

RE-INVESTIGATION OF A HETEROCYCLIC METACYCLOPHANE (1).

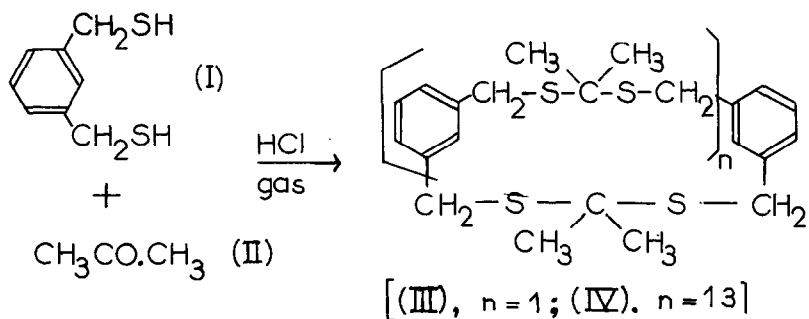
R.E. Busby and \*D. Huckle

(Brunel University, London)

(Received 8 September 1966)

THERE has been little recent work on meta-bridged heterocyclic cyclophanes. Much of the earlier work, as suggested by Griffin in a recent review (2), bears re-examination using modern techniques.

As a prelude to further studies it was necessary to look at the cyclophane (III) (1), prepared by Autenrieth and Buettel (3).



The original conditions (3), of mixing the dithiol (I) and acetone (II) and passing in dry hydrogen chloride at low temperature were not reproducible, possibly because the mixture rapidly set solid. This was overcome by mixing the reagents (I) and (II) in anhydrous ether at 0°C, adding ethereal-HCl, and leaving at ca. 4°C for several days until no more solid separated; equivalent to 80% reaction. N.M.R. showed that both routes afforded

\*Parke, Davis & Co., Staines Road, Hounslow, Middx.

mixtures of similar composition. Neither mixture could be separated into its components using Autenrieth and Beuttel's purification process (3).

The crude produce (10g.) was extracted with ethanol for 6 days in a Soxhlet apparatus, and the material remaining in the thimble (5.1g.) recrystallized from benzene-petroleum ether (60-80°) giving what appeared to be a single compound (IV) as prisms of m.p. 103-5°C. (3.3g.). Analysis was within error for  $(C_{11}H_{14}S_2)_{n+1}$  and molecular weight determination 3,280 (ebullioscopically in benzene), 2,720 (vapour pressure in benzene), suggested n was probably 13. N.M.R. ( $CDCl_3$ ) gave peaks at  $\tau_{CH_2}$  6.12 (sharp singlet: 8 protons),  $\tau_{CH_3}$  8.40 (sharp singlet: 12 protons),  $\tau_{aromatic}$  2.70, 2.58 (sharp major, and broad minor peaks respectively: total, 8 protons): U.V. (5%  $CHCl_3$  in EtOH) showed lack of fine structure,  $\lambda_{max}$  276, 267  $\mu$ ,  $\epsilon$ , 9,200, 12,700: I.R. (KBr) showed aromatic bands at 1600, 1582, 1482, 723, 692  $cm^{-1}$ , and gem-dimethyl bands at 1378, 1361  $cm^{-1}$ . A group of strong bands at 1147, 1106, 1080  $cm^{-1}$  was attributed to the S-C  $(CH_3)_2$ -S group (5).

The cooled ethanol, from the Soxhlet extraction, yielded fine needles (3.1g.), which were recrystallized several times from chloroform-ethanol giving the cyclophane (III) of m.p. 250-1°C. (1.5g) [lit. (3) m.p. 254°C.], molecular weight 444 (vapour pressure in benzene), 445 (ebullioscopically in benzene); U.V. ( $CHCl_3$ ) showed lack of fine structure,  $\lambda_{max}$  273, 267  $\mu$ ,  $\epsilon$  488, 728; I.R. (KBr)  $\nu_{max}$  1596, 1582, 1479, 1376, 1356, 1144, 1105, 1076, 727, 691  $cm^{-1}$ . N.M.R. ( $CDCl_3$ ) gave peaks at  $\tau_{CH_2}$  5.98 (sharp singlet: 8 protons),  $\tau_{CH_3}$  8.30 (sharp singlet: 12 protons),  $\tau_{aromatic}$  2.65, 2.22 (major multiplet and broad minor peak respectively; total 8 protons).

The cyclophane (III), on treatment with glacial acetic acid - 100 vol. hydrogen peroxide, yielded a tetrasulphone of m.p. 320-4°C [lit. (3) quotes m.p. of < 300°C]. Quantitatively the I.R., U.V., and N.M.R.

spectra of the cyclophane (III) and the polymer (IV) were in very close agreement, as would be expected from a dimer-polymer relationship.

The N.M.R. spectra also agreed closely with predicted values. The value for  $\tau_{\text{CH}_2}$  in the  $\text{PhCH}_2\text{SR}$  system calculated by employing Shoolery's shielding contributions (6) gave 6.3. The peak in the cyclic structure should appear at lower field by about 0.2 ppm (7) i.e. 6.1. Observed values were (IV), 6.12; (III), 5.98. Due to the less electronegative sulphur,  $\tau_{\text{CH}_3}$  in  $(\text{CH}_3)_2\text{C}(\text{SR}_2)$  should be at higher field, i.e. ca 8.6-9.0. If allowance is made for the cyclic structure  $\tau_{\text{CH}_3}$  should be lowered giving a predicted range of 8.4-8.8. The found values of 8.4 for (IV) and 8.3 for (III) are therefore in close agreement with the predicted value.

The aromatic proton resonances were of interest. The expected values were as found, but in the cyclophane (III) there was a separation of 0.43 ppm into minor and major peaks, whilst in the polymer (IV) this was only 0.12 ppm. This was not unexpected since conformational differences between the two compounds could result in different shielding, especially of the proton between the bridges. The greater separation in the cyclophane (III) might be due to the greater interaction of this proton with the bridge. Such an interaction should not be so apparent in the far less crowded polymer (IV). This is compatible with the lack of fine-structure in the U.V. which in other cyclophanes has been attributed to trans-annular interaction and/or aromatic distortion (4).

- 
- (1) On cyclophane nomenclature (III) is 3,3,14,14-tetramethyl-2,4,13,15-tetrathia [5,5] metacyclophane. On Chemical Society nomenclature (III) is, 4,4,14,14-Tetramethyl-tricyclo [15.3.1.1.<sup>7.11</sup>] 3,5,13,15-tetrathia-tetraconsane-1(21),7,9,11(22),17,19-hexaene.
- (2) R.W. Griffin Chem. Revs. 63, 45(1963).

- (3) W. Autenrieth and F. Beuttel Ber. 42. 4357 (1909).
- (4) B. Smith, "Bridged Aromatic Compounds" Academic Press, London, 1964 p.359.
- (5) N. Sheppard Trans. Far. Soc. 46 533 (1950).  
J. Inst. of Petroleum 37 102 (1951).
- (6) J.W. Shoolery Technical Information Bulletin, Varian Assoc. California  
1959, 2 No. 3.
- (7) L.M. Jackman Physical Methods in Organic Chemistry, Ed. J.C.P. Schwarz,  
Oliver and Boyd, London, 1964. p.168.