

220. Macrocyclic Acetylenic Compounds. Part IV.¹ 1,6-Dithia-cyclodeca-3,8-diyne.

By G. EGLINTON, I. A. LARDY, R. A. RAPHAEL, and G. A. SIM.

Reaction of 1,4-dichlorobut-2-yne with inorganic sulphides produces 1,6-dithiacyclodeca-3,8-diyne (II) which undergoes base-catalysed rearrangement to the bicyclic thiophen, 4,9-dithiabicyclo[5,3,0]deca-1,(10),2,7-triene (III).

THE properties of the Hückel-type hydrocarbon, [18]annulene,² prompted an attempt to synthesise the iso- π -electronic 1,6,11-trithiacyclopentadeca-2,4,7,9,12,14-hexaene. An obvious starting material for this compound is the isomeric triacetylene 1,6,11-trithiacyclopentadeca-3,8,13-triyne (I), and the reaction between 1,4-dichlorobut-2-yne and sodium sulphide was explored in the hope that (I) would be at least one of the products formed. In the event much polymer was encountered but a crystalline high-melting sparingly-soluble product was isolated in low yield (much improved by use of ammonium sulphide) with the expected empirical formula C_4H_4S . A conventional molecular-weight determination was precluded by the low solubility of the compound. However, mass-spectrometry measurements showed no peak higher than a mass number of 167 corresponding to a molecular ion, $C_8H_7S_2^+$ of a cyclic diacetylene, $C_8H_8S_2$ of structure (II). This indication was fully confirmed by X-ray crystallography. The crystal was found to be monoclinic with lattice parameters $a = 7.38$, $b = 4.44$, $c = 13.25$ Å, $\beta = 109^\circ 30'$, space group $P2_1/c$. The sharpened Patterson projection on (010) was interpreted by a superposition method,³ and gave a direct determination of the molecular structure. There are two molecules in the unit cell and as there are four equivalent positions in the space group $P2_1/c$ the molecule is required to be centrosymmetric; thus it cannot possess a boat-like conformation but must be either flat or, much more probably, chair-like (IIa). The atomic co-ordinates were refined by several cycles of structure-factor and Fourier

¹ Part III, Behr, Eglinton, Lardy, and Raphael, preceding paper.

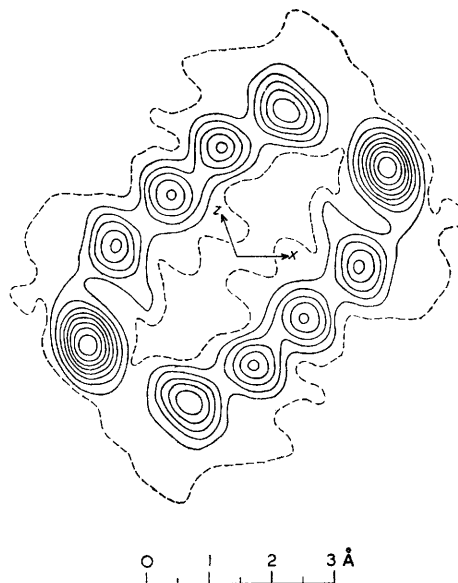
² Jackman, Sondheimer, Amiel, Ben-Efraim, Gaoni, Wolovsky, and Bothner-By, *J. Amer. Chem. Soc.*, 1962, **84**, 4307.

³ Robertson and Beevers, *Acta Cryst.*, 1951, **4**, 270.

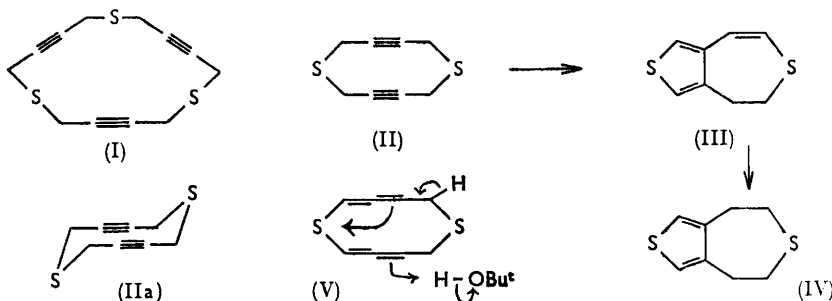
calculations and the value of R is now 17%. The electron-density projection along the b axis is shown in the Figure.

It is noteworthy that an early claim⁴ to have obtained the oxygen analogue of (II) in minute yield by interaction of acetylenedimagnesium bromide and bischloromethyl

Electron density along the b axis. Contour interval $1e\text{\AA}^{-3}$, except around the sulphur atom where it is $2e\text{\AA}^{-3}$ above the 2-electron line. The one-electron contour is broken.



ether has recently been substantiated;⁵ the two heterocycles have very similar melting points. The crystallographic data reported for the oxygen analogue show that it is not isomorphous with the sulphur compound. Nevertheless, it too crystallises in the space group $P2_1/c$ with two molecules in the unit cell and must also adopt the chair conformation.⁵



Sondheimer and his co-workers⁵ were also able to isolate the fifteen-membered trioxa-compound, although the yield (0.5%) was much lower than that (2%) of the ten-membered dioxo-compound. In our case the relatively high yield of the ten-membered dithia-compound may reflect the favourable effect which the rigid chains of four carbon atoms may exercise in bringing about cyclisation once the probable intermediate, $(ClCH_2C\equiv CCH_2)_2S$, has been formed. This would seem especially plausible in view of the relatively high concentrations and the inhomogeneous conditions employed.

The diacetylenic disulphide (II) was surprisingly amenable to catalytic reduction and rapidly absorbed hydrogen with the formation of the corresponding *cis,cis*-diene; however,

⁴ Lespieau, *Compt. rend.*, 1929, **188**, 502.

⁵ Sondheimer, Gaoni, and Bregman, *Tetrahedron Letters*, 1960, **26**, 25.

even vigorous conditions failed to reduce the diene further to the saturated heterocycle. Drastic reduction of (II) with Raney nickel caused desulphurisation and reduction to give *n*-butane, identified by g.l.c. Hydrogen peroxide oxidation of (II) gave the very sparingly soluble disulphoxide and disulphone.

Base-catalysed prototropic rearrangement^{2,6} of (II) to the fully conjugated tetraene was then attempted. Treatment with potassium *t*-butoxide caused a rapid transformation into an isomeric low-melting substance with a naphthalene-like odour. This product gave a strongly positive colour test⁷ with isatin-sulphuric acid. More positive identification as the substituted thiophen (III) was obtained from u.v., i.r., n.m.r., and mass-spectral evidence. Catalytical hydrogenation of (III) smoothly gave the dihydro-compound whose spectral properties were in complete accord with the symmetrical structure (IV). A tentative mechanistic suggestion for the conversion (II) \rightarrow (III) would involve the prototropic generation of the diallene (V) (cf. the base-catalysed isomerisation of allylic sulphides to propenyl sulphides⁸) followed by carbanion-induced transannular bond formation as shown; the formation of a thiophen ring is an obviously powerful driving force.

EXPERIMENTAL

General.—Melting points were determined on a Kofler block and are uncorrected. Ultra-violet and infrared spectral data were recorded with Unicam S.P. 500 and Perkin-Elmer 237 spectrophotometers, respectively, while the n.m.r. (in deuteriochloroform unless otherwise stated and with tetramethylsilane as internal standard) and the mass-spectral measurements were made with A.E.I. spectrometers RS2 (60 Mc/sec.) and MS2, respectively. Gas-liquid chromatographic data were recorded with a Pye "Argon" chromatograph equipped with a strontium-90 detector. Thin-layer chromatography (t.l.c.) was carried out with Kieselgel G silica support.

1,6-Dithiacyclodeca-3,8-diyne (II).—1,4-Dichlorobut-2-yne (18 g.) was added to a stirred solution of ammonium sulphide (600 ml.), prepared by saturating ammonium hydroxide solution (*d* 0.88; 300 ml.) with hydrogen sulphide and then adding an equal volume of ammonium hydroxide solution. The reaction mixture was stirred for 18 hr. and the product then extracted with chloroform. The crude crystalline *diyne* (3.5 g., 28%) which separated from the washed, dried, and partially-evaporated extract, crystallised from a large volume of light petroleum, b. p. 100—120°, as needles, m. p. 200° (decomp.) (Found: C, 57.0; H, 4.6%. $C_8H_8S_2$ requires C, 57.1; H, 4.8%). There were prominent peaks in the mass spectrum at 167 (parent-1) and, *inter al.*, at 153 (loss of CH_2), 135 (loss of S), 122, and 110 mass numbers; ν_{max} . (KCl disc) 2225 ($C\equiv C$) and 1404 (CH_2) cm^{-1} ; λ_{max} . (in EtOH) end absorption at 200 μ (ϵ 4800). The diyne was sparingly soluble in all solvents examined and suitable n.m.r. measurements could not be made. The compound sublimed at 100°/0.1 mm.

The mother-liquors remaining after the initial deposition of the diyne (II) were chromatographed without success, although there were indications from t.l.c. that other substances were present. Various reaction procedures, for example, treatment with sodium sulphide monohydrate in *N*-methylpyrrolidone or in water-ether, or with ammonium sulphide solution and light petroleum (b. p. 40—60°), were much less fruitful than that described.

The diyne presents interesting possibilities for ligand formation involving the π electrons of the triple bond and the *d*-orbitals of the sulphur atoms. Highly-insoluble *complexes* were obtained with silver nitrate (white powder, decomp. above 170°), mercuric chloride [colourless rods, m. p. 148—150° (Found: C, 21.7; H, 1.7; Cl, 11.3. $C_8H_8S_2.HgCl_2$ requires C, 21.85; H, 1.8; Cl, 16.1%)], and with dipotassium tetrachloropalladate (black precipitate), but not from nickel bromide, nickel chloride, iron pentacarbonyl, or iron enneacarbonyl. The diyne was recovered unchanged after u.v. irradiation as the solid and in solution in hydrocarbon solvents, and it did not appear to form sulphonium salts with acetonitrile solutions of methyl iodide, 1,4-dichlorobut-2-yne, or benzyl chloride.

⁶ Jones, Mansfield, Shaw, Whitham, and Whiting, *J.*, 1954, 3201, 3208, 3212, 3217.

⁷ Hartough, "The Chemistry of Heterocyclic Compounds. Thiophene and its Derivatives," Interscience Publishers Inc., N.Y., 1952, p. 13.

⁸ Tarbell and Lovett, *J. Amer. Chem. Soc.*, 1956, 78, 2259.

Oxidation of the diyne (II) with hydrogen peroxide (30%) in acetic acid during 14 hr. at room temperature gave an almost quantitative yield of a disulphoxide, 1,6-dithiacyclodeca-3,8-diyne 1,6-dioxide, as minute prisms decomposing slowly above 250° without melting (Found: C, 47.7; H, 4.8. $C_8H_8S_2O_2$ requires C, 48.0; H, 4.0%). ν_{\max} (KCl disc) 1045 vs cm^{-1} (sulphoxide). Further purification by crystallisation was precluded by the extreme insolubility of this compound.

Similar treatment, but with excess of hydrogen peroxide, and during 3 days, gave the corresponding disulphone, 1,6-dithiacyclodeca-3,8-diyne 1,1,6,6-tetraoxide (93%) as prisms, which decomposed, without melting, above 240° (Found: C, 41.6; H, 3.6. $C_8H_8S_2O_4$ requires C, 41.1; H, 3.5%); ν_{\max} (KCl disc) 1326, 1310, and 1120 vs cm^{-1} (sulphoxide). On continued heating above 220°, the sulphone sublimed and did not lose sulphur dioxide to form cyclooctatetraene as might have been expected.

Reductive desulphurisation of the diyne (II) was achieved with Raney nickel in bis-2-methoxyethyl ether at 60° during 1 hr. and the liberated n-butane was identified by g.l.c. [25% Apiezon L on Celite, 48 in. \times $\frac{1}{8}$ in. column. 20°].

1,6-Dithiacyclodeca-cis-3,cis-8-diene.—A solution of the diyne (II; 67 mg.) in ethyl acetate (20 ml.) was hydrogenated over palladium-charcoal (10%; 670 mg.), absorption of hydrogen ceasing after 1.5 molecular equivalents had been absorbed. Uptake of 2 equivalents could not be achieved and several products were detectable by t.l.c. The diene (49 mg.) separated from benzene-light petroleum (b. p. 40–60°) as prisms which sublimed above 130° (Found: C, 56.1; H, 6.8. $C_8H_{12}S_2$ requires C, 55.8; H, 7.0%). It showed end absorption in the u.v. region (ϵ 2800 at 222 $m\mu$); ν_{\max} (KCl disc) 3023 w (=CH) 1424 s (CH_2) and, in CS_2 , 769 s (cis-CH=CH) cm^{-1} . The n.m.r. spectrum consisted of a doublet at 6.85 τ (four CH_2) and a triplet at 4.5 τ (four olefinic protons), $J_{CH_2,CH=}$ 6 c./sec. These spectral results define the symmetrical cis,cis-3,8-structure for this diene. An attempt to synthesise this compound from cis-1,4-dichlorobut-2-ene and ammonium sulphide produced only malodorous oils.

The diene resisted all attempts at further hydrogenation with prerduced catalysts (derived from 10% palladium-charcoal and platinum oxide alone or in the presence of perchloric acid) in ethyl acetate using a Clauson-Kaas microhydrogenation unit.⁹ It was unaffected by u.v. irradiation of the solid and was recovered unchanged from a solution containing molybdenum hexacarbonyl in n-hexane. However, a solution of the diene (33 mg.) and mercuric chloride (52 mg.) in hot ethanol (20 ml.) did deposit a crystalline bis(mercuric chloride) complex (69 mg.) as plates, decomposing at 213° with sublimation. After sublimation at 100°/1 mm. this complex had ν_{\max} (KCl disc) 1424 s (CH_2) and 758 s (cis-CH=CH?) cm^{-1} (Found: C, 13.5; H, 1.6; Cl, 17.7. $C_8H_{12}S_2, Hg_2Cl_4$ requires C, 13.4; H, 1.7; Cl, 19.8%).

Oxidation of the diene (25 mg.) with hydrogen peroxide (30%, 0.5 ml.) in acetic acid (25 ml.) for 4 days at 20° provided the bis-sulphone, 1,6-dithiacyclodeca-cis-3,cis-8-diene 1,1,6,6-tetraoxide as highly-insoluble needles (31 mg.), decomposing without melting at 300° (Found: C, 40.6; H, 5.4. $C_8H_{12}S_2O_4$ requires C, 40.7; H, 5.1%); ν_{\max} (KCl disc) 3052 w (=CH), 1422 s (CH_2), 1325 and 1120 vs (sulphoxide) and 720 vs (cis-CH=CH?) cm^{-1} .

4,9-Dithiabicyclo[5,3,0]deca-1,(10),2,7-triene (III).—A solution of the diyne (II; 320 mg.) and freshly prepared potassium t-butoxide (1670 mg.) in t-butyl alcohol (200 ml.) was allowed to cool from 60° during 15 min. The mixture was acidified with dilute sulphuric acid, and the product isolated with ether and chromatographed in benzene over alumina (Grade I). Evaporation of the eluate gave the thiophen (III; 207 mg.) as needles, m. p. 54–56°, which after sublimation at 50°/0.01 mm. or crystallisation from aqueous ethanol had m. p. 56–57° (Found: C, 57.0; H, 4.8. $C_8H_8S_2$ requires C, 57.1; H, 4.8%); λ_{\max} 290 $m\mu$ (ϵ 15,800) and end absorption; ν_{\max} (in CS_2) 3096 w (thiophen=CH), 3013 w (cis-CH=CH), 1398 m (CH_2), 797 vs, 788 vs thiophen γ -CH and 745 s (cis-CH=CH). The n.m.r. spectrum (in CCl_4) showed ill-defined multiplets at 7.05 and 6.75 τ (CH_2 adjacent to S and to thiophen ring, respectively), an AB, quartet at 4.2 and 3.54 τ ($J = 11$ c./sec.; cis-CH=CH, protons adjacent to S and to thiophen ring, respectively), and two doublets at 3.27 and 3.1 τ ($J \sim 3$ c./sec.; thiophen α -protons).¹⁰ There were prominent peaks in the mass spectrum at mass numbers 168 (parent molecular ion) 167, 153 (loss of CH_2), 140 (loss of $CH_2=CH_2$) 136, 135, 134, 123, 121, 97, 91, 77, 69, 65, 63, 51, 45, and 39.

The triene possessed a distinct naphthalenic odour and gave a strong violet coloration with

⁹ Clauson-Kaas and Limborg, *Acta Chem. Scand.*, 1947, **1**, 884.

¹⁰ Gutowsky and Porte, *J. Chem. Phys.*, 1961, **35**, 839.

isatin and concentrated sulphuric acid (thiophen nucleus).⁷ It did not form a derivative with mercuric chloride.

The formation of the triene could also be effected in lower yield by using ethanolic potassium hydroxide under reflux, but not with triethylamine, solid potassium hydroxide, alumina, potassium t-butoxide in hot benzene or sodium methoxide in methanol under reflux. Even prolonged reflux with the potassium t-butoxide-butyl alcohol reagent had no effect on 1,6-dithiacyclodeca-*cis*-3,*cis*-8-diene.

No definite product could be isolated from the oxidation of the triene (III) with alkaline potassium permanganate, potassium permanganate in acetone, or performic acid at 70°. Reductive desulphurisation with Raney nickel in various solvents and at various temperatures (50—100°), and dehydrogenation with 10% palladium-charcoal (100—300°) were similarly unsuccessful. Heating under reflux with *N*-bromosuccinimide in carbon tetrachloride for 72 hr. resulted in unchanged starting material and not the hoped for 8-thiabicyclo[4,3,0]nona-1,(9)-2,4,6-tetraene.¹¹

4,9-Dithiabicyclo[5,3,0]deca-1,(10),7-diene (IV).—A solution of the triene (III; 60 mg.) in methanol (30 ml.) was hydrogenated in the presence of 10% palladium-charcoal (320 mg.) and one double-bond equivalent of hydrogen was taken up in 1 min. Evaporation of the solvent from the filtered solution gave the diene (IV; 58 mg.) as needles, m. p. 50—52°, from aqueous ethanol (Found: C, 56.4; H, 5.8. C₈H₁₀S₂ requires C, 56.4; H, 5.9%); λ_{max} 244 mμ (ε 5330) with a shoulder at 250 mμ (ε 4060); ν_{max} (solid) 3085w (thiophen =CH), 805s, and 793s (thiophen γ-CH). The n.m.r. spectrum consisted of two complex bands centred on 7.35 and 6.83 τ (CH₂ adjacent to S and thiophen ring, respectively) and a sharp singlet at 3.17 τ (thiophen α-protons). This spectrum demands ββ'-disubstitution of the thiophen ring.

The diene (IV) was recovered unchanged after attempts at selective desulphurisation, either with Raney nickel in acetone under reflux¹² or with alkaline hydrazine hydrate in triethylene glycol at 160° for 5 hr.¹³

We are indebted to Drs. J. S. Rollett and J. G. Sime for the DEUCE computer programmes.¹⁴ Mr. J. M. L. Cameron, B.Sc., and his staff for the microanalyses, Mrs. F. Lawrie for the i.r. spectra, Dr. R. I. Reed and his colleagues for the mass spectra, and Drs. A. L. Porte and J. C. D. Brand and Miss Muriel McKay for the n.m.r. spectra. One of us (I. A. L.) gratefully acknowledges a D.S.I.R. award.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, GLASGOW W.2. [Received, August 30th, 1963.]

¹¹ Mayer, Kleinert, Richter, and Gewald, *Angew. Chem.*, 1962, **74**, 118.

¹² Pettit and van Tamelen, *Org. Reactions*, 1962, **12**, 356.

¹³ Georgian, Harrison, and Gubisch, *J. Amer. Chem. Soc.*, 1959, **81**, 5834.

¹⁴ "Computing Methods and the Phase Problem in X-ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961; Rollet, p. 87; Sime, p. 301.