Synthesis of Derivatives of Cyclobuteno[c]thiophen

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Summary *cis*- and *trans*-3,4-Dibromocyclobuteno[*c*]thiophen derivatives have been made by the action of sodium iodide on 2,5-dihalogeno-3,4-bisdibromomethylthiophens.

ALTHOUGH a few aza-analogues (pyridino- and quinoxalino-) of benzocyclobutene have been prepared,[1] no oxa- or thia-analogues have been made despite many attempts.[2] The most closely related known compounds are 2-thianorbiphenylene and the thiophen (**1**) which were made from intermediates already containing a 4-membered ring.[3] We now report the synthesis of four derivatives of cyclobuteno[*c*]thiophen.†

When 2,5-dichlorothiophen-3,4-dicarbaldehyde was treated with phosphorus pentabromide in benzene under various conditions it gave mixtures containing the 3,4-bisdibromomethyl compounds (**2**; R = Cl) and (**2**; R = Br). When compound (**2**; R = Cl) was treated with sodium iodide in *NN*-dimethylformamide it gave a mixture of *cis*- and *trans*-3,4-dibromo-2,5-dichlorocyclobuteno[*c*]thiophen (**3**; R = Cl) (total yield 23·5%), m.p. 149—150° and 95°, respectively. The overall structure of the *trans*-isomer is supported by its mass spectrum, M^+ 335·7595, 337·7562 ($C_6H_2Br_2Cl_2S$ requires 335·7598, 337·7574‡). The assignment of the isomers is based on analogy with the corresponding 1,2-dibromobenzocyclobutenes. The n.m.r. spectrum ($CDCl_3$) of the isomer (**3**; R = Cl), m.p. 149—150°, showed a singlet at τ 3·98, and the isomer, m.p. 95° at τ 4·43. *cis*- and *trans*-1,2-Dibromobenzocyclobutene are reported to have m.p. 101° and 52°, respectively, and τ ($CDCl_3$) 4·19 and 4·59, respectively.[4] The *cis*-isomer of (**3**; R = Cl) had identical mass spectral properties to those of the *trans*-isomer.

Thiophen (**2**; R = Br) yielded a mixture of *cis*- and *trans*-bicyclic compounds (**3**; R = Br) (total yield 24%), m.p. 138—139° and 91—92°, respectively. The mass spectrum of the *trans*-isomer showed M^+ 379·7076, 381·7043 ($C_6H_2Br_3ClS$ requires 379·7094, 381·7072‡), and the i.r. spectrum included bands at 3225w, 1442s, 1265s, 1130s, 925m, and 670s cm^{-1}. The *cis*-isomer had an identical mass spectrum, but the i.r. spectrum was slightly different,

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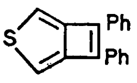
† Satisfactory high resolution mass spectra were obtained for all new compounds isolated.

‡ Allowing for weighted mean of halogen isotopes.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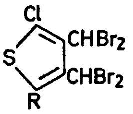
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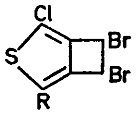
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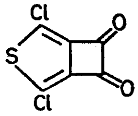
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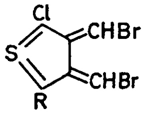
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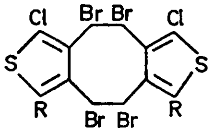
(6)

having bands at 3220m, 1440s, 1240m, 1140s, 905m, and 705s cm^{-1}. In the n.m.r. spectra of the *cis*- and *trans*-isomers (**3**; R = Br), the protons are non-equivalent and give rise to a double doublet τ 3·64 and 3·92, *J* 3 Hz, and τ 4·02 and 4·36, *J* 8 Hz, respectively.

The structure (**3**), as opposed to (**5**) or its dimer (**6**), was assigned to the compounds on the grounds that the isolated compounds were colourless and did not undergo cycloaddition when heated with *N*-phenylmaleimide in ethanol. Also, the mass spectra showed no peaks above the parent ions recorded above. Attempts to brominate the dibromide (**3**; R = Cl) with *N*-bromosuccinimide to give the 3,3,4,4-tetrabromide, which might have given the dione (**4**) on hydrolysis, were unsuccessful. Instead, at 77° (boiling carbon tetrachloride), ring opening occurred to regenerate the bis-dibromomethyl compound (**2**; R = Cl). In contrast the much less highly strained 1,2-dibromobenzocyclobutene readily undergoes substitution to give the 1,1,2,2-tetrabromide[5] and only undergoes ring cleavage when heated with bromine at 160°.[6] Alternative routes for the synthesis of dione (**4**) and related compounds are being studied.

(*Received, 27th March* 1972; *Com.* 520.)

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