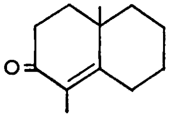
NOTES.

966. *Synthesis of a Dihydrosantonin Isomer.**

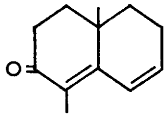
By J. K. CHAKRABARTI, P. DUTT, and P. C. DUTTA.

THIS note reports variations in published methods for the synthesis of santonin D by way of its 1 : 2-dihydro-derivative.

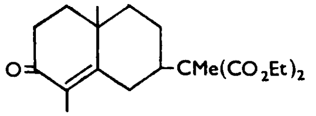
2-Methyl*cyclo*hexanone was condensed in the presence of sodamide with 2-chloroethyl ethyl ketone (instead of with the 2-diethylaminoethyl ketone used by Gunstone and Heggie [1]), and the crude product was refluxed with alkali (this treatment is essential in view of McQuillin's work [2]), giving the ketone (I).



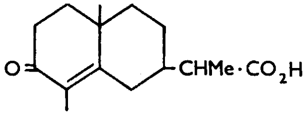
(I)



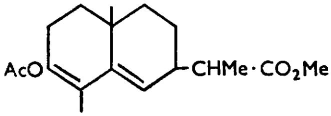
(II)



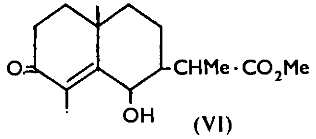
(III)



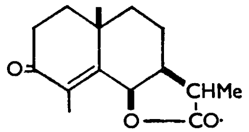
(IV)



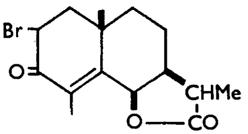
(V)



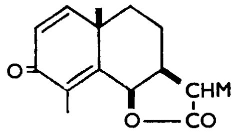
(VI)



(VII)



(VIII)



(IX)

The hexalone (II) was condensed with ethyl methylmalonate in presence of potassium *tert.*-butoxide, but the yield was less than that obtained by Abe *et al.*[3] and our product was contaminated, probably with the ethyl ester of the acid (IV) arising by partial decarboxylation. Hydrolysis and decarboxylation then gives a mixture of acids (IV), separated only by tedious crystallisation; the form isolated in larger amount was esterified and then afforded the enol acetate (V) ($\lambda_{max.}$ 238 mμ; log ε 4·35 in EtOH) which with monoperphthalic acid afforded an oil. This oil has a spectrum with infrared bands at 2·9 (OH), 6·0 (C:C·CO), and 5·78 μ (CO_2Me), and thus probably has structure (VI); alkaline hydrolysis and acidification affords the dihydrosantonin (VII) [infrared bands at 5·7 (γ-lactone) and 6·0 μ (C:C·CO)],

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* For preliminary communications see *Chem. and Ind.*, 1955, 170; 1956, 99.

[1] Gunstone and Heggie, *J.*, 1952, 1437.

[2] McQuillin, *J.*, 1955, 528.

[3] Abe *et al.*, *J. Amer. Chem. Soc.*, 1956, 78, 1416, 1422.

which gives the monobromo-derivative (VIII) identical with a specimen kindly provided by Dr. Abe and converted into santonin D when heated with collidine (cf. Abe *et al.*[4]).

Since epoxide rings are opened diaxially [5] in the above reaction, and since $C_{(11)}$ is attached equatorially,[3] the lactone ring in the dihydrosantonin must be *cis*-fused, in conformity with the known structure [6] of santonin D. The relatively high m. p. (135—136°) of the dihydrosantonin (VII) (cf. the isomers,[4] m. p. 87° and 115°) may be due to compact packing in the molecule, in conformity with the *cis*-fusion of the lactone ring.

Experimental.—2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-*Octahydro*-1 : 10-*dimethyl*-2-*oxonaphthalene* (I). 2-Methyl*cyclo*hexanone (28 g.), freshly prepared sodamide (11·2 g.), and dry ether (300 c.c.) were refluxed for 2 hr. with stirring, then evaporated to half the volume and cooled in a freezing mixture. 2-Chloroethyl ethyl ketone (31·25 g.) was added dropwise with stirring, refluxing continued for another 2 hr., and the solution then concentrated and left overnight. It was decomposed with ice-cold hydrochloric acid and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated. Distillation gave unchanged 2-methyl*cyclo*hexanone, followed by the product, b. p. 110—140°/3 mm. (22·5 g.). This was refluxed with potassium hydroxide (22·5 g.) in methanol (450 c.c.) for 10 hr. in nitrogen, then neutralised with acetic acid, and the alcohol was evaporated almost completely. The residue was diluted with water and extracted twice with ether. The ethereal solution was washed with water, sodium carbonate solution, and very dilute hydrochloric acid. After removal of solvent the ketone (I) (17 g.) distilled at 110—120°/2 mm., had $\lambda_{max.}$ 247 mμ (log ε 4·1 in EtOH) and gave a 2 : 4-dinitrophenylhydrazone, m. p. 197—198° (lit., 198—199°).

Ethyl α-methyl-α-(1 : 2 : 3 : 4 : 5 : 6 : 7 : 10-*octahydro*-8 : 10-*dimethyl*-7-*oxo*-2-*naphthyl*)-*malonate* (III). To a cooled solution from potassium (2·1 g.) and *tert.*-butyl alcohol (108 c.c.) was added ethyl methylmalonate (48 g.), then after 30 min. the ketone (II) (24 g.). The mixture was refluxed in nitrogen for 8 hr. and worked up in the usual way. Distillation gave a forerun of starting materials and then (by evaporative distillation) the desired diester (10·6 g.), b. p. 170—190°/0·2 mm. The product was sublimed and distilled (b. p. 180—185°/0·4 mm.; lit., 203°/1·5 mm.) (Found: C, 68·5; H, 8·5. Calc. for $C_{20}H_{30}O_5$: C, 68·5; H, 8·5%). A 2 : 4-*dinitrophenylhydrazone*, prepared therefrom in the usual way, melted at 102—104°, but repeated crystallisation from ethyl acetate yielded a small amount of red needles, m. p. 196—197° (Found: C, 65·9; H, 6·6. $C_{23}H_{30}O_6N_4$ requires C, 60·2; H, 6·5%), which was the derivative of the ethyl ester of an acid (IV).

α-(1 : 2 : 3 : 4 : 5 : 6 : 7 : 10-*Octahydro*-8 : 10-*dimethyl*-7-*oxo*-2-*naphthyl*)*propionic acid* (IV). The above keto-diester (10·5 g.) was boiled under reflux for 6 hr. with potassium hydroxide (16·8 g.), water (42 c.c.), and methanol (126 c.c.) in nitrogen. A brown oil was obtained (3 g.). This product (52 g.) from several batches was taken up in hot ethyl acetate and on recrystallisation yielded the dicarboxylic acid as needles (22·4 g.), m. p. 191—192° (lit., 204°) (Found: C, 65·0; H, 7·5. Calc. for $C_{16}H_{22}O_5$: C, 65·3; H, 7·4%).

The acid was decarboxylated at 195—200°. The brown mass was taken up in hot ethyl acetate and treated with charcoal, and the solution was concentrated and kept overnight at 0° after addition of 5—10% (by vol.) of light petroleum (b. p. 40—60°). Colourless crystals (8 g. from 22 g. of dibasic acid), m. p. 110—115°, were collected. Laborious fractional crystallisation from ethyl acetate [containing at first a few drops of light petroleum (b. p. 40—60°)] gave acids, m. p. 133—134° (lit., 135°) (1·2 g.) and 144° (lit., 145°) (0·1 g.).

The acid, m. p. 133° (2·6 g.), with diazomethane in methanol–ether gave the ester (2·5 g.) whose 2 : 4-*dinitrophenylhydrazone* formed needles (from ethyl acetate), m. p. 169—170° (Found: C, 59·2; H, 6·4. $C_{22}H_{28}O_6N_4$ requires C, 59·4; H, 6·3%). The other acid (0·2 g.) gave the *methyl ester* 2 : 4-*dinitrophenylhydrazone*, cubes (from ethyl acetate), m. p. 163—164° (Found: C, 59·2; H, 6·5%). The mixed m. p. of the two derivatives was 150—155°.

Methyl α-(7-*acetoxy*-2 : 3 : 4 : 5 : 6 : 10-*hexahydro*-8 : 10-*dimethyl*-2-*naphthyl*)*propionate* (V). The former of the above methyl esters (2 g.) was refluxed with acetic anhydride (10 c.c.) and acetyl chloride (10 c.c.) for 5 hr. in nitrogen, giving the *enol-acetate* (1·8 g.), b. p. 155°/0·2 mm. (Found: C, 70·3; H, 8·2. $C_{18}H_{26}O_4$ requires C, 70·5; H, 8·4%).

1 : 2-*Dihydrosantonin D.* To the enol acetate (1·5 g.) in ether (5 c.c.) at 0° was added 0·813N-ethereal monoperphthalic acid (13 c.c.), and the mixture was kept at 0° for 48 hr., most of the acid being consumed. The solution was washed with cold 10% sodium carbonate solution,

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[4] Abe, Harukawa, Ishikawa, Miki, Toki, Sumi, and Toha, *Proc. Japan Acad.*, 1954, **30**, 116, 119; cf. Matsui, Toki, Kitamura, Suzuki, and Hamuro, *Bull. Chem. Soc. Japan*, 1954, **27**, 7.

[5] Turner, Anliker, Helbling, Meier, and Heusser, *Helv. Chim. Acta*, 1955, **38**, 413.

[6] Cf. *Annual Reports*, 1954, **51**, 208.

then with water, dried (Na_2SO_4), and evaporated, finally in a vacuum. The pasty residue (*ca.* 1 g.) was refluxed with potassium carbonate (0·8 g.) in methanol (40 c.c.) and water (8 c.c.) for 30 min. under nitrogen, cooled, and acidified with acetic acid (1 c.c.), and methanol was distilled off at 14 mm. Adding water (20 c.c.) gave an oil which was extracted with ether. The aqueous layer was made more acid with acetic acid (0·5 c.c.) and again extracted. The combined extracts were washed with water, dried (Na_2SO_4), and evaporated. The oil (*ca.* 0·8 g.) obtained was kept in ethyl acetate containing a few drops of light petroleum (b. p. 40—60°) at 0°. The dihydrosantonin (0·22 g.; m. p. 134°) which separated, when crystallised from ethyl acetate, had m. p. 135—136°, $\lambda_{max.}$ 245 mμ (log ε 3·9 in EtOH) (Found: C, 72·3; H, 8·2. Calc. for $C_{15}H_{20}O_3$: C, 72·5; H, 8·0%).

Santonin D (IX). To a solution of the 1 : 2-dihydrosantonin (0·5 g.) in ether (70 c.c.) was added bromine (0·24 g.) in acetic acid (2 c.c.). The monobromo-derivative slowly crystallised at 0° and formed needles, m. p. 175° (decomp.), from methanol. When mixed with an authentic sample of the bromo-derivative, m. p. 179° (decomp.), it melted at 176° (decomp.). The derivative (0·4 g.) and collidine (1·5 c.c.) were refluxed for 30 min. in nitrogen, then poured into ice-cold dilute sulphuric acid. The solid which separated was extracted with ether, washed with water, and dried (Na_2SO_4). On evaporation, crystals separated which on recrystallisation from methanol melted at 189° (lit., 190°) alone or mixed with santonin D and had $\lambda_{max.}$ 248 mμ (log ε 4·1 in EtOH) (Found: C, 72·8; H, 7·2. Calc. for $C_{15}H_{18}O_3$: C, 73·1; H, 7·3%).

Thanks are recorded to Dr. Abe for a sample of santonin D and for comparing the bromo-derivatives. Analyses were carried out by Mrs. Chhabi Dutta at the microchemical laboratory of the University College of Science, Calcutta, and infrared curves were measured by Dr. N. K. Bhattacharyya at Iowa State College. Thanks are also recorded for gifts of chemicals from the East India Pharmaceutical Works Ltd., Calcutta.

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
JADAVPUR, CALCUTTA-32.

[*Received, April 24th,* 1956.]

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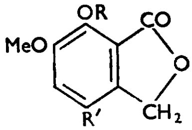
967. *Lactones. Part IV.* A New Preparation of 7-Ethoxy-6-methoxyphthalide.*

By W. R. LOGAN and G. T. NEWBOLD.

DURING examination of the feasibility of B_{AL} phthalide fission,[1] meconin (I) was found, on reaction with ethyl sodiomalonate, ethyl sodioacetoacetate, or ethanolic sodium ethoxide to give 7-ethoxy-6-methoxyphthalide [2] (II) which has been prepared by ethylation of 7-hydroxy-6-methoxyphthalide.[2,3] The structure of the last compound has now been confirmed by infrared measurement, thus establishing rigidly that of the ether (II) (cf. refs. 2 and 4). Chloromethylation of the phthalide (II) gave the derivative (III) identical with that prepared [5] from 2-ethoxy-3-methoxybenzoic acid. The phthalide (II) has been characterised by conversion into 2-ethoxy-6-hydroxymethyl-3-methoxybenzhydrazide and by reduction with lithium aluminium hydride to 3-ethoxy-4-methoxyphthalyl alcohol [2-ethoxy-3 : 4-di(hydroxymethyl)-1-methoxybenzene].



(I): R = Me, R′ = H
(II): R = Et, R′ = H
(III): R = Et, R′ = CH_2Cl

Experimental.—7-*Ethoxy*-6-*methoxyphthalide.* (*a*) Meconin (3·0 g.) was heated under reflux with ethyl sodiomalonate in ethanol [from ethyl malonate (4·96 g., 2 mols.), sodium (0·71 g.), and ethanol (25 c.c.)] for 17 hr. The solution was concentrated under reduced pressure to 12 c.c., an equal volume of water added, and the precipitated oil (2·4 g.), which rapidly solidified, was separated. Crystallisation from aqueous ethanol gave 7-ethoxy-6-methoxyphthalide (2·0 g.)

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* Part III, *J.*, 1956, 3608.

[1] Cf. Wislicenus, *Annalen*, 1886, **233**, 102.
[2] Rodionow, Kanewskaja, and Davankoff, *Ber.*, 1933, **66**, *B*, 1623.
[3] Bowman, *Ber.*, 1887, **20**, 890.
[4] Späth and Burger, *Ber.*, 1926, **59**, 1486.
[5] Manske and Ledingham, *Canad. J. Res.*, 1944, **22**, *B*, 115.

as needles, m. p. 66—67·5° (Found: C, 63·9; H, 5·9. Calc. for $C_{11}H_{12}O_4$: C, 63·45; H, 5·8%). Light absorption in EtOH: Max. at 2150 (ε 27,000) and 3090 (ε 4500); inflexion at 2400 Å (ε 7200); infrared bands in Nujol mull at 1754 (CO stretching frequency) and 1592 cm.$^{-1}$ (benzene ring). The same product (2·1 g.), m. p. and mixed m. p. 66—67°, was obtained by using ethyl acetoacetate (4·03 g.) in place of ethyl malonate. The compound was undepressed in m. p. when mixed with 7-ethoxy-6-methoxyphthalide, m. p. 65·5—66° (lit.,[2] m. p. 68—69°) obtained by ethylation of 7-hydroxy-6-methoxyphthalide which had light absorption in EtOH: Max. at 2190 (ε 23,000) and 3120 (ε 3800) and inflexion at 2350—2400 Å (ε 6500) and strong infrared bands at 1751 (in CCl_4) and 1739 cm.$^{-1}$ (in $CHCl_3$) (CO stretching frequency) consistent with the structure assigned [6] (we are indebted to Mr. J. F. Grove and Dr. L. A. Duncanson for this determination). The compound gives an indigo-blue ferric chloride colour in aqueous ethanol.

(*b*) A solution of meconin (3·0 g.) in ethanol (25 c.c.) containing sodium ethoxide from sodium (0·71 g.) was refluxed for 20 hr., then concentrated, diluted with water, and extracted with ether; removal of the ether gave a negligible residue. The aqueous phase was acidified with hydrochloric acid (Congo-red) and extracted with ether. The dried (Na_2SO_4) ethereal extract on evaporation gave an amber oil (2·95 g.) which was extracted with boiling light petroleum (b. p. 60—80°) (5 × 30 c.c.). The combined extracts were concentrated and the solid which slowly separated was repeatedly crystallised from light petroleum (b. p. 60—80°) to give 7-ethoxy-6-methoxyphthalide (1·0 g.) as needles, m. p. and mixed m. p. 66—67·5° (Found: C, 63·8; H, 6·0%). 7-Ethoxy-6-methoxyphthalide was unaffected by prolonged treatment under reflux with methanolic sodium methoxide.

4-*Chloromethyl*-7-*ethoxy*-6-*methoxyphthalide*. 7-Ethoxy-6-methoxyphthalide (250 mg.) was chloromethylated as described for meconin.[7] Evaporation of the chloroform extract gave a gum (0·28 g.) which rapidly solidified. A solution of the gum in benzene (25 c.c.) was passed through a column of Grade II alumina (3 × 1·5 cm.), the eluate and benzene washings (125 c.c.) were evaporated, and the residue was five times crystallised from benzene–light petroleum (b. p. 60—80°) and sublimed at 100°/10^{-3} mm., to give 4-chloromethyl-7-ethoxy-6-methoxyphthalide, m. p. 128—129·5 (lit., 130°) alone or mixed with a specimen prepared from 2-ethoxy-3-methoxybenzoic acid [5] (Found: C, 56·5; H, 5·25. Calc. for $C_{12}H_{13}O_4Cl$: C, 56·15; H, 5·1%).

2-*Ethoxy*-6-*hydroxymethyl*-3-*methoxybenzhydrazide*. 7-Ethoxy-6-methoxyphthalide (150 mg.) was refluxed with 90% hydrazine hydrate solution (5 c.c.) and ethanol (10 c.c.) for 4 hr. The mixture was concentrated under reduced pressure, then diluted with water, and the product isolated by using chloroform. Crystallisation from benzene–light petroleum (b. p. 60—80°) gave the *hydrazide* (45 mg.) as needles, m. p. 149·5—150·5° (Found: C, 54·9; H, 6·6. $C_{11}H_{16}O_4N_2$ requires C, 55·0; H, 6·7%). Light absorption in EtOH: Max. at 2100 (ε 23,000) and 2840 (ε 2500), inflexions at 2325 (ε 13,000) and 3050 Å (ε 1600).

3-*Ethoxy*-4-*methoxyphthalyl alcohol*. 7-Ethoxy-6-methoxyphthalide (250 mg.) was reduced with lithium aluminium hydride as described for *m*-meconin.[8] The *diol* (120 mg.) separated from benzene–light petroleum (b. p. 40—60°) as felted needles, m. p. 64—65° depressed to 50—59° when mixed with starting material (Found: C, 62·2; H, 7·7. $C_{11}H_{16}O_4$ requires C, 62·25; H, 7·6%). Light absorption in EtOH: Max. at 2090 (ε 18,500), 2240 (ε 7800), and 2820 Å (ε 2000).

THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, June 12th*, 1956.]

[6] Duncanson, Grove, and Zealley, *J.*, 1953, 1331.
[7] Brown and Newbold, *J.*, 1952, 4878.
[8] Blair, Logan, and Newbold, *J.*, 1956, 3608.

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968. *Spectra of Transition-metal Complexes of the Type* $[Co(NH_3)_5X]^{2+}$.

By J. S. GRIFFITH and L. E. ORGEL.

DATA are available on the spectra of a number of complexes of the cobaltic ion of the type $[Co(NH_3)_5X]^{2+}$, *e.g.*, where X = I, Br, Cl, or F.[1] These complexes are of the diamagnetic, spin-paired type. Here we correct and extend the results of a previous publication.[2] We discuss the spectra first on the assumption that the complexes have regular octahedral

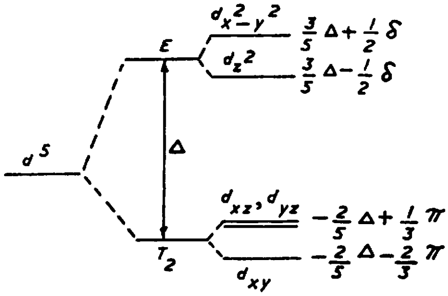
[1] Linhard and Weigel, *Z. anorg. Chem.*, 1951, **266**, 49.
[2] Orgel, *J.*, 1952, 4756.

symmetry, and then consider, as a tetragonal perturbation, the effect of the departure from it. In the former case the *d* orbitals split into two kinds, a lower t_{2g} orbital triplet and an upper e_g doublet. The ground state of the complex is represented by $(t_{2g})^6\ {}^1A_{1g}$ and the longest-wavelength spin-allowed absorptions arise from transitions to the singlets of the configuration $(t_{2g})^5(e_g)^1$. Group-theoretical arguments show that the latter singlets give rise to two triply degenerate states ${}^1T_{1g}$ and ${}^1T_{2g}$. The energies can be worked out in terms of atomic spectral parameters. In previous work one of us [3] has used Racah's parameters A, B, C, and the other [4] the Slater–Condon parameters F_0, F_2, F_4, so, for convenience of reference, we give the energies, relative to a suitable zero, here in terms of both :

$$\left.\begin{aligned} E[(t_{2g})^6\ {}^1A_{1g}] &= 15A - 30B + 15C = 15F_0 - 30F_2 - 60F_4 \\ E[(t_{2g})^5(e_g)^1\ {}^1T_{1g}] &= 15A - 30B + 14C + \Delta = 15F_0 - 30F_2 - 95F_4 + 10Dq \\ E[(t_{2g})^5(e_g)^1\ {}^1T_{2g}] &= 15A - 14B + 14C + \Delta = 15F_0 - 14F_2 - 175F_4 + 10Dq \end{aligned}\right\} \quad (1)$$

where $\Delta = 10Dq$ is the energy difference between the orbitals t_{2g} and e_g.

It is seen that the separation between ${}^1T_{1g}$ and ${}^1T_{2g}$ is $16B = 16F - 80F_4$ and this, therefore, should be the separation between the two longest-wavelength intense absorption bands of octahedral cobaltic complexes. Experimentally, the separation is about 8500 cm.$^{-1}$, whilst the value predicted by our theory is about twice as much. It is possible, of course, that the assignment of the bands is wrong and that the shorter-wavelength absorption band is due to a singlet from $(t_{2g})^4(e_g)^2$. Calculations indicate, however, that this is much less likely. The reason for the bad numerical agreement may be due partly to the approximations of the theory and partly to a reduction in the values of the atomic spectral parameters in forming the complex (cf. Owen [5]).



Effect of tetragonal perturbation on the d *orbitals.*

In an earlier paper by one of us [2] the energy differences in terms of Slater–Condon parameters between the ${}^1T_{1g}$ and the ${}^1T_{2g}$ state of Co^{3+} were stated to be equal to that between the corresponding states of ${}^4T_{1g}$ and ${}^4T_{2g}$ of Cr^{3+}. The latter was given correctly as $12F_2 - 60F_4$, and is in fact only three-quarters of the separation for Co^{3+}. Also the relative order of the T_{1g} and T_{2g} levels is inverted in passing from Cr^{3+} to Co^{3+}.

We now pass on to the effect of a tetragonal distortion, to a first order in the perburbation. We suppose the ligand X to lie along the Z axis and have the *d* orbital splitting shown in the Figure, where $d_{x^2-y^2}$ lies above d_{z^2} because the effect of halogens on the *d* orbitals is less than that of NH_3.[6] One may expect d_{xy} to lie below (d_{xz}, d_{yz}) because π interaction with the filled shells of halogens (especially for Cl, Br, or I) destabilizes the latter.

Then we write $\psi(a \longrightarrow b)$ to represent that singlet function of $(t_{2g})^5(e_g)$ in which there is one electron taken from the orbital of a of t_{2g} and put in the orbital b of e_g. The matrix of electrostatic energy is then

$$M = (15A + 14C)I - 2KB = (15F_0 - 245F_4)I - 2K(F_2 - 5F_4) \quad . \quad . \quad (2)$$

[3] Griffiths, *J. Inorg. Nucl. Chem.*, 1956, **2**, 1, 229.

[4] Orgel, *J. Chem. Phys.*, 1955, **23**, 1819.

[5] Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183.

[6] Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

where I is the unit matrix and

$$K = \begin{array}{l|ccc|ccc}
 & \psi(d_{yz} \rightarrow d_{z^2}) & \psi(d_{zx} \rightarrow d_{z^2}) & \psi(d_{xy} \rightarrow d_{z^2}) & \psi(d_{yz} \rightarrow d_{x^2-y^2}) & \psi(d_{zx} \rightarrow d_{x^2-y^2}) & \psi(d_{xy} \rightarrow d_{x^2-y^2}) \\
\hline
\psi(d_{yz} \rightarrow d_{z^2}) & 13 & 0 & 0 & 2\sqrt{3} & 0 & 0 \\
\psi(d_{zx} \rightarrow d_{z^2}) & 0 & 13 & 0 & 0 & 2\sqrt{3} & 0 \\
\psi(d_{xy} \rightarrow d_{z^2}) & 0 & 0 & 7 & 0 & 0 & 0 \\
\hline
\psi(d_{yz} \rightarrow d_{x^2-y^2}) & 2\sqrt{3} & 0 & 0 & 9 & 0 & 0 \\
\psi(d_{zx} \rightarrow d_{x^2-y^2}) & 0 & 2\sqrt{3} & 0 & 0 & 9 & 0 \\
\psi(d_{xy} \rightarrow d_{x^2-y^2}) & 0 & 0 & 0 & 0 & 0 & 15 \\
\hline
\end{array} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From (2) the zero-order wave-functions are easily seen to be

$$\left.\begin{array}{c}
\tfrac{1}{2}\sqrt{3}\psi(d_{yz} \longrightarrow d_{z^2}) + \tfrac{1}{2}\psi(d_{yz} \longrightarrow d_{x^2-y^2}) \\
\tfrac{1}{2}\sqrt{3}\psi(d_{zx} \longrightarrow d_{z^2}) + \tfrac{1}{2}\psi(d_{zx} \longrightarrow d_{x^2-y^2}) \\
\psi(d_{xy} \longrightarrow d_{x^2-y^2})
\end{array}\right\} \in {}^1T_{1g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\left.\begin{array}{c}
-\tfrac{1}{2}\psi(d_{yz} \longrightarrow d_{z^2}) + \tfrac{1}{2}\sqrt{3}\psi(d_{yz} \longrightarrow d_{x^2-y^2}) \\
-\tfrac{1}{2}\psi(d_{zx} \longrightarrow d_{z^2}) + \tfrac{1}{2}\sqrt{3}\psi(d_{zx} \longrightarrow d_{x^2-y^2}) \\
(d_{xy} \longrightarrow d_{z^2})
\end{array}\right\} \in {}^1T_{2g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Application of the tetragonal perturbation to these functions now gives $(\frac{3}{4}\delta + \pi)$ and $(\frac{3}{4}\delta - \pi)$ as the respective splittings of the two levels ${}^1T_{1g}$ and ${}^1T_{2g}$. In a previous paper[2] it was incorrectly stated that the upper excited state is not split to a first order in perturbation. If, however, our choice of positive signs for δ and π are correct, it is still true that the lower excited state is split more than the upper one. Furthermore, for the lower excited states the doublet should indeed be lower than the singlet in accord with the intensity measurements of Linhard and Weigel.[1] Provided that $\frac{3}{4}\delta > \pi$, the reverse is true for the upper states.

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969. *2-Acyl Derivatives of Cyclic 1 : 3-Diones. Part IV.** *The Structure of Dehydroleptospermone.*

By W. R. CHAN and C. H. HASSALL.

IT has been shown[1] that pyrolysis of the crude product of bromination of leptospermone (I) leads to dehydroleptospermone, $C_{15}H_{20}O_4$. The same compound may be prepared by dehydrobromination of monobromoleptospermone with collidine or with fused potassium acetate in methanol. Some interest attaches to the structure of dehydroleptospermone in view of early proposals, which have, however, been refuted recently,[2] that natural products such as flavaspidic acid[3] and protokosin[4] contain dehydro-2-acyl*cyclo*hexane-1 : 3-dione units in their molecular constitution.

Dehydroleptospermone does not behave like a 2-acyl*cyclo*hexane-1 : 3-dione. It is insoluble in alkali carbonates, does not form a chloroform-soluble copper derivative, and gives no colour with ferric chloride solution. The ultraviolet absorption spectrum has maxima at 231 (ε 11,000) and 260 mμ (ε 11,800) while 2-acyl*cyclo*hexane-1 : 3-diones regularly[5] have maxima near 230 and 280 mμ. Acetylation of dehydroleptospermone

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* Part III, Chan and Hassall, *J.*, 1956, 3495.

[1] Briggs, Hassall, and Short, *J.*, 1945, 706.

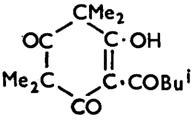
[2] Birch, *J.*, 1951, 3026; Birch and Todd, *J.*, 1952, 3102.

[3] Boehm, *Annalen*, 1903, **320**, 310.

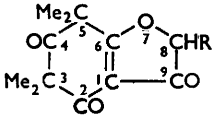
[4] Hems and Todd, *J.*, 1937, 562.

[5] Chan and Hassall, *J.*, 1956, 3495.

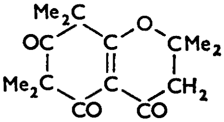
gives a monoacetate with a single ultraviolet absorption maximum at 267 mμ (ε 6100). A comparison of the infrared absorption spectrum of this compound with that of dehydroleptospermone suggests that it is an enol acetate. This evidence indicates that dehydroleptospermone may have the constitution (II) or (IV). To distinguish these possibilities the dehydrobromination of the monobromo-derivative of 6-acetyl-2 : 2 : 4 : 4-tetramethyl*cyclo*hexane-1 : 3 : 5-trione has been studied. The product of the reaction, which i formulated as 3 : 3 : 5 : 5-tetramethyl-7-oxa*bicyclo*[4 : 3 : 0]non-1(6)ene-2 : 4 : 9-trione (III), has properties very similar to those of dehydroleptospermone. The ultraviolet absorption spectra of the two compounds have similar maxima. The infrared absorption spectra have corresponding maxima in the carbonyl and double-bond region 1800–1450 cm.$^{-1}$, and are in agreement with the constitutions (II) and (III) which are proposed. The close similarity of absorption spectra would not be expected if the dehydro-derivatives of leptospermone and 6-acetyl-2 : 2 : 4 : 4-tetramethyl*cyclo*hexane-1 : 3 : 5-trione have the structures (IV) and (III) respectively. This indicates that dehydroleptospermone should be assigned the constitution (II).



(I)



(II) : R = Prⁱ
(III) : R = H



(IV)

Experimental.—Light petroleum refers to the fraction of b. p. 60—80°.

Ultraviolet spectra were determined for methanol solutions with a Beckman spectrophotometer, model DU.

Dehydroleptospermone (3 : 3 : 5 : 5-*tetramethyl*-8-iso*propyl*-7-*oxa*bicyclo[4 : 3 : 0]*non*-1(6)-*ene*-2 : 4 : 9-*trione*). A solution of leptospermone (5·0 g.) and bromine (3·5 g.) in chloroform (5 c.c.) was set aside for 5 days. Bromine and solvent were then removed *in vacuo*. The oily residue did not crystallise. Attempts to distil it at 0·3 mm. led to decomposition. The active bromine in this residue was estimated by using potassium iodide and sodium thiosulphate (Found : Br, 25·7. Calc. for $C_{15}H_{21}O_4Br$: Br, 23·2%).

When the residue was heated at atmospheric pressure for 4 hr. at 130—140° there was considerable evolution of hydrogen bromide, and a solid was obtained. This was recrystallised from ethyl acetate and light petroleum to give a poor yield of dehydroleptospermone, white needles, m. p. 125—130° [Found : C, 68·4; H, 7·7%; *M* (cryoscopic in camphor), 248. Calc. for $C_{15}H_{20}O_4$: C, 68·2; H, 7·6%; *M*, 264]. It gave no colour with tetranitromethane or ferric chloride. A higher yield was obtained when the residue from the bromination reaction was refluxed with γ-collidine (15 c.c.) for 1½ hr. The solid obtained by pouring the mixture into excess of dilute hydrochloric acid was collected after 12 hr., washed successively with 3N-hydrochloric acid (100 c.c.), 10% sodium carbonate solution (100 c.c.), and water (300 c.c.), then chromatographed on acid-washed alumina. The material eluted with benzene (3·7 g.; m. p. 110—114°) was recrystallised repeatedly from light petroleum, to yield white needles, identical with the previous product by m. p., mixed m. p., and ultraviolet absorption.

Alternatively, the residue from the bromination (310 mg.), fused potassium acetate (135 mg.), and methanol (10 c.c.) were refluxed for 2 hr. Water (25 c.c.) was added to the residue after removal of the methanol, and the mixture acidified with hydrochloric acid to give a white solid (167 mg.) affording dehydroleptospermone on recrystallisation from light petroleum. The *acetate* was obtained by refluxing dehydroleptospermone (102 mg.) with 5 c.c. of acetic anhydride–acetyl chloride (4 : 1 v/v) for 2½ hr. It recrystallised from light petroleum as large cubes, m. p. 94—95° (Found : C, 67·4; H, 7·3; Ac, 16·6. $C_{17}H_{22}O_5$ requires C, 66·7; H, 7·2; 1Ac, 14·1%), $\lambda_{max.}$ 267 mμ (ε 6100). It gave a yellow colour with tetranitromethane.

6-*Acetyl*-2 : 2 : 4 : 4-*tetramethyl*cyclo*hexane*-1 : 3 : 5-*trione*. This compound was prepared according to the directions of Riedl and Risse.[6] It was obtained from the fraction soluble in potassium hydrogen carbonate, by steam-distillation, as long needles, m. p. 35·5—36°, $\lambda_{max.}$ 234 and 277 mμ (ε 8500 and 10,500 respectively). The *piperonylidene derivative* recrystallised from

[6] Riedl and Risse, *Annalen*, 1954, **585**, 209.

methanol as yellow plates, m. p. 153—154° (Found: C, 67·6; H, 5·6. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·7%).

3 : 3 : 5 : *5-Tetramethyl-7-oxa*bicyclo[4 : 3 : 0]*non-1(6)-ene-2 : 4 : 9-trione* (III). The triketone (615 mg.) and bromine (397 mg.) in chloroform (3 c.c.) were kept for 20 hr. at room temperature. After removal of the solvent, the oily product (832 mg.) was mixed with dry methanol (20 c.c.) and fused potassium acetate (410 mg.). After 1 hour's refluxing on a water-bath the methanol was distilled off and water (100 c.c.) added. The aqueous solution was extracted with ether (4 × 50 c.c.). The semi-liquid residue obtained after evaporation of ether from the combined extracts was triturated with ether (2 × 3 c.c.), to give a relatively insoluble *product* which recrystallised from methanol as white needles (166 mg.), m. p. 173—175° [Found: C, 65·4; H, 6·3; *M* (Rast), 228. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·35%; *M*, 222], $\lambda_{max.}$ 232 and 260 mμ (ε 10,000 and 11,400 respectively). The compound gave no colour with tetranitromethane. The *acetate*, prepared as described for dehydroleptospermone, crystallised as needles (from light petroleum), m. p. 100—101° (Found: C, 63·6; H, 6·1; Ac, 16·9. $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1; 1Ac, 16·3%). $\lambda_{max.}$ 263 mμ (ε 6000). It gave a yellow colour with tetranitromethane.

Infrared absorption spectra. The infrared spectra were determined in potassium bromide pellets by Dr. S. M. Nagy, Massachusetts Institute of Technology, using a Baird Associates instrument. The principal bands observed between 4000 and 1400 cm.$^{-1}$ were as follows (s = strong, m = medium, w = weak, sh = shoulder):

Dehydroleptospermone: 3310 w, 3150 w, 2900 m, 2860 m, 1724 s, 1695 s, 1650 m, 1587 s, 1473 s, 1425 s.

Compound (III): 3310 m, 2900 m, 2860 m, 1724 s, 1695 s, 1645 s, 1587 s, 1470 s, 1425 s, 1404 m.

Dehydroleptospermone acetate: 3310 w, 2900 m, 1754 m, 1709 m, 1667 s, 1592 m, 1462 m, 1450 sh.

Enol acetate of (III): 3310 w, 2874 m, 1739 s, 1700 m, 1660 s, 1603 m, 1550 w, 1470 m, 1450 m.

One of us (W. R. C.) acknowledges with thanks the award of a Geddes Grant Research Fellowship and a grant from Messrs. Roche Products Ltd.

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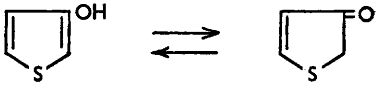
970. 3-*Hydroxythiophen.*

By M. C. Ford and Donald Mackay.

Until recently neither of the monohydroxythiophens was known. 2-Hydroxythiophen, however, has been obtained [2] pure (cf. Mentzer and Billet [1]), but in low yield, from the mixture of magnesium complexes formed by the action of oxygen, at 0—5°, on ethereal 2-thienylmagnesium bromide in the presence of *iso*propylmagnesium bromide. It was a low-melting solid with a non-phenolic odour: two non-phenolic tautomers, 2 : 3-dihydro- and 2 : 5-dihydro-2-oxothiophen, are possible, indeed the infrared spectrum of a carbon tetrachloride solution exhibited a strong carbonyl band but only weak hydroxyl absorption, and, in addition to *O*-acyl derivatives, a benzylidene derivative could be prepared.

The similar oxidation of 3-thienylmagnesium bromide was stated to yield a crude material that could not be purified, though qualitative tests showed it to contain phenolic material. Other possible routes to 3-hydroxythiophen (I) do not seem to have been explored.



(I) (II)

As an authentic specimen was needed the Grignard method was re-examined: the production of a crude phenolic material was confirmed, and two distillations gave the pure hydroxythiophen, which was, however, unstable, developing a reddish tinge and a disagreeable odour within a day, and finally resinifying.

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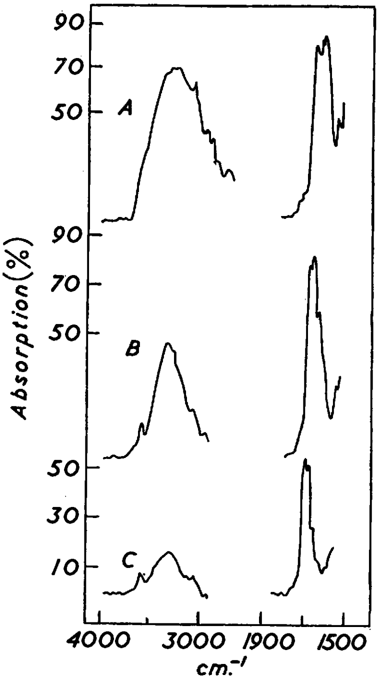
[1] Mentzer and Billet, *Bull. Soc. chim. France*, 1945, 292.

[2] Hurd and Kreuz, *J. Amer. Chem. Soc.*, 1950, **72**, 5543.

The spectrum of a liquid film (*A*) in the range 4000—1500 cm.$^{-1}$ exhibits a broad band centred at 3300 cm.$^{-1}$ characteristic of a hydrogen-bonded phenolic hydroxyl group, whilst the triple peak (1665, 1644, and 1630 cm.$^{-1}$), which is of a very similar intensity, shows the presence of the αβ-unsaturated carbonyl system; hydrogen-bonding of the carbonyl group may perhaps account for the complexity of the band. In the spectra (*B* and *C*) of increasingly dilute carbon tetrachloride solutions the shoulder originally present at 3585 cm.$^{-1}$ emerges as a separate peak at 3600 cm.$^{-1}$, indicating a progressive increase in the proportion of free hydroxyl group. There is a marked accompanying increase in the relative intensity of the unsaturated carbonyl band, together with a displacement of its maximum towards higher frequencies (see Figure).



Tautomerism of 3-*hydroxythiophen* : *hydroxyl and carbonyl bands.*
A, liquid film.
B, 15% v./v. in CCl_4.
C, 8% v./v. in CCl_4.

The absorption characteristic of an unsaturated carbonyl group clearly establishes the presence of the tautomeric 2 : 3-dihydro-3-oxothiophen (II) in the liquid and in solutions. The changes in the relative intensities of the carbonyl and hydroxyl bands suggest a shifting of equilibrium in favour of the oxo-form with increasing dilution, though a difference between the transition moments for the free and the hydrogen-bonded carbonyl group could also be responsible for this effect. However, the strength of the hydroxyl band in the spectrum of the liquid film, and the odour, suggest that the pure substance must be phenolic to a comparable extent.

There is thus a marked contrast between 2-hydroxythiophen which probably exists, not unexpectedly, largely in a ketonic form (indeed the crystalline solid may be in reality 2 : 5-dihydro-2-oxothiophen) and 3-hydroxythiophen which, though also tautomeric, is nevertheless noticeably phenolic.

Experimental.—A solution of ethyl bromide (18·5 g.) and 3-bromothiophen[3] (b. p. 157—158·5°/759 mm.; 37·0 g.) in ether (150 ml.) was added to a briskly reacting mixture of ethyl bromide (18·5 g.), magnesium (13·7 g.), and ether (200 ml.) in such a way that the vigour of the original reaction was maintained; the whole was then refluxed for 18 hr. in nitrogen. A solution of *iso*propylmagnesium bromide [from *iso*propyl bromide (35·0 g.), magnesium (7·0 g.), and ether (100 ml.)] was added, the mixture was cooled to −10°, and dry oxygen was passed, the temperature being maintained below 5°. When absorption of the gas had ceased the product was set aside at 5° for 20 hr. and then poured on powdered solid carbon dioxide. After

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[3] Hartough, " Thiophene and its Derivatives," Interscience, New York, 1952, p. 499.

addition of a slight excess of chilled 2N-sulphuric acid the ether layer was separated, and the aqueous layer saturated with salt and further extracted. The ethereal solutions were combined and, after a preliminary washing with 2N-potassium hydrogen carbonate, extracted with 5N-sodium hydroxide. The alkaline solution was immediately acidified with ice-cold 2N-sulphuric acid and the liberated phenolic material then taken up in ether.

Removal of the solvent under reduced pressure from the dried ($MgSO_4$) solution gave an almost black product (2·2 g.) which was first stored (5°/400 mm.) over phosphoric oxide and then distilled from glass wool: a pale yellow liquid, b. p. 38—39°/0·01 mm., was obtained, which when redistilled under nitrogen at 0·02 mm. (bath $\ngtr$ 80°) yielded the unstable 3-*hydroxythiophen* 5%) as an almost colourless, slightly viscous, oil with a phenolic odour (Found: C, 47·1; H, 4·3. C_4H_4OS requires C, 48·0; H, 4·0%). The analytical and infrared results were obtained within 2 hr. of the final distillation, during which time the deterioration of a reference sample was almost imperceptible.

With aqueous ferric chloride the hydroxythiophen gave an intensely red colour, and with diazotised aniline in presence of alkali, a dark red precipitate.

The *benzoate*, prepared under Schotten–Baumann conditions, was obtained as irregular prisms, m. p. 40°, from light petroleum (b. p. 30—40°) (Found: C, 64·7; H, 4·2; S, 15·4. $C_{11}H_8O_2S$ requires C, 64·7; H, 3·95; S, 15·7%): its m. p. was strongly depressed by admixture with the isomeric 2-thienyl benzoate,[2] m. p. 44°, a liquid being formed at room temperature; the 3 : 5-*dinitrobenzoate*, prepared in pyridine solution and recrystallised from methanol, formed minute, faintly yellow, prisms, m. p. 150° (Found: C, 45·1; H, 2·3. $C_{11}H_6O_6N_2S$ requires C, 44·9; H, 2·1%). The *phenylcarbamate* was prepared in the absence of a solvent and in the cold, a trace of pyridine being used as catalyst; recrystallised from light petroleum (b. p. 70—80°) it gave felted needles, m. p. 120° (Found: C, 60·3; H, 4·4; N, 6·1. $C_{11}H_9O_2NS$ requires C, 60·25; H, 4·1; N, 6·4%). The derivatives all appeared to be stable indefinitely.

3-Bromothiophen (20 g.) was recovered from the ethereal solution of alkali-insoluble material.

Grateful acknowledgment is made to Dr. D. C. McKean with whom the infrared results were discussed. One of us (D. M.) also thanks the Carnegie Trust for the Universities of Scotland for a scholarship, and the Murdo Macaulay Trust for a grant.

THE UNIVERSITY, OLD ABERDEEN. [*Received, July* 12*th*, 1956.]

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971. *The Fission of Alkyl Allyl Ethers by Boron Trichloride.*

By W. GERRARD, M. F. LAPPERT, and H. B. SILVER.

EXPERIMENTS with boron trichloride and mixed dialkyl or alkyl aryl ethers have indicated that, in general, ether fission occurs readily and that the nature of the products depends on the proportions in which the reagents are mixed [see schemes (1) and (2)].

$$\text{(1)}\quad \mathrm{ROR'} + \mathrm{BCl_3} \longrightarrow \mathrm{RO{\cdot}BCl_2} + \mathrm{R'Cl}$$

$$\text{(2)}\quad \mathrm{2ROR'} + \mathrm{BCl_3} \longrightarrow \mathrm{(RO)_2B{\cdot}Cl} + \mathrm{2R'Cl}$$

Moreover, it has been shown that the alkyl chloride is produced exclusively from the more electron-releasing (R′) of the two groups and that the mechanism of the fission is of the S_N1 type.[1]

We have described the fission of diallyl, di-2-methylallyl, and allyl 2-methylallyl ethers [2] and now report results obtained with allyl butyl (*n*-, *sec*.-, and *tert*.-) and allyl propyl (*n*- and *iso*-) ethers. The purpose of the investigation was partly that the results are of interest *per se*, but also to determine the degree of electron-release of the allyl group relative to these saturated alkyl groups. We believe that the fission of mixed ethers by boron trichloride provides a general method of determining relative electron-release of hydrocarbon radicals.

Reaction (2) was employed except in the allyl *n*-butyl ether system, because dichloroboronites, $RO{\cdot}BCl_2$, particularly those wherein R = a *sec*.- or *tert*.-alkyl or an allyl group,

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[1] Gerrard and Lappert, *J.*, 1951, 1020; 1952, 1486; Edwards, Gerrard, and Lappert, *J.*, in the press.

are unstable.[2,3] Whilst the corresponding chloroboronates, $(RO)_2B{\cdot}Cl$, are likewise unstable,[2,4] their manner of decomposition is known [see scheme (3)], and therefore permits the fate of the group R to be traced by isolation and identification of the borate, $B(OR)_3$.

$$(3) \quad 3(RO)_2B{\cdot}Cl \longrightarrow 3RCl + B_2O_3 + B(OR)_3$$

The experiments show that the primary alkyl allyl ethers give allyl chloride and the primary alkoxyboron chloride, whereas the *sec.*- or *tert.*-alkyl allyl ethers produce the reverse mode of fission. We conclude, therefore, that the electron-releasing power of the allyl group is intermediate between that of primary and secondary alkyl groups. This view is supported by Vernon's measurements of first-order rate coefficients for the solvolysis of allyl and *n*-propyl chloride.[5] Our earlier experiments on allylic systems had also indicated that the reactivity of the allyl group is greater than that of a primary alkyl group.

Experimental.—General procedures have been described before.[2] The allyl propyl ethers were prepared by a Williamson synthesis from the appropriate sodium propoxide and allyl bromide. The allyl butyl ethers were obtained by the method of Talley, Hunter, and Yanovsky.[6]

Allyl n-*butyl ether.* The ether (4·98 g., 1 mol.) in *n*-pentane (10 c.c.) was added (20 min.) to boron trichloride (5·67 g., 1·1 mol.) in *n*-pentane (10 c.c.) at −80°. An orange-red lower layer separated, but at 20° the mixture was homogeneous. After 2 hr. at 20°/15 mm., *n*-butyl dichloroboronite (5·81 g., 90%) remained as a pale brown, liquid residue, having b. p. 29°/9 mm., n_D^{21} 1·4158 (Found : Cl, 45·2; B, 7·0. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%).

Allyl sec.-*butyl ether.* The ether (11·50 g., 2 mols.) in *n*-pentane (15 c.c.) was added (20 min.) to the trichloride (5·90 g., 1 mol.) in *n*-pentane at −80°, whereupon a yellow lower layer separated. Matter volatile at 20°/15 mm. was removed by suction (1 hr.). A non-volatile residue (7·47 g.) remained. This was heated (1 hr.) at 140° under reflux, the outlet of the condenser being connected to a cold (−80°) trap. A condensate of crude allyl chloride (2·05 g.), b. p. 42—46°/760 mm., n_D^{20} 1·4105, was collected, leaving a residue (4·98 g.), which afforded triallyl borate (2·95 g., 91%), b. p. 72°/10 mm., n_D^{20} 1·4285 (Found : B, 6·0. Calc. for $C_9H_{15}O_3B$: B, 5·95%), and a residue of boron trioxide (1·075 g., 93%) on distillation.

Allyl tert.-*butyl ether.* The ether (6·91 g., 2 mols.) was slowly added to the trichloride (3·55 g., 1 mol.) at −80°, in the absence of solvent. A pale orange solution was formed. Evacuation at 20°/18 mm. yielded crude *tert.*-butyl chloride (3·56 g., 64%), b. p. 50°/730 mm., n_D^{20} 1·3805 [Found : Cl (all hydrolysable in the cold, characteristic of *tert.*-butyl, but not allyl chloride), 36·8. Calc. for C_4H_9Cl : Cl, 38·4%]. The residue (6·70 g.), after being heated (3 hr.) under reflux at 110°, afforded a condensate (2·93 g.), collected at −80°, which was a mixture of *tert.*-butyl and allyl chloride, b. p. 46—48°/760 mm., n_D^{20} 1·4025 (Found : easily hydrolysable Cl, 21·3; total Cl, 42·0%), and triallyl borate (1·45 g., 79%), b. p. 70°/12 mm. (Found : B, 5·8%).

Allyl n-*propyl ether.* The ether (5·94 g., 2 mols.) in *n*-pentane (10 c.c.) was added dropwise (20 min.) to the trichloride (3·48 g., 1 mol.) in *n*-pentane (5 c.c.) at −80°. A yellow lower layer separated; at 20° the mixture appeared homogeneous and was a deep orange colour. Evacuation at 20°/15 mm. afforded a liquid condensate (5·04 g.), which on distillation gave di-*n*-propyl chloroboronate (4·10 g., 84%), b. p. 38·5°/6 mm., n_D^{20} 1·4036 (Found : Cl, 22·0; B, 6 7. Calc. for $C_6H_{14}O_2ClB$: Cl, 22·0; B, 6·7%).

Allyl iso*propyl ether.* The ether (7·51 g., 2 mols.) was added to the trichloride (4·40 g., 1 mol.) in *n*-pentane (15 c.c.) at −80°. A white solid was formed, but disappeared when the addition had been completed. To the mixture at −80° was added ferric chloride (0·05 g.), to facilitate decomposition of the chloroboronate,[4] and the product was warmed to 20°. Matter volatile at 20°/18 mm. was removed by suction and the residue (3·16 g.) was distilled, to afford triallyl borate (1·67 g., 74%), b. p. 66°/13 mm., n_D^{20} 1·4267 (Found : B, 6·0%), and a residue containing boron trioxide (0·871 g., 100%).

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[*Received, July* 19*th*, 1956.]

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[2] Gerrard, Lappert, and Silver, *J.*, 1956, 3285.
[3] Gerrard and Lappert, *J.*, 1951, 2545; 1955, 3084.
[4] Lappert, *J.*, 1956, 1768.
[5] Vernon, *J.*, 1954, 423.
[6] Talley, Hunter, and Yanovsky, *J. Amer. Chem. Soc.*, 1951, **73**, 3528.