between hexamine metal complex ions and polarizable anions.* It should also be of great value to correlate the spectroscopic effect with the geometry of the perturbing field.**

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* A synthesis of $Co(en)_3$ EDTA for the purpose of an X-ray structure determination is under way.

** It has been found in this laboratory that $Co(en)_3^{3+}$ is labilized by UV-irradiation so that EDTA, probably already co-ordinated in the outer sphere, can form Co(III)EDTA. In this reaction the absolute configuration of the chelate complex is not retained.[12]

Heteroaromatic Boron Compounds

V. On the Synthesis of a Dithienoborepin

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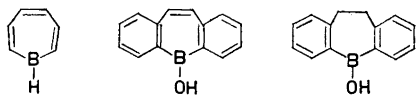
In connection with our work on heteroaromatic boron compounds, we are interested in studying the physical and chemical properties of borepin (I) derivatives, which are isoelectronic with the



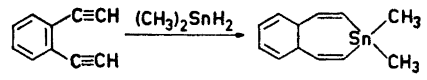
I II III

aromatic tropylium cations. A first attempt to reach the borepin system was made by van Tamelen *et al.*[1] in 1960, who prepared the dibenzoborepin (II) starting from *o,o'*-dilithiobibenzyl and butyl borate to obtain the anhydride of the borinic acid (III), which was dehydrogenated to II by side-chain bromination with *N*-bromosuccinimide followed by dehydrohalogenation with methanolic sodium methoxide. In their preliminary report van Tamelen *et al.* did not make clear the extent of aromatic stabilization in II. According to Dewar [2] great stabilization should not be expected, in view of the low stabilization of the dibenzotropylium ion.[3-5]

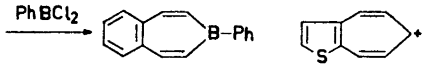
In another preliminary communication Leusink *et al.*[6] describe the synthesis of the 3-phenyl-3-benzoborepin IV, which was prepared by reacting the tin derivative V, obtained from *o*-diethynylbenzene (VI) and dimethyltinhydride, with phenyl boron dichloride.[6]

From the stability of IV towards air-oxidation and from its UV and NMR spectral data, Leusink *et al.* concluded that IV had aromatic properties.

Pettit and coworkers [7] on the other hand have shown that annelation of a thiophene ring to the tropylium ion increases its stability. Thus the thienotropylium ion VII has $pK_{R^+} = +6.0$, while that of the

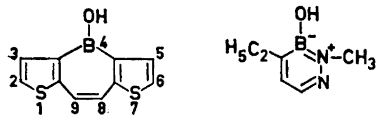


VI V



IV VII

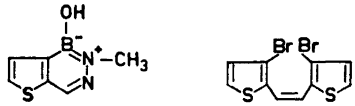
tropylium cation is 4.7. Earlier investigations by Heilbronner *et al.*[8] indicate that the benzotropylium cation is about 1000 times less stable than the tropylium cation. We therefore hoped that the thiophene analogue of I (VIII) would show greater stability. Furthermore, it may be possible to obtain the monocyclic borepin system by Raney-nickel desulphurization. We have



VIII IX

recently shown that this route is feasible for the preparation of 4-ethyl-3-hydroxy-2-methyl-3,2-borazaropyridine (IX) from 4-hydroxy-5-methyl-4,5-borazarothieno[2,3-c]pyridine (X).[9]

For the preparation of VIII, we used a shorter version of the van Tamelen route. From the early experiments of Wittig and Haag [10] it is known that appreciable amounts of *cis*-isomers are formed in the Wittig reaction and that by the choice of correct experimental conditions the *cis* isomer can become the dominant one (for review of *cf.* Ref. 11). During recent years Wittig reactions have been carried out with heterocyclic aldehydes and ylids derived from thenyl- and furfuryl triphenylphosphonium salts and the formation of both *trans* and *cis* ethylenes was observed.[12–15] We therefore anticipated that it would be possible to direct the Wittig reaction between 3-bromo-2-thenyl triphenyl phosphonium chloride and 3-bromo-2-thiophene aldehyde so as to obtain *cis*-1,2-di(3-bromo-2-thienyl)-ethene (XI) as the main product, and then to obtain VIII *via* halogen-metal exchange between XI



X XI

and ethyllithium followed by reaction with ethyl borate.

After using many different modifications of the Wittig reaction, we found that the use of sodium methoxide in *N,N*-dimethylformamide yielded the highest proportion of *cis* isomer, with only small amounts of the *trans* isomer.

By means of a process of fractional precipitation and crystallisation described in the experimental part, pure *cis* isomer, m.p. 60–61°C, was obtained in 54 % yield. After precipitating the triphenylphosphin oxide, fractional distillation at 0.2 mm Hg may also be used for the separation of the *cis-trans* isomers.

The *trans* isomer, m.p. 150–151°C, is obtained most conveniently and in high yield by applying the phosphonate method [16] to 3-bromo-2-thenyldiethylphosphonate and 3-bromo-2-thiophenealdehyde as previously demonstrated by Wynberg *et al.*[14] in the thiophene and furan series.

The *cis-trans* assignments are easily made on the basis of IR spectroscopical data.[12,18] The higher melting isomer shows a strong band at 940 cm^{-1} which is considered characteristic of the trans CH out-of-plane deformation of the vinyl group, and which is absent in the *cis* isomer.

Treatment of the low-melting isomer with two equivalents of ethyllithium, followed by one equivalent of ethyl borate yielded the ether of VIII, m.p. 256–258°C, in 25 % yield.

The structure of the product is evident from its NMR (in CS_2) and mass spectrum. The NMR spectrum shows a sharp peak at 2.68 τ assigned to the ethylenic bridge and two AB doublets at 2.47 τ and 3.30 τ with a coupling constant of 5.0 c/s. A high resolution mass spectrum of the peaks in the region of *m/e* 416–419 also confirmed the structure of the borepin ether.

Experimental. (3-Bromo-2-thenyl)triphenylphosphonium chloride. 273 g (1.29 mole) of 3-bromo-2-thenylchloride [19] was added to a solution of 340 g (1.29 mole) of triphenyl phosphine in 1300 ml of anhydrous benzene and the mixture refluxed with stirring. At intervals

the precipitate was filtered off, washed with benzene, and the refluxing of the filtrate was continued. After 100 h 581 g (94 %) of 3-bromo-2-thenyltriphenylphosphonium chloride was obtained.

cis-1,2-Di(3-bromo-2-thienyl)ethene. In a nitrogen-swept three-necked flask 150 g (0.316 mole) of (3-bromo-2-thenyl)triphenylphosphonium chloride was mixed with 40.5 g (0.75 mole) of sodium methoxide. With stirring and ice-cooling 250 ml of anhydrous dimethyl formamide was added. After 30 min 61.2 g (0.325 mole) of 3-bromo-2-thiophene aldehyde[20] dissolved in 200 ml of anhydrous *N,N*-dimethyl formamide was added dropwise with ice-cooling.

The mixture was stirred overnight and then poured into ice-water. The pH was adjusted to 7 with 1 N hydrochloric acid. The oil that separated was taken up in ether and the aqueous layer extracted with ether. The combined ether phases were washed with sodium bisulphite solution and water and dried over magnesium sulphate. The ether solution was evaporated to about half its volume, and the precipitated triphenylphosphine oxide filtered off. The filtrate was evaporated to dryness, the residue dissolved in benzene, and chromatographed on silica gel, which removed residual triphenylphosphine oxide. The benzene solution was evaporated to dryness and the residue heated with 100 ml of boiling petroleum ether. The liquid was decanted off and cooled to −70°. On scratching an orange-yellow precipitate was formed which was filtered off. The filtrate was used for renewed extraction of the original solvent and the separation procedure repeated until the *trans* isomer started to separate, as detected by the appearance of the characteristic absorption at 940 cm^{-1}. 60 g (54 %) of *cis*-1,2-di(3-bromo-2-thienyl)ethene, m.p. 60−61°, was thus obtained. [Found: C 34.1; H 1.88; S 18.1. Calc. for $C_{10}H_6Br_2S_2$ (350.0): C 34.28; H 1.71; S 18.28].

Bis-(4-dithieno[3,2-b:2',3'-f]borepinyl) ether. 45 ml of 0.83 N ethereal ethyllithium was added dropwise under nitrogen to a stirred solution of 5.0 g (0.014 mole) of cis 1,2-di-(3-bromothienyl)ethene in 200 ml of anhydrous ether cooled to −70°C. The reaction mixture was stirred for 2 h at −70°C and then pressed with nitrogen into a stirred solution of 2.50 g (0.0171 mole) of triethylborate in 100 ml of anhydrous ether cooled to −70°C. After 4 h the cooling-bath was removed and when the temperature of the mixture had risen to 0°C, 100 ml of ice-cold 2 N hydrochloric acid was added with stirring. After 15 min, the water phase was separated and the ether layer extracted with 10 portions of 50 ml of ice-cold 1 N sodium hydroxide solution. Each aqueous layer was immediately acidified with 2 N hydrochloric acid and extracted with ether. The first extract gave upon evaporation an oil from which small amounts of the borepin ether crystallised. The other combined ether extracts yielded after drying with magnesium sulphate 0.750 g (25 %) of bis-(4-dithieno[3,2-b:2',3'-f]-borepinyl)ether, m.p. 256−258°C after recrystallisation from chloroform. Mass spectrum (*m/e*, %): 45, 5.7; 156, 5.1; 157, 13.7; 158, 7.1; 175, 4.5; 190, 46.4; 191, 7.6; 192, 7.8; 200, 5.3; 201, 10.3; 202, 9.6; 209, 4.5; 218, 5.4; 227, 4.3; 384, 10.3; 385, 7.0; 415, 4.1; 416, 17.5; 417, 57.8; 418, 100; 419, 33.8; 420, 21.1; 421, 5.6. [Found: C 57.44; H 3.05; Mwt. 416.002, 416.999, 417.996. Calc. for $C_{20}H_{12}OS_4{}^{10}B_2$, 416.002; $C_{20}H_{12}OS_4{}^{10}B^{11}B$, Mwt. 416.999; $C_{20}H_{12}O_4S_4{}^{11}B_2$, Mwt. 417.996: C 57.74; H 2.89].

NMR spectra were obtained with a Varian A-60 high resolution spectrometer, and mass spectra with an LKB 900 mass spectrometer and with an AEI M9 double focussing mass spectrometer.

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On the Friedel-Crafts Acylation of *p*-Methylacetanilide

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For a polarographic investigation of *o*-aminoacetophenones [1] 2′-amino-5′-methylacetophenone (I) was needed; this compound has been prepared in yields varying from 0 to 10 % by Friedel-Crafts acetylation [2,3] of 4-methylacetanilide (II) with acetyl chloride; no other products have been reported isolated from this reaction. In the reinvestigation of the reaction described below the yield of characterised compounds reached nearly 90 %.

The acetylation of 4-methylacetanilide (II) was performed with excess of aluminium chloride and acetyl chloride in carbon disulphide; from the reaction mixture were isolated the following three compounds: 2′-amino-5′-methylacetophenone (I) 8 % yield, 5′-amino-2′-methylacetophenone (IV) 54 % yield, and 2,6-dimethyl-4(1H)-quinolone (III) 24 % yield. The presence of small amounts of 3—4 other compounds was indicated by thin-layer chromatography, but they were not characterised.

Variation of the experimental conditions influenced the yield somewhat, but not significantly.

The major product (IV) was proved to be the hitherto unknown 5′-amino-2′ methylacetophenone from the analysis, IR (non-hydrogenbonded carbonyl absorption 1675 cm^{-1}), and the NMR-spectrum; the aromatic proton at highest field (H4, neighbour to the amino group and not influenced appreciably by the carbonyl group) shows a *meta* and an *ortho* coupling. IV was reduced electrolytically to the hitherto unknown 1-(5′-amino-2′-methylphenyl)ethanol.

The structure of III was established from the analysis, the NMR-spectrum, and the identity with the product obtained by condensation of *p*-toluidine with ethylacetate.[4]

The quinolone III seems not to be formed by further reaction of 2′-acetamino-5′-methylacetophenone (I) as I on treatment with acetyl chloride and aluminium chloride under a variety of conditions failed to produce III; neither did *N,N*-diacetylated *p*-toluidine under similar conditions produce III.

Ethyl-3-(4′-toluidino) crotonate (V) yields on heating to 160° III; V reacted with carbon disulphide in the presence of aluminium chloride, but treatment of V with acetyl chloride and aluminium chloride only yielded acetylated products and no III. The reaction mechanism for the formation of III is thus not clear, although it seems probable that a derivative of 3-(4′-toluidino)crotonic acid is an intermediate.

Chlorination in acetic acid of II yields 3-chloro-4-acetaminotoluene, and nitration of II in a 3:1 mixture of nitric and sulphuric acid yields 3-nitro-4-acetaminotoluene, whereas nitration with a mixture containing a high concentration of sulphuric acid produces a mixture of 2- and 3-nitro-4-acetaminotoluene. Under acidic conditions protonation of the amino group induces a higher proportion of the 2-isomer.

The Friedel-Crafts acetylation of II using aluminium chloride as Lewis acid produces the 2- and 3-isomers in a ratio of 7:1 which indicates a high degree of