: see G.C. Levy and G.L. Nelson, *C-13 NMR for Organic Chemists*, Wiley-Interscience, NY, 1972, p.68-9.

9. The ir spectrum showed a band at 1950 cm^{-1}, attributed to the allene.

10. Satisfactory microanalytical and/or high resolution mass spectral data were obtained for this compound.

11. ^{1}H NMR, $CDCl_3$, δ: 7a, 6.99 (s,2H), 5.20 (s, 4H): 8a, 6.92 (2H), 3.6-2.5 (m, 6H): 3, 5.63 (d, 1H) 5.43 (d, 1H), 2.18 (s, 2H), 1.08 (s, 9H), 0.98 (s, 9H): 4, 5.87 (d, 1H), 5.47 (d, 1H), 3.47 (s, 2H), 1.22 (s, 9H), 1.06 (s, 9H); 7b, 7.05 (s, 2H), 4.67 (s, 2H), 1.08 (s, 18H): 8b, 7.31 (s, 2H), 3.70 (m, 2H), 2.63 (m, 2H), 1.37 (s, 18H): 10, 7.47 (s, 2H), 1.25 (s, 18H).

12. ^{13}C NMR spectra, $CDCl_3$ ppm: 7a, 118.0 (C-7,9) 72.1 (C-2,5): 7b, 136.7 (C-1,6), 118.4 (C-7,9) 88.3 (C-2,5), 36.1 (C Me$_3$), 27.3 (C (CH$_3$)$_3$); 8b, 170.4 (C-4,6), 120.2 (C-10,12), 137.4 (C-1,9), 48.5 (C-2,8), 45.9 (C-3,7), 32.9 (CMe$_3$), 29.7 (C(CH$_3$)$_3$): 10, 205.1 (C=O), 142.1 (C-3,4), 125.9 (C-2,5), 44.2 (CMe$_3$), 27.3 (C(CH$_3$)$_3$).

13. 2b can exist in two diastereomeric forms, but no evidence could be obtained for the presence of two compounds. The stereochemistries of 2b, 7b, and 8b are under current investigation.

14. Thermolysis of 4 under a wide variety of conditions did not lead to 9, either 4 being recovered unchanged or a complex mixture of products being formed. Base catalysed rearrangement of 4 on KOH impregnated Al_2O_3 gave 2b and 3.

15. C.M. Bowes, D.F. Montecalvo and F. Sondheimer, *Tetrahedron Letters*, 3181 (1973): C.M. Bowes and F. Sondheimer, unpublished observations, see C.M. Bowes, Ph.D. Thesis, University of London, 1974.

16. Attempts to trap 5a, b with dimethyl fumarate have so far been unsuccessful.

17. H.A. Staab and B. Draeger, *Chem. Ber.*, 105, 2320 (1972).

18. W. Roth and G. Erker, *Angew. Chem. Int. Ed. Engl.*, 12, 503, 505 (1973), W. Roth, H. Heiber, and G. Erker, *ibid*, 504 (1973): see also W. Grimme and H.J. Rother, *ibid*, 12, 505 (1973).