A Correction to " meta-*Interactions and Inductive Effects in Heterocyclic Systems."*

By D. A. Brown and M. J. S. Dewar.

[Reprint Order No. 4802a.]

Professor Herbert C. Brown has drawn our attention to several passages in our paper of the above title (*J.*, 1953, 2406) in which we attributed to him and his co-author (H. C. Brown and W. A. Murphey, *J. Amer. Chem. Soc.*, 1951, **73**, 3308) the view that the prototropic reactivity which they had discovered for the methyl group in β-picoline is due to *m*-quinonoid structures stabilizing the conjugate carbanion. This view we criticised and rejected on the basis of molecular-orbital calculations.

Professor Brown points out that, in actual fact, he and his co-author clearly and explicitly stated in their paper that stabilization by *m*-quinonoid structures could *not* be the explanation and that an alternative one must be sought.

We entirely agree with this statement of the facts. We greatly regret that, through inadvertence, we so completely misrepresented their views.

Queen Mary College, London, E.1. [*Received, November 17th,* 1953.]

The Chemistry of Ribose and its Derivatives. Part III. The Separation of Anomeric Methyl Ribosides.*

By G. R. Barker and D. C. C. Smith.

[Reprint Order No. 5107.]

Synthesis of derivatives of ribose from methyl ribosides would be greatly facilitated if single anomeric forms of these compounds were readily available. Minsaas (*Annalen*, 1934, **512**, 286) obtained methyl β-D-ribopyranoside by a lengthy process of crystallisation of the mixture of anomers, and Jeanloz, Fletcher, and Hudson (*J. Amer. Chem. Soc.*, 1948, **70**, 4055) obtained it from 2 : 3 : 4-tri-*O*-benzoyl-β-D-ribopyranosyl bromide. The corresponding α-isomer has not been described and the methyl ribofuranosides (Barker, *J.*, 1948, 2035) were obtained only as a mixture of anomeric forms. We therefore attempted to isolate all four isomers by the method of Hough, Jones, and Wadman (*J.*, 1950, 1702) which has been used successfully also by Augestad, Berner, and Weigner (*Chem. and Ind.*, 1953, 376).

Mixtures of the methyl α- and β-ribosides were separately placed on columns of powdered cellulose, and elution from the columns was followed polarimetrically. In each case early fractions showed an increasing negative rotation and yielded the β-isomer. Thereafter, a mixture of α- and β-isomers was obtained, and was resolved by repeated chromatography. Methyl β-ribopyranoside crystallised immediately and had almost the same physical properties as those reocrded by Minsaas (*loc. cit.*); the other three isomers have not crystallised after three years, but it is probable that in each case complete separation of α- and β-forms had been achieved since each was chromatographically homogeneous. The identities of the isomers were confirmed by the fact that each consumed the expected quantity of sodium metaperiodate and the rotations of the solutions after completion of the oxidation corresponded to the specific rotations of the expected dialdehydes previously recorded (Jackson and Hudson, *J. Amer. Chem. Soc.*, 1937, **59**, 994). From the specific rotations of the four glycosides it was calculated that the original mixtures of furanoside and pyranoside anomers contained 68 and 74%, respectively, of the β-forms.

If the molecular rotations of these anomeric pairs were known the ring structure of crystalline ribose itself might be indicated. Phelps, Isbell, and Pigman (*ibid.*, 1934, **56**,

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* Part II, *J.*, 1950, 23.

747) considered that the crystalline sugar is probably β-D-ribofuranose on account of the initial direction of the mutarotation and of its similarity in behaviour to the mannose–calcium chloride compound which also exhibits complex mutarotation (Dale, *ibid.*, 1929, **51**, 2225) and gives a γ-lactone on oxidation with bromine (Isbell, *ibid.*, 1933, **55**, 2166). Unfortunately, crystalline D-ribose is known in only one form, and hence calculation of the partial molecular rotation of carbon atoms 2—5 has not so far been possible. However, by application of the rules of isorotation the molecular rotation of the anomer of crystalline D-ribose can be predicted approximately from the molecular rotations of the four methyl D-ribosides. Thus the algebraic sums of the molecular rotations * of the methyl α- and β-D-ribofuranosides and of the methyl α- and β-D-ribopyranosides are respectively +139° and −5°; these figures represent the relative partial rotation due to carbon atoms 2—5. It being assumed that the partial molecular rotation of this part of the molecule is the same in the free sugar, and the molecular rotation of crystalline D-ribose being taken as −36° †, then the molecular rotation of its anomer would be approximately +175° if furanose, or +31° if pyranose. According to the rules of isorotation the algebraic difference between the molecular rotations of the α- and the β-form of any sugar derivative is a measure of the partial molecular rotation of $C_{(1)}$, and hence depends largely on the nature of the substituent at this position. In accordance with this, the difference between the molecular rotations of the methyl D-ribopyranosides (+345°) agrees well with the published differences for the other methyl pentopyranosides (D-xylose, +360°; D-lyxose, +308°; L-arabinose, +375°; cf. Bates, "Polarimetry, Saccharimetry, and the Sugars," National Bureau of Standards, 1942, p. 708 *et seq.*). The methyl D-ribofuranosides show a similar difference (+343°) which suggests that $C_{(1)}$ has the same partial molecular rotation in both furanoside and pyranoside structures. In the free sugars, the ribofuranoses or ribopyranoses might be expected to show molecular-rotation differences between α- and β-forms similar to those observed for other sugars (galactose, +176°; glucose, +168°; lactose, +187°; mannoheptose, +177°; cf. Bates, *loc. cit.*). The difference between the molecular rotations of α- and β-ribose, derived from the observed rotation of crystalline D-ribose and the predicted rotation of its anomer would be +211° if furanose and +77° if pyranose. These figures suggest that crystalline D-ribose has the furanose configuration. However, there are sugars whose molecular-rotation differences do not fall into line with those quoted (lyxose, +117°; mannose, +83°; talose, +99°), and since ribose behaves anomalously in other ways, it is impossible to draw a firm conclusion. The properties of the four methyl ribosides are, however, recorded below in order that a decision may be reached when further data become available.

	Methyl D-ribofuranoside			Methyl D-ribopyranoside		
	α-form		β-form	α-form		β-form
$[\alpha]_D^{20}$ (*c*, 1·0 in MeOH)	+146·8°		−62·4°	+103·3°		−106·5°
Molecular rotation, [*M*]	+241		−102	+170		−175
$[M]_\alpha - [M]_\beta$		+343			+345	
$[M]_\alpha + [M]_\beta$		+139			−5	
Mols. $NaIO_4$ reduced [1]	0·99		0·94, 1·06	1·9		1·97
[α] of oxidation product	+116·3°		−145·3°	+122°		−125·5°
[α] of expected dialdehyde [2]	+117·3 to +121·1		−148·1 to −150·6	+124·2 to +125·2		−123·7 to −124·3

[1] By Barneby's method (*J. Amer. Chem. Soc.*, 1916, **38**, 330). [2] Jackson and Hudson, *loc. cit.*

Experimental.—Methyl α- and β-ribofuranosides. The mixed glycosides were obtained by Barker's method (*loc. cit.*). Paper chromatography with *n*-butanol–water as the solvent system gave two spots of R_F values 0·32 and 0·45. The syrupy mixture (5·4 g.) in *n*-butanol (30 c.c.) was saturated with water and loaded on to a column of "Solkafloc" prepared by Campbell, Mellangy, and Work's method (*Biochem. J.*, 1951, **48**, 109) and eluted with *n*-butanol saturated with water, 6-c.c. fractions being collected. Fractions having a progressively increasing negative rotation were combined and yielded, after removal of the solvent, chromatographically homogeneouss yrupy methyl β-D-ribofuranoside (0·89 g.; R_F, 0·45) which was sublimed at 0·01 mm.

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* For convenience, molecular rotations [*M*] as quoted in this paper are defined as [α] × mol. wt./100.

† Extrapolation of the mutarotation curve given by Phelps *et al.* (*loc. cit.*) to zero time gives a specific rotation of −24·0° for crystalline D-ribose.

(Found: OMe, 19·7. Calc. for $C_6H_{12}O_5$: OMe, 18·9%). Fractions having a progressively decreasing negative rotation were discarded. Fractions having a positive rotation were combined and after removal of the solvent a syrup was obtained which was not chromatographically homogeneous. The material was rechromatographed by the same method, the fractions being examined by paper chromatography. Those containing only the component of R_F 0·32 were combined, the solvent was removed as before, and the remaining syrupy methyl α-D-ribofuranoside (0·23 g.) was sublimed at 0·01 mm. (Found: OMe, 19·5. Calc. or $C_6H_{12}O_5$: OMe, 18·9%).

Methyl α- and β-*ribopyranosides*. The mixed glycosides were prepared by Minsaas's method (*loc. cit.*). Paper chromatography in the *n*-butanol–water system gave two spots of R_F values 0·32 and 0·45. The mixture (6 g.) was dissolved in the upper layer of a mixture of pyridine, ethyl acetate, and water (1 : 2 : 2), and loaded on to a column as described above and eluted with the same mixture of solvents. Eluates were examined polarimetrically as before and from the early fractions chromatographically homogeneous syrupy methyl β-D-ribopyranoside (0·95 g.; R_F, 0·45) was obtained. After being sublimed at 0·01 mm. the compound crystallised within 1 hr. and had m. p. 78° (Found: OMe, 18·0. Calc. for $C_6H_{12}O_5$: OMe, 18·9%). Later fractions, after being re-chromatographed twice, gave chromatographically homogeneous syrupy methyl α-D-ribopyranoside (0·065 g.; R_F, 0·32), and was sublimed at 0·01 mm. (Found: OMe, 18·5. Calc. for $C_6H_{12}O_5$: OMe, 18·9%).

One of us (D. C. C. S.) gratefully acknowledges the receipt of a maintenance grant from the Department of Scientific and Industrial Research.

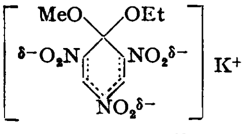
THE UNIVERSITY, MANCHESTER. [*Received, February 10th,* 1954.]

Potassium Ethyl 1-*Methoxypicrate.*

By R. FOSTER and D. LL. HAMMICK.

[Reprint Order No. 5109.]

WE have measured the infra-red absorption of the product of interaction of *s*-trinitroanisole with potassium ethoxide. The spectrum shows several interesting features. The N–O symmetrical stretching frequencies appear to have shifted from 1343 cm.$^{-1}$ in *s*-trinitroanisole to 1291 cm.$^{-1}$ in the product. Similarly the N–O asymmetrical stretching frequencies have shifted from 1552 to 1492 cm.$^{-1}$. These bands have been assigned by Randle and Whiffen (*J.*, 1952, 4153) the values 1349 ± 9 and 1518 ± 13 cm.$^{-1}$ respectively. Another feature of the spectrum is that the Ar–H stretching frequency at 3090—3000 cm.$^{-1}$ is absent. It is suggested that these differences are due to an increased negative charge on the nitro-groups, supporting the annexed structure (Sidgwick, " Organic Chemistry of Nitrogen," ed. Taylor and Baker, Oxford Univ. Press, 1937, p. 260).



Confirmation of the conclusions of Meisenheimer (*Annalen*, 1902, **323**, 219) and of Jackson and Earle (*Amer. Chem. J.*, 1903, **29**, 89) that the two alkoxy-groups are symmetrically disposed in the molecule is given by the identity of the products obtained (*a*) from *s*-trinitroanisole and potassium ethoxide and (*b*) from *s*-trinitrophenetole and potassium methoxide (Meisenheimer, *loc. cit.*).

Experimental.—The spectra measured were those of solid films dispersed as mulls in liquid paraffin as observed with a Perkin–Elmer double-beam spectrometer with a rock-salt prism.

We thank Dr. F. B. Strauss for helpful discussions, and the Department of Scientific and Industrial Research for a maintainance grant to one of us (R. F.).

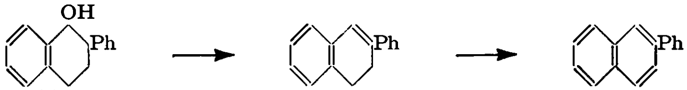
DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, February 10th,* 1954.]

Synthesis of 2-Phenylnaphthalene.

By Neil Campbell and David Kidd.

[Reprint Order No. 5096.]

Only a few convenient syntheses of 2-phenylnaphthalene are known (Spring, *J.*, 1934, 1332; Hey and Wilkinson, *J.*, 1940, 1030; Weizmann, Bergmann, and Bograchov, *Chem. and Ind.*, 1940, **59**, 402; Price and Ciskowski, *J. Amer. Chem. Soc.*, 1938, **60**, 2502). We now report an easy method starting from readily accessible substances. Benzyl cyanide and phenethyl bromide afford a product which is hydrolysed to $\alpha\gamma$-diphenylbutyric acid. Ring-closure of the acid gives 2-phenyl-1-tetralone, which is reduced quantitatively by lithium aluminium hydride to 2-phenyl-1-tetralol (I). The tetralol is converted into 2-phenylnaphthalene (III) either by treatment with thionyl chloride or by dehydration to 3 : 4-dihydro-2-phenylnaphthalene (II) and subsequent dehydrogenation with chloranil. In the first process dehydration must be accompanied by chlorination followed by dehydrochlorination.



(I) (II) (III)

The yields at all stages except the first (62%) are 90% or more.

Experimental.—2-*Phenyl*-1-*tetralol.* Freshly distilled benzyl cyanide (82·5 g.) was added during ½ hr. to " molecular " sodium (16·2 g.) covered by dry ether (300 ml.). The mixture was stirred and boiled for 2 hr. and cooled in ice-water, and to it was added with brisk stirring phenethyl bromide (60 g.) during 2 hr. Stirring was continued overnight, and the ether boiled off and replaced by a similar volume of dry benzene. The mixture was boiled for 3 hr., and hydrolysed with dilute hydrochloric acid. The organic layer was separated, washed with water, dried, and evaporated to give α-diphenylbutyronitrile (44 g.), b. p. 152—156°/1 mm. The nitrile was hydrolysed with 70% sulphuric acid and acetic acid for 2 days: the resulting $\alpha\gamma$-diphenylbutyric acid (94%), crystallised twice from light petroleum (b. p. 60—80°), had m. p. 72—73° (lit., 70—72°).

The acid was converted into the acid chloride which underwent ring-closure by the inverse Friedel–Crafts reaction (Johnson and Glenn, *J. Amer. Chem. Soc.*, 1949, **71**, 1094), giving 2-phenyl-1-tetralone (almost quantitative yield), m. p. 75·5—76·5° after crystallisation from ethanol (lit., 76—77°). The tetralone (7·40 g., 0·033 mol.) in dry ether (100 ml.) was added to a solution of lithium aluminium hydride (1 g., 0·025 mol.) in dry ether (200 ml.) during 30 min. The solution was boiled (3 hr.) and the excess of hydride was decomposed by addition of water and then dilute sulphuric acid to the cooled solution. The organic layer was separated, washed with water, and dried (Na_2SO_4). Removal of the ether gives 2-phenyl-1-tetralol (7·10 g., 95%), needles (from light petroleum, b. p. 60—80°), m. p. 67—68°.

2-*Phenylnaphthalene.* (*a*) The tetralol (3·90 g.) reacted vigorously with thionyl chloride (12 ml.), and the solution after 1 hr. was boiled for the same period. Excess of thionyl chloride was removed *in vacuo* and finally by co-distillation with dry benzene. The residue was crystallised from methanol, giving 2-phenylnaphthalene (3·18 g., 90%), which was further purified by passing its solution in benzene–light petroleum (1 : 3) down a short alumina column. A yellow impurity remained on the column and pure 2-phenylnaphthalene was obtained from the filtrate.

(*b*) The tetralol (2·00 g., 0·009 mole) was shaken (5 hr.) with phosphoric oxide (2·56 g., 0·018 mole) in dry benzene (50 ml.). Water and then ether were added and the ether layer was washed successively with 5% sodium carbonate solution and water. The dried solution was evaporated and the residual 3 : 4-*dihydro*-2-*phenylnaphthalene* (1·84 g.) crystallised from methanol in colourless blades, m. p. 64—66° (Found: C, 93·1; H, 6·9. $C_{16}H_{14}$ requires C, 93·1; H, 6·9%). The *trinitrobenzene* derivative formed golden-yellow blades (from ethanol), m. p. 110—111° (Found: N, 13·5. $C_{28}H_{20}O_{12}N_6$ requires N, 13·3%). The dihydro-compound (1·03 g., 0·005 mole) and chloranil (1·27 g., 0·005 mole) were boiled (15 hr.) in sulphur-free xylene.

Ether was added and the solution shaken with successive portions of 4% aqueous potassium hydroxide until the alkaline washings were colourless. The organic layer was washed with water and dried (Na_2SO_4), and the solvents were removed by distillation *in vacuo*. The residue in benzene–light petroleum (b. p. 60—80°) (1 : 2) was passed down a short alumina column. Elution of a pale blue fluorescent band gave 2-phenylnaphthalene (90%), m. p. 101—102° (lit., 101—102°), identified by its m. p. and those of the trinitrobenzene derivative, m. p. 112—113·5° (lit., 113·5—115·5°), and the trinitrofluorenone derivative, m. p. 170—171° (lit., 169·5—170·5°).

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UNIVERSITY OF EDINBURGH. [*Received, February 8th*, 1954.]

Branched-chain Sugars. Part II. The Action of Grignard Reagents on* 1 : 2-3 : 4-*Di*-O-iso*propylidene*-6-O-*toluene*-p-*sulphonyl*-α-D-*galactose*.

By W. G. OVEREND and G. VAUGHAN.

[Reprint Order No. 5094.]

GILMAN and his co-workers (Gilman and Beaber, *J. Amer. Chem. Soc.*, 1923, **45**, 839; Gilman and Heck, *ibid.*, 1928, **50**, 2223) concluded that reaction of organomagnesium halides with aryl esters of sulphonic acids gives sulphones and phenols, whereas with alkyl sulphonates alkylation occurs together with the formation of some alkyl halide, in accordance with the equations :

$$\mathrm{ArO{\cdot}SO_2{\cdot}R + R'{\cdot}MgX \longrightarrow ArO{\cdot}MgX + R'{\cdot}SO_2{\cdot}R} \qquad (1)$$

$$\mathrm{AlkO{\cdot}SO_2{\cdot}R + R'{\cdot}MgX \longrightarrow Alkyl{\cdot}R' + R{\cdot}SO_2{\cdot}O{\cdot}MgX} \qquad (2)$$

$$\mathrm{AlkO{\cdot}SO_2{\cdot}R + R{\cdot}SO_2{\cdot}O{\cdot}MgX \longrightarrow Alkyl{\cdot}X + (R{\cdot}SO_2{\cdot}O)_2Mg} \qquad (3)$$

(X = halide, R′ = alkyl.)

If toluene-*p*-sulphonyl esters of carbohydrates could be induced to react with alkylmagnesium halides according to reactions 2 and 3, the products would be of interest from several viewpoints. Reaction 2 would yield a *C*-alkyl sugar, and it was hoped to realise an independent synthesis of the *C*-alkyl sugars formed by the action of Grignard reagents on methyl 2 : 3-anhydrohexosides (Newth, Richards, and Wiggins, *J.*, 1950, 2356; Foster, Overend, Stacey, and Vaughan, *J.*, 1953, 3308). Reaction 3 would produce halogenated sugars which are useful intermediates in the synthesis of deoxy-sugars (see Overend, Stacey, *et al.*, *J.*, 1949, 1235, and later papers). However, 1 : 2-3 : 4-di-*O*-*iso*propylidene-6-*O*-toluene-*p*-sulphonyl-α-D-galactose and methylmagnesium iodide in ether gave 6-deoxy-6-iodo-1 : 2-3 : 4-di-*O*-*iso*propylidene-α-D-galactose as sole isolatable product. A similar result was obtained with ethylmagnesium iodide. Attempts to demonstrate the presence, respectively, of ethyl- and propyl-pentose derivatives were unsuccessful. The identity of each product was confirmed by its smooth reduction to 6-deoxy-1 : 2-3 : 4-di-*O*-*iso*propylidene-α-D-galactose (di-*O*-*iso*propylidene-D-fucose). Variation of the proportions of the Grignard reagent and the toluene-*p*-sulphonyl derivative of di-*O*-*iso*propylidene-galactose had no effect on the nature of the product and little effect on the yield. No reaction occurred between phenylmagnesium iodide and this D-galactose derivative, or with methylmagnesium iodide and toluene-*p*-sulphonyl esters formed from secondary hydroxyl groups : 1 : 2-5 : 6-di-*O*-*iso*propylidene-3-*O*-toluene-*p*-sulphonyl-D-glucofuranose and methyl 2-*O*-toluene-*p*-sulphonyl-β-L-arabinoside and its diacetate were recovered almost quantitatively. In view of the yields of 6-deoxy-6-iodo-1 : 2-3 : 4-di-*O*-*iso*propylidene-α-D-galactose obtained in our experiments it is probably formed by the reaction scheme originally proposed by Kenyon *et al.* (Kenyon, Phillips, and Turley, *J.*, 1925, 399;

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* Part I, *J.*, 1953, 3308.

Holmberg, *Ber.*, 1926, **59**, 1558; see also Rossander and Marvel, *J. Amer. Chem. Soc.*, 1928, **50**, 1491) rather than according to reactions 2 and 3 above.

Experimental.—Reaction of 1 : 2-3 : 4-*di*-O-iso*propylidene*-6-O-*toluene*-p-*sulphonyl*-α-D-*galactose with alkylmagnesium iodides.* (*a*) With methylmagnesium iodide. To methylmagnesium iodide prepared from magnesium (0·243 g.) and methyl iodide (1·46 g.) in ether was added an ethereal solution of 1 : 2-3 : 4-di-*O*-*iso*propylidene-6-*O*-toluene-*p*-sulphonyl-α-D-galactose (4·14 g.). The mixture was heated under reflux for 5 hr. and then kept at room temperature overnight. After dilution with ether and water, 2N-hydrochloric acid was added until the precipitate had redissolved. The ethereal layer was separated, washed successively with water, saturated sodium hydrogen carbonate solution, dilute sodium thiosulphate solution, and water, and then dried (Na_2SO_4). Evaporation of the solvent yielded an oil which distilled as a colourless syrup, b. p. 140—145° (bath-temp.)/0·003 mm., which crystallised on trituration. Recrystallisation from ethanol gave 6-deoxy-6-iodo-1 : 2-3 : 4-di-*O*-*iso*propylidene-α-D-galactose (2·5 g.), m. p. 70° alone or on admixture with an authentic specimen, $[\alpha]_D^{14}$ −50·2° (*c*, 1·59 in $CHCl_3$) (Found : C, 38·8; H, 4·8. Calc. for $C_{12}H_{19}O_5I$: C, 38·9; H, 5·1%).

Reductive dehalogenation gave quantitatively 6-deoxy-1 : 2-3 : 4-di-*O*-*iso*propylidene-α-D-galactose, m. p. 37—38°, $[\alpha]_D^{13}$ −52·9° (*c*, 2·04 in $CHCl_3$) (Found : C, 59·1; H, 8·2. Calc. for $C_{12}H_{20}O_5$: C, 59·0; H, 8·2%), and removal of the *iso*propylidene group gave 6-deoxy-6-iodo-D-galactose, m. p. 110° alone or on admixture with an authentic specimen prepared according to Raymond and Schroeder (*J. Amer. Chem. Soc.*, 1948, **70**, 2785).

(*b*) With ethylmagnesium iodide. The reaction was carried out in a similar manner with ethylmagnesium iodide [prepared from magnesium (0·243 g.) and ethyl iodide (0·83 c.c.) in ether] and 1 : 2-3 : 4-di-*O*-*iso*propylidene-6-*O*-toluene-*p*-sulphonyl-α-D-galactose (4·14 g.), and again 6-deoxy-6-iodo-1 : 2-3 : 4-di-*O*-*iso*propylidene-α-D-galactose (2·4 g.), m. p. 70°, was isolated.

The authors thank Professor M. Stacey, F.R.S., for his interest and Dr. R. Allerton for providing some of the initial materials. One of them (G. V.) thanks the Dunlop Rubber Co. Ltd. for financial support.

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The Heats of Formation of Phosphorus Trichloride, Sulphuryl Chloride, and Thionyl Chloride.

By E. NEALE and L. T. D. WILLIAMS.

[Reprint Order No. 5022.]

WE recently reported (*J.*, 1952, 4535) heats of hydrolysis of phosphorus trichloride and oxychloride significantly larger than those due to Thomsen ("Thermochemische Untersuchungen," 1882, Vol. 2), and our results were substantially confirmed by Charnley and Skinner (*J.*, 1953, 450). In computing heats of formation from the experimental results, data given in " Selected Values of Chemical Thermodynamic Properties " (National Bureau of Standards, Circular 500) were used for the heats of formation of the hydrolysis products. Charnley and Skinner in commenting on the reliability of the latter pointed out that while the value for phosphoric acid is based on two independent measurements which are in good agreement, that for phosphorous acid depends solely on the work of Thomsen (*op. cit.*). In view of this it was decided to repeat measurements on phosphorus trichloride, carrying out the hydrolysis in bromine water and thus producing phosphoric acid directly and avoiding reference to phosphorous acid.

This work was preliminary to an investigation of the thermochemistry of organic phosphorus compounds (to be reported shortly). As certain oxidation reactions in this programme required the use of sulphuryl chloride, it was also necessary to check its heat of hydrolysis and that of its reduction product—thionyl chloride—since here again published data are based on unconfirmed work by Thomsen (*op. cit.*) for the former and by Ogier (*Compt. rend.*, 1882, **94**, 82) for the latter chloride.

Experimental.—Purification of compounds. Phosphorus trichloride and sulphuryl chloride were fractionally distilled through a Dufton column (PCl_3 in an atmosphere of nitrogen). Thionyl chloride was distilled first over quinoline and finally over linseed oil.

Calorimeter. This was that used in the earlier work (*loc. cit.*); calibration was done electrically. The samples were contained in glass ampoules which were broken under the surface of the liquid. The calorimeter liquid was 500 ml. of distilled water in all cases, with the addition of 7—8 g. of bromine in the case of phosphorus trichloride and a little powdered iodine in that of sulphuryl chloride.

All measurements were carried out between 22° and 23°.

In the experiments with phosphorus trichloride the products were analysed for phosphoric acid (by Wilson's quinoline phosphomolybdate method, *Analyst*, 1951, **76**, 65) after removal of the excess of bromine with sodium sulphite. The hydrolysis products from both sulphuryl and thionyl chloride were analysed for chloride.

The observed heats ($\Delta H_{\text{obs.}}$) in the Tables refer to the reactions:

$$PCl_3(\text{l.}) + Br_2(\text{aq.}) + 4H_2O(\text{l.}) \longrightarrow H_3PO_4(\text{aq.}) + 3HCl(\text{aq.}) + 2HBr(\text{aq.})$$

$$SO_2Cl_2(\text{l.}) + 2H_2O(\text{l.}) \longrightarrow H_2SO_4\ (\text{aq.}) + 2HCl(\text{aq.})$$

$$SOCl_2(\text{l.}) + 2H_2O(\text{l.}) \longrightarrow H_2SO_3(\text{aq.}) + 2HCl(\text{aq.})$$

The subsidiary thermochemical data used in deriving heats of formation ($\Delta Hf°$) were taken from National Bureau of Standards, Circular 500. The results are summarised in the Table.

(a) *Reaction of phosphorus trichloride with bromine water.*

Wt. (g.)	Moles of H_2O per mole of PCl_3	$\Delta H_{\text{obs.}}$ (kcal.)	$\Delta Hf°$ PCl_3(l.) (kcal.)	Wt (g.)	Moles of H_2O per mole of PCl_3	$\Delta H_{\text{obs.}}$ (kcal.)	$\Delta Hf°$ PCl_3(l.) (kcal.)
1·0749	3500	−137·8	−74·5	0·5848	6300	−137·5	−74·8
0·6741	5500	−138·6	−73·7	0·6573	5600	−138·1	−74·2
0·6819	5400	−137·3	−75·0	0·7810	4700	−138·4	−73·9
					Mean values	−137·9	−74·4

Recovery of H_3PO_4 in the reaction products varied from 100·0 to 100·9%.

(b) *Hydrolysis of sulphuryl chloride with iodine as catalyst.*

Wt. (g.)	Moles of H_2O per mole of SO_2Cl_2	$\Delta H_{\text{obs.}}$ (kcal.)	$\Delta Hf°$ SO_2Cl_2(l.) (kcal.)	Wt. (g.)	Moles of H_2O per mole of SO_2Cl_2	$\Delta H_{\text{obs.}}$ (kcal.)	$\Delta Hf°$ SO_2Cl_2(l.) (kcal.)
0·9175	4100	−63·1	−93·3	1·2310	3100	−63·5	−92·9
0·8426	4500	−62·6	−93·8				
					Mean values	−63·1	−93·3

Recovery of chloride in the hydrolysis products was 99·4%.

(c) *Hydrolysis of thionyl chloride.*

Wt. (g.)	Moles of H_2O per mole of $SOCl_2$	$\Delta H_{\text{obs.}}$ (kcal.)	$\Delta Hf°$ $SOCl_2$(l.) (kcal.)	Wt. (g.)	Moles of H_2O per mole of $SOCl_2$	$\Delta H_{\text{obs.}}$ (kcal.)	$\Delta Hf°$ $SOCl_2$(l.) (kcal.)
1·1388	2900	−32·7	−58·3	0·9702	3400	−32·4	−58·6
0·7051	4700	−32·4	−58·6	1·0295	3200	−32·3	−58·7
					Mean values	−32·5	−58·5

Recovery of chloride in the hydrolysis products was 99·7%.

Discussion.—The mean value of $\Delta Hf PCl_3(\text{l.}) = -74{\cdot}4$ kcal. is significantly different from the value of −79·6 kcal. obtained by simple hydrolysis and use of Thomsen's data for $\Delta Hf H_3PO_3$. A few experiments (not given in detail here) in which the heat of oxidation of hydrolysed phosphorus trichloride in bromine water was measured gave results in good agreement with those from the combined oxidation–hydrolysis of this chloride. Measurement of the heat of solution of crystalline phosphorous acid in aqueous hydrochloric acid showed it to be approximately +1·0 kcal./mole, which is insufficient to account for the difference. Our view is that Thomsen's value is probably in error owing to the difficulty of obtaining very pure phosphorous acid.

The present results for sulphuryl chloride agree with that derived from Thomsen's work within the limits of our experiments, but there is a marked discrepancy between our results for thionyl chloride and those obtained by Ogier (*loc. cit.*), *viz.*, $\Delta H_{\text{obs.}}$ −39·2; ΔHf° −49·2 kcal. Ogier's experimental details were not available, so we were unable to compare the dilutions in his experiments with those reported above. The ΔHf° value calculated from Ogier's work is that given in the National Bureau of Standards, Circular 500.

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The Ultra-violet Absorption of Triethyl Phosphite.

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DE HAUSS (*Chim. Analyt.*, 1952, **34**, 249) stated that solutions of trialkyl phosphites $(RO)_3P$ have pronounced ultra-violet absorption. For trimethyl phosphite in methanol and triethyl phosphite in hexane, maximum absorption is said to occur at 2600 Å and the minimum at about 2150 Å (see Fig. 1, *loc. cit.*). This result could be of value in the identification and determination of trialkyl phosphites in the presence of the isomeric dialkyl alkylphosphonates $R{\cdot}PO(OR)_2$ which do not absorb in this region.

On measuring the absorption of an ethanolic solution of triethyl phosphite prepared by the usual procedure from ethanol, phosphorus trichloride, and diethylaniline, an absorption curve was obtained which was similar in shape to that of De Hauss, but of much lower intensity: thus the molar extinction coefficient $\varepsilon = (1/cl) \log I_0/I$ (where c is the concentration of the phosphite in mole/l. and l the length of the cell in cm.) was only 1·45 for 2600 Å, while De Hauss reported the value of 14.

Since it is difficult to remove traces of diethylaniline from triethyl phosphite even after careful fractional distillation, it was considered possible that the above samples of triethyl phosphite were contaminated with the tertiary amine. Diethylaniline absorbs very strongly in the ultra-violet region: a 0·0001M-solution of diethylaniline in ethanol gave an absorption spectrum similar to that of a 1M-solution of our triethyl phosphite (cf. Bowden and Braude, *J.*, 1952, 1075).

It was possible to prepare pure triethyl phosphite which was almost transparent in the ultra-violet region by substituting triethylamine for diethylaniline in the synthesis of triethyl phosphite. The boiling point of triethylamine is much lower than that of triethyl phosphite and separation was easy by fractional distillation. The molar extinction coefficients of this triethyl phosphite in different solvents are tabulated below.

Solvent Å:	2700	2600	2500	2400	2300	2250
Methanol	0·013	0·030	0·065	0·234	0·446	1·32
Ethanol	0·067	0·083	0·14	0·29	0·47	1·31
n-Hexane	0·027	0·06	0·12	0·29	0·474	—
n-Heptane	0·013	0·016	0·045	0·194	0·271	1·09

It is thus not possible to use the ultra-violet absorption spectrum to distinguish between trialkyl phosphites and dialkyl alkylphosphonates.

For identification of diethyl ethylphosphonate in the presence of triethyl phosphite, the infra-red absorption spectrum is useful. The former substance absorbs strongly at

1230 cm.$^{-1}$, while triethyl phosphite is relatively transparent in the 1260—1180 cm.$^{-1}$ region (Meyrick and Thompson, *J.*, 1950, 225).

Experimental.—Triethyl phosphite was prepared as described by Ford-Moore and Perry (*Org. Synth.*, 1951, **31**, 111), except that freshly distilled triethylamine was substituted for diethylaniline. The product was fractionated four times through a semimicro-column (Gould, Holzmann, and Niermann, *Analyt. Chem.*, 1948, **20**, 361), b. p. 59°/19 mm. (Found: C, 43·7; H, 9·2. Calc. for $C_6H_{15}O_3P$: C, 43·4; H, 9·0%). The cuprous iodide addition compound had m. p. 112° (from ethanol) (Arbusow and Arbusow, *Ber.*, 1932, **65**, 195). The infra-red spectrum of this triethyl phosphite was identical with that described by Meyrick and Thompson (*loc. cit.*).

Solvents were purified as described previously (Dostrovsky and Halmann, *J.*, 1953, 505, 513). The ultra-violet absorption spectra were measured with a DU Beckmann Spectrophotometer.

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