NOTES.

286. *The Interaction of Boron Trichloride with Esters of Sulphurous and Sulphuric Acid.*

By J. Charalambous, H. J. Davies, M. J. Frazer, and W. Gerrard.

Alkyl sulphites readily exchanged an alkoxyl group for chlorine attached to boron (eqns. 1 and 2); but the alkoxyl group in the chlorosulphinate was not so replaced, although n-butyl dichloroborinate and even the chloroboronate did react with the sulphite.

$$(Bu^nO)_2S{:}O + BCl_3 \longrightarrow Bu^nO{\cdot}BCl_2 + Bu^nO{\cdot}S(:O)Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$3(Bu^nO)_2S{:}O + BCl_3 \longrightarrow (Bu^nO)_3B + 3Bu^nO{\cdot}S(:O)Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Diphenyl sulphite reacted similarly, but owing to the resistance of the phenyl group to the nucleophilic chlorine anion, the chlorosulphinate is more stable thermally and could be forced to undergo further reaction (3), and the boron chloro-esters gave phenyl borate and boron trichloride by mutual exchange.[1]

$$PhO{\cdot}S(:O)Cl + BCl_3 \longrightarrow SOCl_2 + PhO{\cdot}BCl_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Ethylene sulphite and *o*-phenylene sulphite reacted as shown.

$$2[CH_2{\cdot}O]_2{>}SO \xrightarrow{BCl_3} [ClS(:O){\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O]_2BCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$C_6H_4O_2SO \xrightarrow{BCl_3} C_6H_4O_2BCl + SOCl_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

[1] Colclough, Gerrard, and Lappert, *J.*, 1955, 907.

All these reactions may be formulated as involving a four-centre transition state, the driving force being mainly the nucleophilic power of alkoxylic oxygen in co-operation with the electrophilic function of the non-metals.

By contrast, n-propyl, n-butyl, and n-octyl sulphate reacted with boron trichloride in a solvent to give alkyl chloride (s-RCl from Pr^n and Bu^n)[2] and a yellow precipitate approximating to the mixed anhydride $[B_2S_3O_{12}]_n$. In the absence of solvent the reaction was vigorous at 20°, hydrogen chloride and sulphur dioxide being evolved.

Methyl or phenyl chlorosulphonate did not react with boron trichloride, but the ethyl, n-propyl, and n-butyl compounds did so violently, even at −80°, giving sulphur dioxide, hydrogen chloride, and a brown (hydrocarbon polymer) residue; only the ethyl compound gave the alkyl chloride.

The results relate to factors involved in the formation of mixed polyanhydrides,[3,4] *e.g.*, with boron trichloride, trialkyl phosphites give a mixture of chloro-esters, whereas trialkyl phosphates give alkyl chloride and compounds having P–O–B linkages.

Experimental.—The sulphite (Table 1) and boron trichloride (in methylene dichloride; volume not critical) were mixed at −80°. Volatile matter was removed at 20°/20 mm., any thionyl chloride being trapped at −80°; boron trichloride was absorbed by potassium hydroxide. The residue was distilled under reduced pressure, uncondensed matter and boron trichloride or thionyl chloride being trapped.

TABLE 1.

R	$(RO)_2S{:}O$ (g.)	$(RO)_2S{:}O$ (mol.)	BCl_3 (mol.)	Yield of RO·S(:O)Cl * (%)	Boron compound,* and yield (%)	
Bu^n	9·97	1	1 [a]	84·5	$Bu^nO{\cdot}BCl_2$	52·4
Bu^n	21·40	3	1	80·4	$(Bu^nO)_3B$	97·0
Ph	10·27	1	1	—	$(PhO)_3B$	91·4 [b]
Ph	25·00	3	1	82·0	$(PhO)_3B$	89·0

* Products were characterised by analysis and b. p.
[a] BCl_3 recovered 0·47 g. Residue 0·9 g. [b] BCl_3 0·59 g., $SOCl_2$ 3·93 g.

Similarly, ethylene sulphite (13·74 g., 2 mol.) and boron trichloride (1 mol.) gave *bis*-(2-*chlorosulphinyloxyethyl*)*chloroboronate* (17·11 g., 80·8%), b. p. 100—103°/2·5 mm. (Found: B, 3·15; Cl, 29·6; S, 19·1. $C_4H_8BCl_3O_6S_2$ requires B, 3·2; Cl, 31·9; S, 19·2%). The infrared spectrum, in particular the band at 1217 $cm.^{-1}$ (S=O), supports the assigned structure. *o*-Phenylene sulphite (7·75 g., 1 mol.) gave *o*-phenylene chloroboronate (5·19 g., 67·8%), b. p. 70°/20 mm., thionyl chloride (4·2 g.), and a residue (2·0 g.) (Found: B, 6·9; Cl, 4·7; S, 4·6%). Thionyl chloride (1·33 g.) was collected in alkali during the initial removal of volatile matter at 20°/20 mm.

n-Butyl chlorosulphinate (94·5%) and boron trichloride (89%) were recovered after being mixed. Phenyl chlorosulphinate (9·85 g., 1 mol.) and boron trichloride (6·46 g., 1 mol.) gave triphenyl borate (3·96 g.), b. p. 180°/2 mm., boron trichloride (2·98 g.), and thionyl chloride (4·92 g.).

Sulphates and boron trichloride. Volatile compounds were characterised by chemical, spectroscopic, and gas-chromatographic analyses. The sulphate (1 mol.) (Table 2) was added dropwise to an excess of boron trichloride at 20°. The vigorous reaction gave a yellow solid which, at 20°/20 mm. (0·5 hr.), gave hydrogen chloride, sulphur dioxide, boron trichloride, and alkyl chloride; there was a brown tarry residue which, at 300°/20 mm. (3 hr.), gave sulphur dioxide, sulphur trioxide, hydrogen chloride, and a black solid containing boron and small amounts (<5%) of sulphur and chlorine.

[2] Cf. Cooper and Gerrard, *Chem. and Ind.*, 1961, 320.
[3] Gerrard, *J. Oil Colour Chemists' Assoc.*, 1959, **42**, 625; *Soc. Chem. Ind. Monograph* **13**, 1961, p. 328; *Ann. Rep. Prog. Appl. Chem.*, 1960, **45**, 394.
[4] Gerrard and Griffey, *Chem. and Ind.*, 1959, 55; *J.*, 1960, 3170; 1961, 4095; Gerrard and Jeacocke, *ibid.*, 1959, 704; Gerrard and Strickson, *ibid.*, 1958, 860; Gerrard and Lindsay, *ibid.*, 1960, 152; Frazer, Gerrard, and Patel, *ibid.*, 1959, 90, 728; 1960, 726; Currell, Frazer, Gerrard, Haine, and Leader, *J. Inorg. Nuclear Chem.*, 1959, **12**, 45; Bedell, Frazer, and Gerrard, *J.*, 1960, 4037; Frazer, Gerrard, and Strickson, *J.*, 1960, 4701; Frazer, Gerrard, and Singh, *J.*, 1961, 4680.

TABLE 2.

R	$(RO)_2SO_2$ (g., 1 mol.)	BCl_3 reacted (mol.)	RCl (mol.)	Residue [a] Wt. (g.)	Found (%) B	S	Cl	HCl (mol.)	SO_2 and SO_3 (mol.)	Solid [b] B † (%)
Me	10·00	0·85	1·5	10·4	7·3	25·0	16·1	0·56	1·00	25·8
Et	22·50	0·71	1·4	18·8	6·3	25·0	7·5	0·39	0·96	16·1
Pr^n	25·00	0·67	1·1 [c]	21·0	5·4	20·5	4·4	0·85	0·94	13·6
Bu^n	10·00	1·20	1·1 [d]	9·4	7·2	13·2	17·4	—	0·93	19·0
In n-pentane										
Pr^n	12·9	0·66	—	5·9	6·5	28·0	2·5 *	0·40	0·77	27·0
Bu^n	13·5	0·60	1·3 [e]	6·5	6·1	30·1	4·6	—	—	—
$n\text{-}C_8H_{17}$ ...	7·8	0·67	1·5 [f]	2·6	6·8	30·0	2·9	—	—	—

* Could not be freed from chlorine without removal of sulphur oxides (Calc. for $B_2O_{12}S_3$: B, 7·0; S, 31·0%)

† All boron from reacted boron trichloride was in this residue.

[a] At 20°/20 mm. [b] At 300°/20 mm. [c] Pr^i, 97%; Pr^n, 3%. [d] Bu^s, 96%; Bu^n, 4%. [e] Bu^s, 85%; Bu^n, 15%. [f] Mixture of n- and s-, b. p. 74—80°/20 mm. n_D^{22} 1·4295, d^{20} 0·870.

Methyl sulphate did not react at 20°, but a white solid formed at 45° (4 hr.). Methyl chloride was then allowed to evaporate and the mixture was treated as before.

In n-pentane (total 530 c.c.), the sulphate (1 mol.) (Table 2) was added to an excess of boron trichloride at −80°. A precipitate corresponding approximately to boron sulphate, $B_2S_3O_{12}$, formed at 20° (12 hr.). The filtrate gave boron trichloride, hydrogen chloride, and alkyl chloride. The precipitate (tested in the case of n-propyl sulphate) decomposed at 300°/20 mm., giving a mixture of sulphur di- and tri-oxide, and a residue of boric oxide.

Chlorosulphonates and boron trichloride. After boron trichloride (6·15 g.) and methyl chlorosulphonate (22·20 g.) in n-pentane (25 c.c.) had been heated at 45° for 26 hr. the chlorosulphonate (20·0 g., 90%), b. p. 50—51°/30 mm., was recovered (Found: Cl, 27·1. Calc. for CH_3ClO_3S: Cl, 27·2%). The other alkyl chlorosulphonates (1 mol.) reacted violently, even at −80°, and yielded viscous liquids (see Table 3).

TABLE 3.

R	BCl_3 reacted (mol.)	HCl at 20°/ 20 mm. (mol.)	At 100°/20 mm. HCl (mol.)	At 100°/20 mm. SO_2 (mol.)	Tarry residue Found (%) B	Cl	S
Et	0·45	0·32 *	0·42	0·20	5·3	21·5	5·5
Pr^n	0·23	0·60	0·37	0·58	3·0	13·0	8·3
Bu^n	0·85	0·99	0·81	0·14	5·5	8·3	13·8

* Ethyl chloride (53·5%) was also obtained.

Phenyl chlorosulphonate. This was prepared from phenol and sulphuryl chloride in the presence of pyridine dissolved in ether, a procedure which with alcohols gives alkyl chloride. The distilled product (46 g.) (Found: Cl, 17·2; S, 14·2%), when treated with boron trichloride (2·3 g.) in n-pentane (50 c.c.) at −80°, gave the chlorosulphonate (40·2 g., 71% overall), b. p. 113°/18 mm., n_D^{25} 1·5265 (Found: Cl, 18·3; S, 16·4. Calc. for $C_6H_5ClO_3S$: Cl, 18·4; S, 16·7%). It was recovered, b. p. 114—116°/23 mm. (Found: Cl, 18·6; S, 16·4%), after being heated at 45° (8 hr.) under reflux with boron trichloride (1 mol.) in methylene dichloride. It had previously been prepared,[5,6] impure and in low yields, from sodium phenoxide and sulphuryl chloride.

NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON, N.7. [*Received, August 28th*, 1961.]

[5] Battegay and Denivelle, *Compt. rend.*, 1932, **194**, 1505.

[6] Lukashevich and Kurdyumova, *J. Gen. Chem. U.S.S.R.*, 1948, **18**, 1963.

287. 1,3,5-*Triazines. Part I. The Reaction of Cyanuric Chloride with* NN-*Diethylaniline.*

By R. C. GOLESWORTHY, R. A. SHAW, and B. C. SMITH.

A HYDROGEN HALIDE acceptor was required for reactions between cyanuric chloride and non-metallic hydrides, and the suitability of *NN*-diethylaniline for this purpose has been investigated. Replacement of the chlorine atoms of cyanuric chloride by primary and

secondary amines has been studied extensively,[1] but reactions with tertiary bases have been neglected. Saure [2] investigated the reaction of cyanuric chloride with aqueous pyridine, but no reaction was observed with anhydrous pyridine, even on boiling. It has also been reported [3] that cyanuric chloride reacts with a mixture of diphenylamine and triethylamine in toluene, to give ethyl chloride and 2-chloro-4-diethylamino-6-diphenylamino-1,3,5-triazine.

Cyanuric chloride and *NN*-diethylaniline in 1 : 2 molar ratio were heated together for an hour at 125°. Ethyl chloride was evolved and *NN*-diethylaniline hydrochloride was isolated. Two derivatives of 1,3,5-triazine were obtained: colourless 2,4-dichloro-6-*N*-ethylanilino- and yellow -6-*p*-*NN*-diethylanilino-1,3,5-triazine, the latter giving intensely fluorescent solutions in hydrocarbon solvents. The structures were confirmed by independent synthesis. The monoethyl derivative was prepared from cyanuric chloride and *N*-ethylaniline by the method of Thurston *et al.*,[4] and the diethyl derivative (from cyanuric chloride and the Grignard reagent from *p*-bromo-*NN*-diethylaniline.

The dealkylation is analogous to the reaction between trimethylamine and hexachlorocyclotriphosphazatriene,[5] and other similarities between the 1,3,5-triazine and phosphazene systems have been reported recently.[6]

Experimental.—Cyanuric chloride (18·5 g., 0·1 mole) and *NN*-diethylaniline (29·8 g., 0·2 mole) were heated at 125° in the absence of solvent for 1 hr., whereafter evolution of ethyl chloride ceased. Addition of benzene gave an insoluble brown solid which was sublimed at 100°/2 mm. and identified as *NN*-diethylaniline hydrochloride (5·1 g., 0·027 mole), m. p. 158—159°. Evaporation of the filtrate and sublimation at 100—120°/0·01 mm. gave a yellow solid (24·2 g.) from which colourless 2,4-*dichloro*-6-N-*ethylanilino*-1,3,5-*triazine* (10·1 g., 37%), m. p. 116·5—117° (Found: C, 49·4; H, 4·0; Cl, 26·0; N, 20·9. $C_{11}H_{10}Cl_2N_4$ requires C, 49·1; H, 3·8; Cl, 26·4; N, 20·8%), and yellow 2,4-*dichloro*-6-p-NN-*diethylanilino*-1,3,5-*triazine* (6·4 g., 21%), m. p. 157—157·5° (Found: C, 52·3; H, 5·1; Cl, 23·7; N, 18·4. $C_{13}H_{14}Cl_2N_4$ requires C, 52·5; H, 4·8; Cl, 23·9; N, 18·9%), were obtained by fractional crystallisation from light petroleum (b. p. 60—80°). These had $\nu_{max.}$ (in KBr) as follows: monoethyl, 1570, 1475, 1325, 1225, 1180, 1105, 843, 808, 793, 768, 760, 697; diethyl, 1615, 1520, 1415, 1355, 1275, 1232, 1192, 1105, 967, 843, 798, and 719 cm.$^{-1}$.

N-Ethylaniline was added slowly to a cooled suspension of cyanuric chloride (18·5 g.) and sodium carbonate (10·6 g.) in aqueous acetone. Extraction with light petroleum gave 2,4-dichloro-6-*N*-ethylanilino-1,3,5-triazine (16·0 g., 60%), m. p. and mixed m. p. 116·5—117°, whose identity was confirmed by analysis and infrared spectroscopy.

p-*NN*-Diethylaminophenylmagnesium bromide [from *p*-bromo-*NN*-diethylaniline (11·4 g., 0·05 mole) and magnesium (1·3 g.)] in tetrahydrofuran (70 ml.) was added to a solution of cyanuric chloride (7·4 g., 0·04 mole) in tetrahydrofuran (50 ml.). The mixture was boiled for ½ hr. and, after removal of solvent, the benzene-soluble material was eluted with benzene on a silica gel chromatography column. Recrystallisation from light petroleum gave 2,4-dichloro-6-*p*-*NN*-diethylanilino-1,3,5-triazine (3·8 g., 30%), m. p. and mixed m. p. 157—157·5°, whose identity was confirmed as above.

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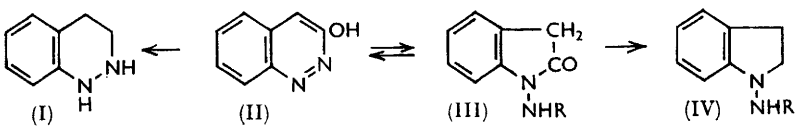
[1] Smolin and Rapoport, " *s*-Triazines and Derivatives," Interscience Publ. Inc., New York, 1959, Chapter 5.
[2] Saure, *Chem. Ber.*, 1950, **83**, 335.
[3] Kober, Schnabel, and Schroeder, Wright Air Development Division Technical Report, 1960, 60—315, p. 4.
[4] Thurston, Dudley, Kaiser, Hechenbleikner, Schaefer, and Holm-Hansen, *J. Amer. Chem. Soc.*, 1951, **73**, 2981.
[5] Burg and Caron, *J. Amer. Chem. Soc.*, 1959, **81**, 836.
[6] Fitzsimmons and Shaw, *Proc. Chem. Soc.*, 1961, 258.

288. 1,2,3,4-*Tetrahydrocinnoline and Related Compounds.*

By D. E. Ames and (Miss) H. Z. Kucharska.

It has been shown that reduction of cinnolines with various reagents generally yields indole derivatives but in some cases di- and tetra-hydrocinnolines can be isolated.[1] However, unsubstituted 1,2,3,4-tetrahydrocinnoline (I) has apparently not yet been described.

We have now found that reduction of 3-hydroxycinnoline (II), which can be regarded as the tautomeric form of an amide, with lithium aluminium hydride in 1,2-dimethoxyethane gives 1,2,3,4-tetrahydrocinnoline (I) which can readily be separated from the neutral products also formed. When 4-hydroxycinnoline was reduced similarly, hydrogenolysis also occurred, giving a mixture of cinnoline and 1,2,3,4-tetrahydrocinnoline, separated as the picrates. Reduction of 4-methoxycinnoline gave similar results, but 4-chlorocinnoline gave only 4,4'-bicinnolinyl (also formed on catalytic hydrogenation of 4-chlorocinnoline [2]).



Baumgarten, Creger, and Zey [3] have shown that 3-hydroxycinnoline (II) and *N*-amino-oxindole (III; R = H) are readily interconverted by oxidation–reduction methods. To confirm that no such rearrangement had occurred during treatment with lithium aluminium hydride, the reduction of *N*-amino-oxindole (III; R = H) was also examined. *N*-Aminoindoline (IV; R = H), thus obtained, was also prepared by reduction of *N*-nitrosoindoline with lithium aluminium hydride [4] or sodium dithionite. Similar reduction of *N*-acetamido-oxindole (III; R = Ac) gave *N*-ethylaminoindoline (IV; R = Et) together with some of the intermediate, *N*-ethylamino-oxindole (III; R = Et).

Experimental.—1,2,3,4-*Tetrahydrocinnoline* [with T. F. Grey]. 3-Hydroxycinnoline [5] (8 g.) was placed in a Soxhlet apparatus and reduced with lithium aluminium hydride (5 g.) in 1,2-dimethoxyethane (300 c.c.), refluxing for 3 hr. being required to extract the solid. Ether (300 c.c.) and 5N-sodium hydroxide (8 c.c.) were then added successively and the mixture was refluxed for 1 hr. The solid was collected and extracted repeatedly with ether, the combined filtrates being evaporated to dryness *in vacuo* (bath <40°). The residual oil was extracted from ethyl acetate repeatedly with 2N-hydrochloric acid; basification with 2N-sodium hydroxide and isolation with ethyl acetate gave 1,2,3,4-*tetrahydrocinnoline* (3·6 g.), b. p. 82—83°/0·2 mm., n_D^{20} 1·6095 (Found: C, 71·8; H, 7·3; N, 20·3. $C_8H_{10}N_2$ requires C, 71·6; H, 7·5; N, 20·9%), $\lambda_{max.}$ (in ethanol) 2810 Å (ε 1560). The *hydrochloride* formed prisms, m. p. 171—173°, from ether–2-methoxyethanol (Found: C, 55·7; H, 6·6; N, 16·2; Cl, 22·1. $C_8H_{10}N_2$,HCl requires C, 56·3; H, 6·5; N, 16·4; Cl, 20·8%). The *picrate*, prisms from ether–ethanol, had m. p. 121—122° (Found: C, 46·5; H, 3·9; N, 19·3. $C_{14}H_{13}N_5O_7$ requires C, 46·3; H, 3·6; N, 19·3%).

Reduction of 4-hydroxycinnoline. 2-Nitroacetophenone was conveniently prepared from *o*-nitrobenzoic acid in about 90% yield by Bowman's method [6] and converted into 4-hydroxycinnoline.[7] This (8 g.) was reduced with lithium aluminium hydride in the same manner as the 3-isomer. Distillation of the basic fraction gave 3·5 g. of material, b. p. 80—81°/0·2 mm. (Found: C, 72·2; H, 6·7; N, 18·8%). Fractional crystallisation of the picrates from ethanol–ether gave 1,2,3,4-tetrahydrocinnoline picrate, m. p. and mixed m. p. 122—123°, and cinnoline

[1] Reviewed by Jacobs in "Heterocyclic Compounds," Vol. VI, ed. Elderfield, Wiley, New York, 1957, p. 159.
[2] Morley, *J.*, 1951, 1971.
[3] Baumgarten, Creger, and Zey, *J. Amer. Chem. Soc.*, 1960, **82**, 3977.
[4] Cf. Hanna and Schueler, *J. Amer. Chem. Soc.*, 1952, **74**, 3693.
[5] Alford and Schofield, *J.*, 1952, 2105.
[6] Bowman, *J.*, 1950, 322.
[7] Keneford and Simpson, *J.*, 1947, 917.

picrate, m. p. 192—193°, undepressed by an authentic specimen.[8] The infrared spectrum of the basic fraction was similar to that of 1,2,3,4-tetrahydrocinnoline but showed additional max. at 1393, 1139, 1094, and 846 cm.$^{-1}$ which were also present in the spectrum of cinnoline.

4-Methoxycinnoline [9] (4 g.) in benzene (200 c.c.) was added to lithium aluminium hydride (3 g.) in ether (150 c.c.). After the mixture had been refluxed for 3 hr., it was worked up similarly. The basic fraction (1·6 g.), b. p. 76—77°/0·1 mm., had an absorption spectrum similar to that of the product from 4-hydroxycinnoline, also showing the bands due to cinnoline.

Reduction of 4-chlorocinnoline. 4-Chlorocinnoline [7] (7·6 g.) in ether (300 c.c.) was added to lithium aluminium hydride (5 g.) in ether (300 c.c.), and the mixture refluxed for 4 hr. After addition of 5N-sodium hydroxide solution (8 c.c.), the mixture was refluxed for 1 hr., then cooled and filtered, the solid being washed repeatedly with boiling ethyl acetate. Evaporation under reduced pressure and recrystallisation from 1,2-dimethoxyethane gave 4,4'-bicinnolinyl, m. p. 232—234° undepressed by admixture with an authentic sample [2] (Found: C, 74·0; H, 4·0; N, 22·1. Calc. for $C_{16}H_{10}N_4$: C, 74·4; H, 3·9; N, 21·7%), $\lambda_{max.}$ (in ethanol) 2350, 3000, and 3300 Å (ε 18,800, 15,700, and 18,800).

1-*Aminoindoline.*—1-Amino-oxindole [3] (8 g.) in benzene (250 c.c.) was added gradually to lithium aluminium hydride (5 g.) in ether (300 c.c.). The mixture was refluxed for 2 hr. and worked up as in the previous examples; distillation of the basic fraction gave 1-*aminoindoline* (4·1 g.), b. p. 62—64°/0·1 mm., n_D^{20} 1·5972 (Found: C, 72·0; H, 7·6; N, 20·2. $C_8H_{10}N_2$ requires C, 71·6; H, 7·5; N, 20·9%). The *picrate*, m. p. 150—151°, crystallised from benzene–ethanol (Found: C, 46·6; H, 3·6; N, 19·2. $C_{14}H_{13}N_5O_7$ requires C, 46·3; H, 3·6; N, 19·2%); the *hydrochloride* formed needles, m. p. 183—184°, from ether–ethanol (Found: C, 56·7; H, 6·5; N, 16·3; Cl, 20·1. $C_8H_{10}N_2$,HCl requires C, 56·3; H, 6·5; N, 16·4; Cl, 20·8%); 1-*acetamidoindoline*, prepared by treatment with pyridine–acetic anhydride overnight, crystallised from aqueous methanol and had m. p. 126—127° (Found: C, 68·8; H, 6·7; N, 15·4. $C_{10}H_{12}N_2O$ requires C, 68·2; H, 6·9; N, 15·9%).

Reduction of 1-nitrosoindoline in the same way also gave 1-aminoindoline (infrared spectrum identical with that of the previous sample; the picrate had m. p. and mixed m. p. 150—151°).

Reduction of 1-acetamido-oxindole. 1-Acetamido-oxindole [3] (8 g.) in 1,2-dimethoxyethane (250 c.c.) was added gradually to lithium aluminium (5 g.) in ether (500 c.c.) and the mixture was refluxed for 3·5 hr. The basic fraction, isolated in the manner described, was distilled, giving 1-*ethylaminoindoline* (1·3 g.), b. p. 73—74°/0·1 mm. (Found: C, 73·7; H, 8·3; N, 17·5. $C_{10}H_{14}N_2$ requires C, 74·0; H, 8·7; N, 17·3%). The *hydrochloride* formed prisms, m. p. 160—162°, from ether–ethanol (Found: C, 61·0; H, 7·4; N, 14·3. $C_{10}H_{14}N_2$,HCl requires C, 60·4; H, 7·6; N, 14·1%). Distillation of the neutral fraction gave 1-*ethylamino-oxindole* (1·2 g.), b. p. 124—128°/0·1 mm. (Found: C, 68·5; H, 7·1; N, 15·8. $C_{12}H_{10}N_2O$ requires C, 68·2; H, 6·9; N, 15·9%), $\nu_{max.}$ 1698 and 1621 cm.$^{-1}$ (1-amino-oxindole: 1695, 1645, and 1613 cm.$^{-1}$).

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[8] Alford and Schofield, *J.*, 1953, 609.
[9] Schofield and Simpson, *J.*, 1945, 512.

289. *The Reaction of Dimethyl Acetylenedicarboxylate with 1-Methylimidazoles.*

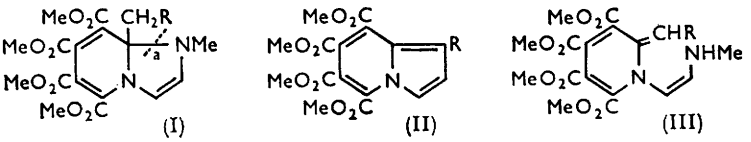
By A. CRABTREE and A. W. JOHNSON.

IN 1932, Diels, Alder, *et al.*[1] studied the addition of dimethyl acetylenedicarboxylate to various imidazoles and in the case of 1,2-dimethylimidazole they identified the product as having structure (I; R = H), formed by a reaction somewhat related to that observed with pyridine.[1,2] With acetic acid the adduct underwent rearrangement to the indolizine (II; R = H) with elimination of methylamine. In a recent re-investigation of the

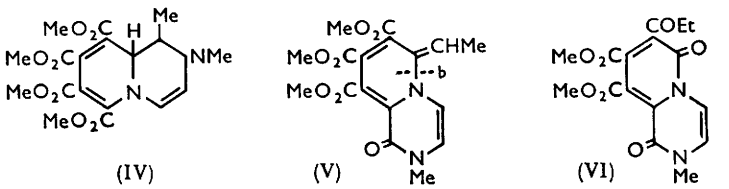
[1] Diels, Alder, Winkler, and Peterson, *Annalen*, 1932, **498**, 1.
[2] Jackman, Johnson, and Tebby, *J.*, 1960, 1579; Acheson and Taylor, *J.*, 1960, 1691.

reaction [3] it is stated that the structures (I; R = H) and (II; R = H) are in accord with the observed absorption spectra.

The rearrangement of the initial adduct (I; R = H), a substituted methylenediamine, probably involves ring fission at bond a of the five-membered ring to give an intermediate (III; R = H) which then cyclises with elimination of methylamine.



In an endeavour to provide a further example of this rearrangement, the preparation of the adduct (I; R = Me), $C_{18}H_{22}N_2O_8$, from dimethyl acetylenedicarboxylate with 2-ethyl-1-methylimidazole has been investigated. Rearrangement of it with acetic acid gave two crystalline products, both containing the two original nitrogen atoms, and only a small quantity of methylamine was obtained. The first of the rearranged compounds, also $C_{18}H_{22}N_2O_8$, was red and is formulated as (IV). It is formed in a manner similar to that suggested for the formation of (II), except that the amino-group of (III; R = Me) is now involved in the cyclisation. The second product, $C_{17}H_{18}N_2O_7$, formed chocolate-brown needles. Its genesis again involves ring fission of (I) in the manner cited, but the secondary reaction is a cyclisation of the ester group adjacent to the cyclic nitrogen atom, with the *N'*-methylvinylamine side chain to yield an *N*-methyl-lactam. The product (V) was rather unstable and, like (IV), it rearranged on treatment with hot dilute hydrochloric



acid to give the hydrochloride of a fluorescent yellow base, $C_{16}H_{16}N_2O_7$. This product is ketonic (positive Zimmermann test; [4] oxime) and is formulated as the oxo-diamide (VI) which is formed from (V) by fission of the bond b, hydration of the terminal double bond to a propionyl group, and condensation of the appropriate ester group with the cyclic nitrogen atom to yield a second lactam.

The basic nature of this product (VI) is attributed partly to the possibility of aromatisation as the lactim form and partly to the cumulative inductive effect of the *N*-alkyl substituents in the bistertiary amide system. None of the indolizine (II; R = Me) was observed in the rearrangement products of compound (I; R = Me), which emphasises the remarkable effect on the course of the reaction caused by the substitution of a 2-ethyl for the 2-methyl group in the parent imidazole. No adduct from dimethyl acetylenedicarboxylate and either 2-benzyl- or 2-phenyl-imidazole was obtained in the pure state.

Experimental.—Ultraviolet and visible absorption spectra were determined for ethanolic solutions, and infrared spectra on potassium bromide discs.

2-Ethyl-1-methylimidazole. Dimethyl sulphate (8 c.c.) was added dropwise to 2-ethylimidazole [5] (6·7 g.), cooled in ice. The mixture was then warmed for 10 min. on the steam-bath and set aside for 1 hr. After addition of 10% aqueous sodium hydroxide (50 c.c.) the mixture was extracted with chloroform, and after removal of the solvent from the extract the residual 2-ethyl-1-methylimidazole (2·4 g.), b. p. 210—215°, was distilled. The *picrate* formed yellow plates, m. p. 139°, from methanol (Found: C, 42·8; H, 4·35; N, 20·7. $C_{12}H_{13}N_5O_7$ requires C, 42·5; H, 3·85; N, 20·65%).

[3] Acheson and Taylor, *J.*, 1960, 4600.
[4] Neunhöffer, Thenalt, and Zimmermann, *Z. physiol. Chem.*, 1961, **323**, 116.
[5] Radziszewski, *Ber.*, 1883, **16**, 490.

Adduct of dimethyl acetylenedicarboxylate and 2-ethyl-1-methylimidazole (I; R = Me). Dimethyl acetylenedicarboxylate (3 g.) in ether (25 c.c.) was added to 2-ethyl-1-methylimidazole (1 g.) in ether (25 c.c.). The mixture was kept at room temperature for 1 hr., after which the precipitated *tetraethyl* 8a-*ethyl*-1,8a-*dihydro*-1-*methylimidazo*[1,2-a]*pyridine*-5,6,7,8-*tetracarboxylate* (I; R = Me) (1·5 g.) was separated and crystallised from methanol, forming red needles, m. p. 157—158° (Found: C, 54·9; H, 5·8; N, 7·1; OMe, 30·5. $C_{18}H_{22}N_2O_8$ requires C, 54·8; H, 5·6; N, 7·1; 4OMe, 31·4%), $\lambda_{max.}$ 221, 259, 299, and 465 mμ (log ε 4·01, 3·99, 4·03, and 3·69, respectively), $\nu_{max.}$ (C=O) 1683, 1689, 1707, 1740, and 1753 cm.$^{-1}$.

Rearrangement of the adduct by acetic acid. The foregoing product (2·4 g.) was heated on the steam-bath in acetic acid for 30 min. After cooling, the solution was poured into ether (150 c.c.) and kept at 0° overnight. The precipitated solid (1·5 g.) was separated and the ethereal solution evaporated. The residue from the evaporation was dissolved in water (50 c.c.), made alkaline by the addition of aqueous sodium hydroxide, and subjected to steam-distillation. The distillate (50 c.c.) was added to saturated aqueous picric acid (30 c.c.), and evaporation of this solution gave a small quantity of methylamine picrate as yellow plates, m. p. and mixed m. p. 213—214° (lit., 215°), from ethyl acetate.

The solid precipitate (1·5 g.) crystallised from methanol (100 c.c.) as chocolate-brown needles of *trimethyl* 6-*ethylidene*-1,6-*dihydro*-2-*methyl*-1-*oxo*-1H-*pyrido*[1,2-a]*pyrazine*-7,8,9-*tricarboxylate* (V) (0·4 g.), m. p. 212—214° (Found: N, 7·6; OMe, 25·7. $C_{17}H_{18}N_2O_7$ requires N, 7·7; 3OMe, 25·8%), $\lambda_{max.}$ 273, 331, and 504 mμ (log ε 4·06, 3·97, and 3·75, respectively), $\nu_{max.}$ (C=O) 1678, 1721, and 1748 cm.$^{-1}$. Evaporation of the methanolic mother-liquors gave *tetramethyl* 2,9a-*dihydro*-1,2-*dimethyl*-1H-*pyrido*[1,2-a]*pyrazine*-6,7,8,9-*tetracarboxylate* (IV) (0·25 g.) as red rods, m. p. 206° (from methanol) (Found: C, 54·4; H, 5·35; N, 6·85; OMe, 31·0. $C_{18}H_{22}N_2O_8$ requires C, 54·8; H, 5·35; N, 7·1; 4OMe, 31·4%), $\lambda_{max.}$ 234, 313, and 467 mμ (log ε 3·90, 3·87, and 4·00, respectively), $\nu_{max.}$ 1661 (probably C=C), 1717, and 1746 cm.$^{-1}$.

Formation of the diamide (VI). (i) The above brown product (V) (0·6 g.) was heated on the steam-bath for 10 min. in 3N-hydrochloric acid (20 c.c.). The solution was cooled and evaporated to dryness *in vacuo*, and the residue (0·3 g.) triturated with acetone. After the addition of a little ether the yellow hydrochloride was separated. An aqueous solution of the hydrochloride (0·1 g. in 5 c.c.) was neutralised with solid sodium carbonate; the fluorescent yellow solid so obtained crystallised from 50% aqueous methanol as yellow needles, m. p. 173°, of *dimethyl* 1,6-*dihydro*-2-*methyl*-6-*oxo*-7-*propionyl*-2H-*pyrido*[1,2-a]*pyrazine*-8,9-*dicarboxylate* (VI) (Found: C, 54·7; H, 4·3; N, 7·8; OMe, 17·8. $C_{16}H_{16}N_2O_7$ requires C, 55·15; H, 4·6; N, 8·0; 2OMe, 17·85%), $\lambda_{max.}$ 246, 304, and 430 mμ (log ε, 3·84, 4·00, and 4·09, respectively), $\nu_{max.}$ (C=O) 1687, 1698, 1701, 1718, 1722, 1733, and 1751 cm.$^{-1}$. The product gave a positive Zimmermann test [4] and the *oxime* formed yellow needles, m. p. 255—257° (from methanol) (Found: C, 53·2; H, 4·85. $C_{16}H_{17}N_3O_7$ requires C, 52·9; H, 4·7%).

(ii) The rearrangement product (IV) (30 mg.) in water (2 c.c.) containing 3 drops of concentrated hydrochloric acid was heated gently for a few minutes until the solid had dissolved. The solution was then cooled and neutralised with sodium hydrogen carbonate. The precipitated yellow solid (20 mg.) crystallised from 50% aqueous methanol; it then had m. p. 161—167°, raised to 169—171° after sublimation at 160°/0·05 mm., and not depressed on admixture with the product from the previous experiment. The infrared spectra of the two products were superimposable.

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290. *The Structure of Cæsium Tungstoferrate.*

By D. H. Brown and J. A. Mair.

In a previous paper,[1] on the basis of analytical evidence, tungstoferric acid was described as an 11-acid although the analytical results were not conclusive, the ratio $\frac{1}{2}Fe_2O_3 : WO_3$ varying from 1 : 11 to 1 : 12. The assumption was made that the most likely impurity was metatungstic acid, and this would account for the slightly high tungsten content. However, *X*-ray powder photography has since shown that tungstoferric acid is probably a 1 : 12 acid. Photographs were taken with the specimen mounted in a fine Lindemann-glass tube and Cu-K_α radiation. The structure was found to be cubic with a unit-cell

[1] Mair, *J.*, 1950, 2364.

Lines and intensities for cæsium 12-tungstoferrate, tungstozincate, and tungstophosphate

$h^2+k^2+l^2$	Calc.	Ferrate Obs.	Zincate Obs.	Phosphate Obs.	$h^2+k^2+l^2$	Calc.	Ferrate Obs.	Zincate Obs.	Phosphate Obs.
6	13·7	15	15	15	38	92·1	90	90	90
8	5·8	5	5	5	40	2·1	Absent	Absent	Absent
10	25·7	25	25	26	41	28·9	25	30	25
12	150·0	150	150	150	42	47·5	45	45	45
14	0·9	Absent	Absent	Absent	44	78·9	80	80	80
16	79·9	75	78	80	46	2·7	Absent	Absent	Absent
18	17·6	17	17	17	48	29·5	30	30	30
20	0·2	Absent	Absent	Absent	50	206·3	210	200	200
22	94·5	90	90	95	52	35·8	35	35	35
24	11·8	10	10	10	54	37·6	40	40	40
26	79·7	80	80	80	56	1·5	Absent	Absent	Absent
27	8·8	10	10	10	58	26·4	25	25	30
30	46·7	50	45	50	62	222·3	230	230	230
32	86·7	90	85	90	64	2·7	Absent	Absent	Absent
33	10·2	10	10	10	65	1·9	Absent	Absent	Absent
34	9·1	10	10	10	66	130·6	130	130	130
36	15·1	15	15	15	68	20·4	20	20	20

length of 11·88 Å, very close to those of cæsium 12-tungstophosphate [2] (11·83 Å), 12-tungstosilicate (11·78 Å), and 12-tungstozincate [3] (11·86 Å). The intensities agreed with those calculated from a structure similar to that proposed for cæsium 12-tungstophosphate,[2] but with ferric iron as the central ion. Comparison photographs of the four cæsium salts appeared identical (lines and intensities, measured visually, are given in the Table).

These results suggest that the structure and hence the formula, of cæsium tungstoferrate and 12-tungstozincate are similar, with ferric ion replacing the central zinc ion. The slightly low tungsten analysis could have been due to some hydrolysis of the 12-tungstoferrate ion on recrystallisation, giving traces of the relatively insoluble ferric paratungstate. The fact that it is a 12-acid and not an 11-acid accounts for the chemical stability described in the previous paper.[1]

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GLASGOW, C.1.

[*Received, November 6th*, 1961.]

[2] Santos, *Proc. Roy. Soc.*, 1935, *A*, **150**, 309.
[3] Brown and Mair, *J.*, 1958, 2597.

291. *The Thermodynamic Functions of Carbon Tetraiodide.*

By J. H. S. GREEN and (MISS) D. J. HOLDEN.

THE vibrational frequencies of carbon tetraiodide have been recently measured [1] and the fundamental frequencies assigned. The results are in accord with the tetrahedral structure confirmed by earlier electron-diffraction studies.[2] Sufficient data are therefore available for calculation of spectroscopic thermodynamic functions (compare previous work on the other iodomethanes [3]). The C–I bond length was taken as 2·135 Å, whence the product of the three equal moments of inertia is $1{\cdot}681 \times 10^{-110}$ g.^{3} cm.^{6}. The vibrational contributions were evaluated with the aid of tables [4] using the frequencies (cm.$^{-1}$): 90(2), 123(2), 178(1), 555(3). Fundamental constants were the same as those used previously.[5] The resulting values of the free energy function $(G°-H_0°)/T$, heat content function $(H°-H_0°)/T$, entropy $(S°)$ and heat capacity $(C_p°)$ are tabulated; all relate to one mole of the molecule in the ideal gas state.

[1] Stammreich, Taveres, and Bassi, *Spectrochim. Acta*, 1961, **17**, 661.
[2] Finbak and Hassel, *Z. phys. Chem.*, 1937, *B*, **36**, 301; Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 393.
[3] Gelles and Pitzer, *J. Amer. Chem. Soc.*, 1953, **75**, 5259.
[4] Johnston, Savedoff, and Belzer, "Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D.C., 1949.
[5] Green, *J.*, 1961, 2236.

T (K)	$-(G° - H_0°)/T$ (cal./deg.)	$(H° - H_0°)/T$ (cal./deg.)	$S°$ (cal./deg.)	$C_p°$ (cal./deg.)
273·16	74·17	17·48	91·65	22·51
298·16	75·68	17·92	93·60	22·91
300	75·79	17·95	93·74	22·94
400	81·16	19·34	100·50	24·00
500	85·59	20·34	105·93	24·59
600	89·36	21·20	110·56	24·94
700	92·65	21·65	114·30	25·16
800	95·58	22·10	117·68	25·31
900	98·19	22·46	120·65	25·41
1000	100·60	22·76	123·36	25·50

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292. *Heterocyclic Compounds of Nitrogen. Part IV.*[1] *A Synthesis of 3-Iodo-2-o-iodophenylindole.*

By J. MALCOLM BRUCE.

TREATMENT of *o*-iodoacetophenone phenylhydrazone with polyphosphoric acid[2] or, preferably, anhydrous zinc chloride afforded 2-*o*-iodophenylindole, from which the 3-iodo-derivative was obtained by reaction with iodine monochloride under conditions similar to those used by Terent'ev *et al.*[3] for the iodination of indole. The absorption spectra of these indoles are consistent with the assigned structures.

When heated with old samples of cuprous oxide, 3-iodo-2-*o*-iodophenylindole afforded 2-*o*-iodophenylindole; reactions with freshly prepared cuprous oxide[4] yielded 2-phenylindole. A cyclobutadiene derivative[5] was not detected.

Experimental.—Phenylhydrazine, iodine monochloride, and solvents were freshly distilled. Dioxan was distilled from sodium, and pyridine from solid potassium hydroxide. Light petroleum had b. p. 60—80°. Peter Spence's grade "H" alumina was used. Solutions in organic solvents were dried with sodium sulphate. Solvents were removed on the water-bath, where necessary under reduced pressure (water-pump). Sublimation and bulb-to-bulb distillation temperatures are those of the heating-bath. Ultraviolet absorption spectra were measured for solutions in purified[6] dioxan in a Perkin-Elmer model 4000 recording spectrophotometer. M. p.s are corrected.

o-Iodoacetophenone. Reaction[7] of *o*-iodobenzoyl chloride[8] (53 g.) with diethyl ethoxymagnesiomalonate, and hydrolysis[7] of the product afforded *o*-iodoacetophenone (41 g., 84%), b. p. 85—86°/0·05 mm. The 2,4-*dinitrophenylhydrazone*, orange hexagonal plates from butan-1-ol, had m. p. 187·5° (Found: C, 39·5; H, 2·8; I, 29·9; N, 13·3. $C_{14}H_{11}IN_4O_4$ requires C, 39·5; H, 2·6; I, 29·8; N, 13·1%). The *semicarbazone*, hexagonal plates from ethanol, had m. p. 181—181·5° (Found: C, 35·8; H, 3·7; I, 41·5; N, 13·8. $C_9H_{10}IN_3O$ requires C, 35·7; H, 3·3; I, 41·9; N, 13·9%). *o*-Iodoacetophenone prepared[9] from *o*-aminoacetophenone[10] afforded identical (m. p. and mixed m. p.) derivatives.

2-o-*Iodophenylindole.* (*a*) *o*-Iodoacetophenone (1·23 g.), phenylhydrazine (0·54 g.), and polyphosphoric acid, from phosphoric acid (1·5 g.; 88—90% H_3PO_4) and phosphoric oxide (1 g.), were stirred at 110°. After the exothermic reaction had subsided, the temperature was raised to 150°, another exothermic reaction then occurring. The mixture was heated at 180° for 2 min., cooled, and diluted with water (12 c.c.). The suspension was extracted with ether, and the extract was washed with water and dried. Removal of the solvent and distillation (bulb-to-bulb; 150°/0·01 mm., then 200°/0·01 mm.) of the residue afforded *o*-iodoacetophenone

[1] Part III, Bruce, *J.*, 1960, 360.
[2] Kissman, Farnsworth, and Witkop, *J. Amer. Chem. Soc.*, 1952, **74**, 3948.
[3] Terent'ev, Belenk'kiĭ, and Yanovskaya, *Zhur. obshchei Khim.*, 1954, **24**, 1265 (*Chem. Abs.*, 1955, **49**, 12,327d).
[4] Cf. Cava and Stucker, *J. Amer. Chem. Soc.*, 1955, **77**, 6022.
[5] Cf. Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187; Baker, Boarland, and McOmie, *J.*, 1954, 1476.
[6] Vogel, "A Text-Book of Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p. 175.
[7] Cf. Walker and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 1386.
[8] Cohen and Raper, *J.*, 1904, **85**, 1271.
[9] von Auwers, Lechner, and Bundesmann, *Ber.*, 1925, **58**, 36.
[10] Bruce, *J.*, 1959, 2366.

(0·12 g.), and the *indole* (0·43 g., 27%) as an orange-yellow viscous oil which gave a deep wine-red colour with Ehrlich's reagent (Found: C, 52·7; H, 3·3; I, 39·6; N, 4·5. $C_{14}H_{10}IN$ requires C, 52·7; H, 3·2; I, 39·8; N, 4·4%), ν (N–H) (in CS_2) 3475 cm.$^{-1}$, $\lambda_{max.}$ 221, 299 mμ (log ε 4·60, 4·10), $\lambda_{min.}$ 266 mμ (log ε 3·80). The 1,3,5-*trinitrobenzene adduct*, deep red needles from benzene–light petroleum, had m. p. 115·5—116° (Found: C, 45·4; H, 2·5; I, 22·9; N, 10·8. $C_{14}H_{10}IN,C_6H_3N_3O_6$ requires C, 45·1; H, 2·5; I, 23·8; N, 10·5%).

(*b*) *o*-Iodoacetophenone (4·82 g.) and phenylhydrazine (2·16 g.) were heated together at 150° for 30 min. and then at 100°/30 mm. for 30 min. Powdered anhydrous zinc chloride (30 g.) was added, and the mixture was stirred at 180° for 15 min., cooled, and digested on the boiling-water bath with 2% hydrochloric acid (50 c.c.) until no further material dissolved. The suspension was cooled, the aqueous phase was removed, and the residue extracted with benzene. The benzene extract was washed with 2% hydrochloric acid, then with water, and dried. After being concentrated to 25 c.c. the solution was chromatographed on alumina (115 × 22 mm.), and the column was eluted with benzene until it was no longer yellow. Removal of the solvent from the eluate and distillation (bulb-to-bulb; 140°/0·01 mm., then 185°/0·008 mm.) of the residue afforded *o*-iodoacetophenone (0·65 g.), and 2-*o*-iodophenylindole (3·61 g., 57%), identical (ultraviolet absorption spectrum, m. p. and mixed m. p. of the 1,3,5-trinitrobenzene adduct) with that prepared by method (*a*).

3-*Iodo*-2-*o*-*iodophenylindole*. As far as possible operations were carried out with exclusion of light. 2-*o*-Iodophenylindole (3·61 g.) in pyridine (15 c.c.) at 0° was treated during 15 min. with iodine monochloride (1·93 g.) in dioxan (15 c.c.) and kept at 0° for 60 hr. Most of the solvent was then removed at 25 mm. (warm-water bath), the residue was diluted with water (25 c.c.) and extracted with ether, and the extract was washed with water, dried, and evaporated. The residue, in benzene (10 c.c.), was chromatographed on alumina (100 × 22 mm.), the column being eluted with benzene until the eluate (80 c.c.) was almost colourless. Removal of the solvent and crystallisation of the residue from cyclohexane (30 c.c.) afforded the *indole* (3·84 g., 76%) as pale fawn prisms, m. p. 124·5—125°. A colourless sample, m. p. 127°, was obtained by sublimation at 125°/0·005 mm., and recrystallisation of the sublimate from cyclohexane (Found: C, 37·7; H, 1·9; I, 56·6; N, 3·3. $C_{14}H_9I_2N$ requires C, 37·8; H, 2·0; I, 57·0; N, 3·2%). It had ν (N–H) (in CS_2): 3460 cm.$^{-1}$, $\lambda_{max.}$ 225, 287 (infl.), 291 mμ (log ε 4·65, 4·00, 4·01), $\lambda_{min.}$ 260 mμ (log ε 3·82). Ehrlich's test was negative. The indole lost iodine above its m. p., and its solution in benzene became yellow when exposed to light. The 1,3,5-*trinitrobenzene adduct*, orange-red laths from benzene–light petroleum, had m. p. 141° (Found: C, 36·4; H, 1·5; I, 38·1; N, 8·0. $C_{14}H_9I_2N,C_6H_3N_3O_6$ requires C, 36·5; H, 1·8; I, 38·6; N, 8·5%).

Reactions with cuprous oxide. (*a*) 3-Iodo-2-*o*-iodophenylindole (1 g.) and cuprous oxide (7·5 g.; from Messrs. Hopkin and Williams Ltd.) were intimately mixed and placed in a 25 mm. diameter test-tube, covered with cuprous oxide (5 g.) followed by a plug of glass wool, and degassed at 100°/20 mm., and then at 100°/0·01 mm. A water-cooled cold-finger was placed above the glass wool, the pressure was again reduced to 0·01 mm., and the tube was immersed in a metal-bath preheated to 350°. The bath was then kept at 340—350° for 30 min., and the pressure above the reaction mixture was held at 0·01 mm. The gum (21 mg.) which collected on the cold-finger was removed and distilled (bulb-to-bulb; 140°/0·01 mm.) to give an orange oil (17 mg., 2·4%) identical (ultraviolet absorption spectrum, m. p. and mixed m. p. of the 1,3,5-trinitrobenzene adduct) with 2-*o*-iodophenylindole. Similar results were obtained with other commercial samples of cuprous oxide.

(*b*) Experiment (*a*) was repeated, with cuprous oxide prepared [11] by reduction of cupric acetate with hydrazine. The white solid (5 mg.) which collected on the cold-finger was triturated with cold light petroleum (1 c.c.), and sublimed at 160°/0·01 mm. Crystallisation of the sublimate from light petroleum afforded 2-phenylindole as plates (3 mg., 0·7%), m. p. 189·5—190°, identical (ultraviolet absorption spectrum,[1] and mixed m. p.) with authentic material.

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[11] Brauer, "Handbuch der präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p. 755.

293. 4-*Chloromethylstyrene*.

By C. L. ARCUS and N. S. SALOMONS.

As part of a study of polymer reactivity,[1] we are investigating the kinetics of replacements in poly-(4-chloromethylstyrene).

[1] Arcus and Halliwell, *J.*, 1961, 3708.

Direct chloromethylation of styrene yields the β-chloromethyl compound, as shown by its conversion by the Sommelet reaction into cinnamaldehyde.[2] The following route to chloromethylstyrene is described in a patent:[3] ethylbenzene is chloromethylated, and the product subjected to bromination in the ethyl group; the bromoethylchloromethylbenzene is then dehydrobrominated. In the chloromethylation of ethylbenzene, Freeman[4] found the isomers to be formed in the following proportions: *p*- 69·2, *o*- 29·0, *m*- 1·9%; hence the isolation of 4-chloromethylstyrene is dependent on the effectiveness of fractionation at some stage in the above reaction sequence. We required an unequivocally *para*-isomer, and this has been prepared as follows.

p-Chloromethylbenzaldehyde was obtained by the known route from *p*-tolunitrile. Reaction with methylmagnesium bromide gave 4-chloromethyl-α-methylbenzyl alcohol which on dehydration with potassium hydrogen sulphate yielded 4-chloromethylstyrene. Polymers and a copolymer with styrene have been prepared.

Experimental.—*p*-Tolunitrile[5] was converted by Barkenbus and Holtzclaw's method[6] into 4-cyanobenzyl chloride. This compound (m. p. 79·5—80·5°; 50 g.) was subjected to the Stephen reaction; the procedure of Baker and his co-workers[7] was followed except that hot water was replaced by cold in the decomposition of the aldimine stannichloride; the latter was suspended by vigorous stirring in ether (750 ml.), and water (750 ml.) was added dropwise. After 20 min. decomposition was complete. The ethereal layer was repeatedly washed with 5% aqueous sodium carbonate, then with water, and dried (Na_2SO_4); concentration yielded *p*-chloromethylbenzaldehyde which, recrystallised from ether, had m. p. 70—71° (24 g.).

Methylmagnesium bromide was prepared from magnesium (8 g.), methyl bromide (54 g.), and ether (320 ml.); the solution was decanted and cooled in ice–salt. *p*-Chloromethylbenzaldehyde (40 g.) in ether (550 ml.) was slowly added with stirring; after a further ½ hr., the whole was poured into iced saturated ammonium chloride solution. The ethereal layer, washed with water until neutral and dried (Na_2SO_4), yielded *4-chloromethyl-α-methylbenzyl alcohol* (22 g.), b. p. 125·5°/3 mm., n_D^{25} 1·5510 (Found: C, 63·2; H, 6·2; Cl, 21·0. $C_9H_{11}ClO$ requires C, 63·35; H, 6·5; Cl, 20·75%).

This alcohol (12·7 g.), fused potassium hydrogen sulphate (0·13 g.), and t-butylcatechol (0·13 g.) were heated at 45 mm. in an oil-bath; the temperature was raised to 210° in 30 min., and so kept for 45 min.; finally the pressure was reduced to 30 mm. The combined distillate from three such dehydrations was dried (Na_2SO_4) and redistilled after the addition of 1% of t-butylcatechol; it gave *4-chloromethylstyrene* (20·7 g.), b. p. 77·5—79°/2 mm., n_D^{25} 1·5725 (Found: C, 70·9; H, 5·85; Cl, 23·5. C_9H_9Cl requires C, 70·85; H, 5·95; Cl, 23·25%).

The monomer (6·39 g.) containing αα′-azoisobutyronitrile (0·064 g.) was heated under nitrogen at 72° for 112 hr. The resultant polymer, dissolved in benzene (55 ml.), was added to rapidly stirred light petroleum (b. p. 40—60°, 550 ml.). The precipitate was collected, washed with light petroleum, and dried. *Poly-(4-chloromethylstyrene)* (2·8 g.), a white powder, had $[\eta]_c$ 0·157 (Found: C, 70·85; H, 5·75; Cl, 23·0%). The monomer (9·60 g.) with αα′-azoisobutyronitrile (0·050 g.) similarly gave polymer (4·9 g.) having $[\eta]_c$ 0·255 (Found: C, 70·6; H, 5·85; Cl, 23·05%). Styrene (7·46 g.) and 4-chloromethylstyrene (5·50 g.; ratio of monomers 1·99 : 1) with αα′-azoisobutyronitrile (0·080 g.) similarly yielded the *copolymer* (7·2 g.), which had $[\eta]_c$ 0·290 (Found: C, 82·3; H, 6·95; Cl, 10·35. Styrene and 4-chloromethylstyrene copolymerised in ratio 1·76 : 1 require C, 82·55; H, 6·95; Cl, 10·55%).

The intrinsic viscosity, $[\eta]_c = (1/c)\ln(\eta_{soln.}/\eta_{solv.})$ (c = g. of solute in 100 ml. of solution), was determined for the polymer or copolymer in solution in toluene at 24·9° and c 1·0.

We thank the Department of Scientific and Industrial Research for a research studentship (to N. S. S.) and Imperial Chemical Industries Limited for aid from a grant.

Battersea College of Technology, London, S.W.11. [*Received, November 7th,* 1961.]

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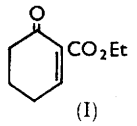
[4] Freeman, *J. Org. Chem.*, 1961, **26**, 212.
[5] *Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 514.
[6] Barkenbus and Holtzclaw, *J. Amer. Chem. Soc.*, 1925, **47**, 2189.
[7] Baker, Brieux, and Saunders, *J.*, 1956, 404.

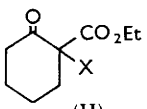
294. *Ethyl 6-Oxocyclohex-1-enecarboxylate.*

By C. W. T. Hussey and A. R. Pinder.

Our interest in the compound (I) named in the title arose because it is a possible intermediate in a synthesis of 2-acetylcyclohex-2-enone.[1] We therefore investigated the halogenation and dehydrohalogenation of ethyl 2-oxocyclohexanecarboxylate (II; X = H), steps which have been reported by Kötz and his co-workers,[2] Ruhkopf,[3] and Mousseron and his co-workers [4] to lead to the ester (I). We have found that in fact this chlorination and dehydrochlorination, or the bromination and dehydrobromination, yield several products, which do not include the desired ester (I). After our studies had been completed (April, 1960), a paper by Brenner [5] appeared, in which most of our experimental work is described. Our results and conclusions are in complete agreement with Dr. Brenner's, and we endorse his correction of some long-standing inaccuracies in the literature. We report here briefly some additional observations.

Ethyl 2-oxocyclohexanecarboxylate with *N*-bromosuccinimide yielded exclusively the 1-bromo-derivative (II; X = Br), which was not enolic but became so when kept, distilled, or treated with hydrogen bromide. This behaviour is consistent with partial rearrangement to the 3-bromo-ester (III) [6] (cf. the rearrangement of ethyl α-bromoacetoacetate to the γ-isomer [7]). Dehydrobromination of the first product (II; X = Br) with aniline in ether (cf. Kötz [2]), or with collidine, gave the saturated ester (II; X = H) and ethyl salicylate only, probably by disproportionation of the intermediate, desired product (I).[5]


(I)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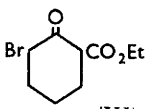
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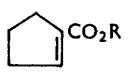
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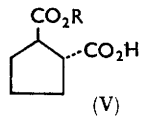
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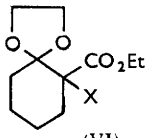
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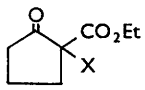
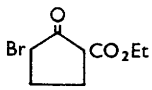
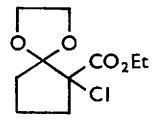
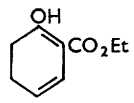

(VII)


(VIII)


(IX)


(X)

The chloro-analogue (II; X = Cl) behaved similarly on dehydrochlorination by collidine, but with potassium acetate it gave ethyl cyclopent-1-enecarboxylate (IV; R = Et), the corresponding acid, *trans*-cyclopentane-1,2-dicarboxylic acid (V; R = H), and the corresponding monoethyl ester (V; R = Et), all the result of a Favorski reaction, and a product formulated as ethyl 1-acetoxy-2-oxocyclohexanecarboxylate (II; X = OAc), on analytical and spectral evidence.

The ethylene ketal (VI; X = Cl) was prepared; it proved resistant to the action of base. Attempts to make the corresponding bromo-ketal (VI; X = Br) failed because of the ease of rearrangement of the bromo-ester (II; X = Br).

In the cyclopentane series the analogues (VII; X = Cl and Br) were obtained by similar methods. Neither was enolic, but the latter was readily transformed into the enolic isomer of (VIII) under the conditions specified for the higher homologue; both yielded ethyl 2-oxocyclopentanecarboxylate (VII; X = H) when heated with collidine. The ketal (IX) resembles its analogue (VI; X = Cl) in its resistance to dehydrochlorination.

The pronounced enolic properties of the synthetic ester (I) [5] show that it resembles our so-called 2-acetylcyclohex-2-enone [1] and 2-acetylcyclohept-2-enone,[8] and it would seem more satisfactory to formulate it as (X), stabilisation of the labile cross-conjugated system having been effected by enolisation.

[1] McEntee and Pinder, *J.*, 1957, 4419.
[2] Kötz, *Annalen*, 1908, **358**, 183; Kötz and Grethe, *J. prakt. Chem.*, 1909, **80**, 473.
[3] Ruhkopf, *Ber.*, 1939, **72**, 1978.
[4] Mousseron, Jacquier, Fontaine, and Zagdoun, *Bull. Soc. chim. France*, 1954, 1246.
[5] Brenner, *J. Org. Chem.*, 1961, **26**, 22.
[6] Sheehan and Mumaw, *J. Amer. Chem. Soc.*, 1950, **72**, 2127.
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[8] Hussey and Pinder, *J.*, 1961, 3525.

Experimental.—Ethyl 1-*bromo*-2-*oxocyclohexanecarboxylate* (II; X = Br). Ethyl 2-oxocyclohexanecarboxylate (8·5 g., 0·05 mole), *N*-bromosuccinimide (9·34 g., 0·06 mole), and carbon tetrachloride (40 c.c.) were refluxed for 30 min., cooled, filtered, and concentrated *in vacuo*. The crude bromo-keto-ester (11·1 g.), ν 1724 (C=O) cm.$^{-1}$ (in CCl_4), was devoid of enolic properties, but these gradually developed on storage, on distillation, or under the influence of hydrogen bromide.

Heating the bromo-keto-ester with aniline in ether, or with collidine, yielded ethyl 2-oxocyclohexanecarboxylate (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 157—158°) and ethyl salicylate (infrared comparison and hydrolysis to salicylic acid, m. p. and mixed m. p. 155°).

Ethyl 1-*chloro*-2-*oxocyclohexanecarboxylate* (II; X = Cl). This chloro-ketone was obtained as described by Brenner,[5] but in the absence of potassium carbonate. It had b. p. 132—134°/8·5 mm., ν 1734 and 1751sh (C=O) cm.$^{-1}$ (liquid film) (Found: Cl, 16·8. Calc. for $C_9H_{13}ClO_3$: Cl, 17·4%), and was not enolic. When heated with collidine it yielded ethyl salicylate, salicylic acid, and cyclohex-2-enone (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 166—167°). The chloro-ketone (8·5 g.), glacial acetic acid (17 g.), and anhydrous sodium acetate (17 g.) were refluxed for 15 min., cooled, diluted with water, basified with sodium hydroxide, and extracted with ether. Evaporation of the dried extract gave a residue separable into two fractions, b. p. 78—82°/12 mm. (0·3 g.) and 80—100°/0·1 mm. (0·5 g.). The former was identical with a synthetic specimen [9] of ethyl cyclopent-1-enecarboxylate (infrared comparison and hydrolysis to cyclopent-1-enecarboxylic acid, see below); the latter, with infrared bands at 1799, 1764sh, 1730, and 1681sh cm.$^{-1}$ (liquid film) is tentatively formulated as 1-*acetoxy*-2-*oxocyclohexanecarboxylate* (II; X = OAc) (Found: C, 57·4; H, 6·7. $C_{11}H_{16}O_5$ requires C, 57·9; H, 7·0%). The 2,4-*dinitrophenylhydrazone* crystallised from ethanol in orange-yellow plates, m. p. 195·5—196° (Found: N, 14·3. $C_{17}H_{20}N_4O_8$ requires N, 13·7%). The alkaline solution was acidified and extracted with ether, and the ethereal extract washed several times with sodium hydrogen carbonate. The washings were acidified and extracted with ether; evaporation yielded a semi-solid mass (3·2 g.). It was triturated with a little ether and the solid collected. Fractional crystallisation from water yielded cyclopent-1-enecarboxylic acid, m. p. 119·5—120°, alone or mixed with an authentic sample,[9] followed by *trans*-cyclopentane-1,2-dicarboxylic acid, m. p. 160—161°, undepressed on admixture with a synthetic specimen.[10] Evaporation of the filtrate gave *ethyl hydrogen* trans-*cyclopentane*-1,2-*dicarboxylate* (V; R = Et), b. p. 172—175°/14·5 mm. (1·4 g.) (Found: C, 58·5; H, 7·6%; equiv., 182. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%; equiv., 186). Alkaline hydrolysis yielded *trans*-cyclopentane-1,2-dicarboxylic acid, m. p. and mixed m. p. 160—161° (see above).

Ethyl 1-*chloro*-2,2-*ethylenedioxycyclohexanecarboxylate* (VI; X = Cl). Ethyl 1-chloro-2-oxocyclohexanecarboxylate (5·1 g.), ethylene glycol (3·1 g.), dry benzene (20 c.c.). and a crystal of toluene-*p*-sulphonic acid were refluxed for 4 hr. under a Dean and Stark apparatus. The cooled solution was washed with sodium hydrogen carbonate solution and water, dried, and concentrated. The *ketal* distilled at 83—84°/0·05 mm. (3·4 g.) (Found: C, 53·2; H, 7·1. $C_{11}H_{17}ClO_4$ requires C, 53·1; H, 6·9%) and had no ketonic C=O absorption in the infrared. Most of the product was recovered when heated at 180° for 7 hr. with collidine.

Ethyl 1-*chloro*-2-*oxocyclopentanecarboxylate* (VII; X = Cl), b. p. 85—89°/0·5 mm. (85% yield) (Found: C, 50·5; H, 6·05; Cl, 18·2. $C_8H_{11}ClO_3$ requires C, 50·4; H, 5·8; Cl, 18·6%), was obtained by an analogous reaction between ethyl 2-oxocyclopentanecarboxylate and sulphuryl chloride. The 2-*bromo-analogue* (VII; X = Br), obtained by bromination of the same keto-ester with *N*-bromosuccinimide, could not be purified owing to its tendency to rearrange when distilled. Both halogenated keto-esters yielded ethyl 2-oxocyclopentanecarboxylate (infrared comparison), with unidentified low-boiling material, when heated with collidine.

Ethyl 1-*chloro*-2,2-*ethylenedioxycyclopentanecarboxylate* (IX). The *ketal* was obtained from the ketone (3·8 g.), ethylene glycol (2·3 g.), benzene, and toluene-*p*-sulphonic acid, as described above for the cyclohexane analogue. It had b. p. 87—88°/0·2 mm. (2·3 g.) (Found: C, 50·8; H, 6·4; Cl, 15·7. $C_{10}H_{15}ClO_4$ requires C, 51·2; H, 6·4; Cl, 15·1%) and no ketonic infrared absorption. Heating the ketal with collidine at 180° for 1 hr. gave mainly unchanged material.

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Department of Chemistry, University College, Cardiff.

[*Received, November* 13*th*, 1961.]

[9] Cook and Linstead, *J.*, 1934, 956.
[10] Aspinall and Baker, *J.*, 1950, 743.

295. *A New Resolution of α-Methoxy-α-phenylacetic Acid.*

By Douglas G. Neilson and David A. V. Peters.

α-Methoxy-α-phenylacetic acid was first resolved by Pirie and Smith [1] who obtained the (+)-acid by crystallisation of its quinine salt. Other alkaloids have been used,[2] quinidine, cinchonine, or cinchonidine giving the (+)-acid and morphine or strychnine the (−)-acid, but of these only quinine and morphine were described as giving reasonable resolution.

We found resolution with quinine to give low yields of the (+)-form and only very impure (−)-acid. Ephedrine was found by Roger [3] to give both forms of mandelic acid in high yield and so we applied it to α-methoxy-α-phenylacetic acid. The (±)-acid was prepared by an adaptation of the method of Truit *et al.*;[4] crystallisation of the ephedrine salt from ethanol gave both forms of the acid optically pure and in high yield. The Table shows the specific rotations obtained by various workers.

$[\alpha]_D$ in EtOH	Temp.	Concn. (*c*) *	Ref.	Method of prep.
−150·6°	13°	0·541	5	From (−)-mandelic acid
−151·1	,,	2·706	,,	,, ,,
−150·7	20	0·574	This paper	Ephedrine resoln.
+150·0	20	0·494	,,	,, ,,
−150·9	20	0·685	6	From sugars
+151·5	—	1·716	1	Quinine resoln.

* The specific rotations of these acids increase with increasing concentration.[5]

Experimental.—A solution of sodium methoxide (59·4 g. of sodium in 500 ml. of methanol) was added dropwise to a solution of methyl (±)-α-bromo-α-phenylacetate [4] (590 g.) in methanol and the whole refluxed for 4 hr. and left for 24 hr. at room temperature. Sodium bromide was filtered off and the filtrate treated with 15% aqueous sodium hydroxide (1 ml.) at 80° for 2 hr. Sodium (±)-α-methoxy-α-phenylacetate, which separated on cooling, was washed with alcohol, decomposed with 25% sulphuric acid, and worked up in the usual way, to give (±)-α-methoxy-α-phenylacetic acid (310 g.), m. p. 69—70°.

Ephedrine (40 g.) and this (±)-acid (40 g.) were dissolved in warm ethanol (150 ml.) and left for 24 hr. at room temperature. The ephedrine salt (40 g.) which was precipitated was filtered off and crystallised once from ethanol (200 ml.) to give a salt (28·8 g.), $[\alpha]_{5461}^{19}$ −87·8° (*c* 0·668 in methanol; *l* 2). One further crystallisation from ethanol (200 ml.) gave a salt of $[\alpha]_{5461}^{20}$ −91·2° (*c* 0·534 in methanol; *l* 2). Decomposition of this salt with 20% sulphuric acid gave (−)-acid (11 g.) which after one crystallisation from light petroleum (b. p. 80—100°)–benzene had $[\alpha]_{5461}^{20}$ −173·3° and $[\alpha]_D^{20}$ −150·7° (*c* 0·574 in ethanol; *l* 2). Evaporation and treatment of the reaction liquor in a similar way yielded (+)-acid (9·5 g.), $[\alpha]_{5461}^{20}$ +172·6°, $[\alpha]_D^{20}$ +150·0° (*c* 0·494 in ethanol; *l* 2). The acids had m. p. 65—66° and gave no depression on admixture with authentic active acids.

We thank the Department of Scientific and Industrial Research for a grant (to D. A. V. P.) and Queen's College, Dundee, for an Edward A. Deeds' Research Fellowship in Chemistry (to D. G. N.).

Queen's College, Dundee, University of St. Andrews. [*Received, November 16th*, 1961.]

[1] Pirie and Smith, *J.*, 1932, 338.
[2] Bamann and Portmann, *Arch. Pharm.*, 1932, **9**, 513.
[3] Roger, *J.*, 1935, 1544.
[4] Truitt, Mark, Long, and Jeanes, *J. Amer. Chem. Soc.*, 1948, **70**, 4214.
[5] McKenzie, *J.*, 1899, **75**, 753.
[6] Weygand and Gölz, *Chem. Ber.*, 1954, **87**, 707.

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296. *Condensation Products of Terephthalaldehyde: Cyclisation of the Michael Adduct by Polyphosphoric Acid.*

By Z. S. Ariyan and B. Mooney.

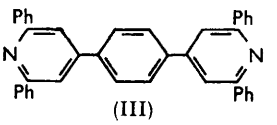
Davey and Gottfried [1] have condensed phthalaldehyde with ketones, obtaining aldols which they dehydrated to benzotropones; we have condensed terephthalaldehyde with

[1] Davey and Gottfried, *J. Org. Chem.*, 1961, **26**, 3699, 3705.

some aromatic and heterocyclic ketones after our earlier preparation [2] of heterocyclic compounds of chalcone type and the related pentane-1,5-diones (Michael adducts) which in polyphosphoric give trisubstituted pyranol and thence pyridine derivatives. Lendenfeld [3] has reported the preparation from terephthalaldehyde of bischalcones of type (I). We have obtained from one of them the Michael addition product (II), cyclised it in

p-$C_6H_4(CH{:}CH{\cdot}COR)_2$ (I)

p-$C_6H_4[CH(CH_2{\cdot}COPh)_2]_2$ (II)



(III)

polyphosphoric acid and then by use of ammonia obtained compound (III) which has seven aromatic nuclei united to one another. Attempts to prepare heterocyclic compounds of type (II) by an established method [4] gave only the related chalcones (I).

Condensation of quinoline-2-aldehyde with acetophenone is reported [2,5] to yield the aldol although the corresponding chalcone has been obtained by a similar method.[6] Attempts to dehydrate the aldol to the chalcone at 60° failed; a similar failure is reported by Marvel *et al.*[7] This aldol is extremely photosensitive, a property noted earlier [8] for some heterocyclic chalcones.

Experimental.—Preparation of chalcones. To a warm solution of the terephthalaldehyde (0·05 mole) and a ketone (0·05 mole) in alcohol (100 ml.), about 2 : 1 aqueous-ethanolic 6% sodium hydroxide solution (25 ml.) was added; chalcone formation was almost instantaneous. The mixture was shaken for 10 min., allowed to cool, and filtered, giving the *chalcones* (see Table) in 70% yield; they were recrystallised from benzene or chlorobenzene.

Chalcones, p-$C_6H_4(CH{:}CH{\cdot}COR)_2$.

		Found (%)			Required (%)	
R	M. p.	C	H	Formula	C	H
Ph [3]	201°					
2-Thienyl	223	68·3	3·8	$C_{20}H_{14}O_2S_2$	68·6	4·0
2-Furyl	229	75·2	4·3	$C_{20}H_{14}O_4$	75·5	4·4

3,3′-p-*Phenylenebis*-(1,5-*diphenylpentane*-1,5-*dione*) (II). Reaction as above of acetophenone (0·3 mole) and terephthalaldehyde (0·1 mole) on a water-bath for 30 min. gave the *tetraketone*, m. p. 187° (from benzene) (Found: C, 83·4; H, 5·9. $C_{40}H_{34}O_4$ requires C, 83·0; H, 5·9%).

4,4′-p-*Phenylenebis*(2,6-*diphenylpyridine*) (III). The ketone (II) (2 g.) and tetraphosphoric acid (25 g.) were stirred at 70° for 4 hr., soon becoming green fluorescent in ultraviolet light (characteristic of the presence of pyrylium salts [9]). Pouring the mixture into ice–water precipitated the pyrylium phosphate which was triturated with aqueous ammonia, yielding the *pyridine derivative* (III), m. p. 304° (from ethyl acetate) (35%) (Found: C, 89·4; H, 5·6; N, 5·1. $C_{40}H_{28}N_2$ requires C, 89·6; H, 5·3; N, 5·2%).

β-*Hydroxy*-β-2′-*quinolylpropiophenone*. This compound [2,5] developed a purple colour in alcohol or benzene solution but after several crystallisations in the dark had m. p. 123° (Found: N, 5·2. Calc. for $C_{18}H_{13}NO$: N, 5·05%). Low m. p.s reported in the literature are probably due to photodecomposition. Exposure of an alcoholic solution to daylight for 6 months afforded a small amount of a reddish-brown material of m. p. 153—154°.

The authors acknowledge the interest and encouragement of Professor H. I. Stonehill of this Department.

Department of Chemistry and Metallurgy, Royal Military College of Science, Shrivenham, Swindon, Wilts. [*Received, November 27th*, 1961.]

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[7] Marvel, Coleman, and Scott, *J. Org. Chem.*, 1955, **20**, 1785.
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