# NOTES.

## *The Preparation of Tristrifluoromethylphosphine Oxide.*

### By Ram Chand Paul.

Trimethylphosphine is very readily oxidised to its oxide by exposure to air (Cahours and Hofmann, *Annalen*, 1857, **104**, 30) whereas trischloromethylphosphine does not react with atmospheric oxygen and yields the oxide only when boiled with nitric acid (Hoffman, *J. Amer. Chem. Soc.*, 1930, **52**, 2996). Tristrifluoromethylphosphine reacts readily with oxygen but undergoes extensive breakdown and the oxide has not been identified among the products. A further possible method for preparing tristrifluoromethylphosphine oxide is by the aqueous hydrolysis of tristrifluoromethylphosphorus dichloride, but this reaction yields bistrifluoromethylphosphinic acid and fluoroform, while hydrolysis with aqueous alkali gives a salt of trifluoromethylphosphonic acid (Eméleus, Haszeldine, and Paul, *J.*, 1955, preceding paper). It was found, however, that tristrifluoromethylphosphorus dichloride reacted smoothly when heated with an excess of anhydrous oxalic acid according to the equation : $(CF_3)_3PCl_2 + H_2C_2O_4 = (CF_3)_3PO + CO + CO_2 + 2HCl$. Tristrifluoromethylphosphine oxide was produced in a 70% yield. It was a liquid (b. p. 23·5°) and was stable at room temperature. On reaction with water, fluoroform was lost: $(CF_3)_3PO + H_2O = (CF_3)_2PO(OH) + CHF_3$, and with an excess of dilute sodium hydroxide solution 2 mols. of fluoroform were lost and sodium trifluoromethylphosphonate was produced. The reaction with water contrasts with that of alkyl or aryl tertiary phosphine oxides, which form stable hydrates.

*Experimental.—Preparation of tristrifluoromethylphosphine oxide.* Tristrifluoromethylphosphorus dichloride (5·32 g.) was heated in a 2-necked flask (50 ml.) with anhydrous oxalic acid (2·0 g.; *ca.* 30% excess) over a small flame. The volatile products were swept out of the flask as formed by means of a stream of dry nitrogen. The condenser returned tristrifluoromethylphosphorus dichloride to the flask but a more volatile fraction passed over and was condensed in two traps cooled in liquid oxygen. This condensate was fractionated in the vacuum system and yielded *tristrifluoromethylphosphine oxide* (3·0 g., 70%) (Found : F, 68·1%; *M*, 254. $C_3OF_9P$ requires F, 67·8%; *M*, 254). Vapour pressures, measured with an isoteniscope, gave a b. p. of 23·6°.

Tristrifluoromethylphosphine oxide (0·2343 g.) was sealed in a Carius tube with 10% sodium hydroxide solution (15 ml.) and kept at room temperature for 48 hr. Fractionation of the

volatile products gave fluoroform (0·1285 g.) (Found : M, 69·8. Calc. for $CHF_3$ : M, 70). The weight of fluoroform expected if two $CF_3$ groups were removed was 0·1291 g. The solution recovered from the tube was freeze-dried and sodium trifluoromethylphosphonate was identified in the solid residue by means of its infrared spectrum.

Tristrifluoromethylphosphine oxide (0·3918 g.) was sealed in a Carius tube with water (9 ml.) and left for 24 hr. Fractionation of the volatile products gave fluoroform (0·1060 g.), the weight corresponding to the loss of one $CF_3$ group being 0·1079 g. The solution left in the Carius tube was found to be completely volatile on freeze-drying. It was treated with excess of alkali-free silver oxide (12 hr.) and then filtered. The solution, on freeze-drying, gave silver bistrifluoromethylphosphinate [Found : Ag (as AgCl), 35·1; $CF_3$ (as $CF_3H$), 22·1. Calc. for $C_2O_2F_6PAg$ : Ag, 35·0; $CF_3$ (if one $CF_3$ group is hydrolysed), 22·3%)].

*Infrared spectrum of tristrifluoromethylphosphine oxide.* The spectrum of this compound (C.S. No. 141)*, recorded on a Perkin-Elmer Model 21 Spectrophotometer, shows strong C–F stretching vibrations at 8·27 and 8·45 μ with overtones at 4·17 and 4·31 μ. The P⋮O vibration is assigned to the 7·53 μ band by analogy with the spectra of other trifluoromethyl compounds of phosphorus (Bennett, Emeléus, and Haszeldine, J., 1954, 3598), and the $CF_3$ deformation vibration to the 13·36 μ band.

The author is indebted to the University of Panjab for leave of absence, during which this work was carried out.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

# Constituents of the Higher Fungi. Part IV.† A Quinone from Polyporus fumosus.

## By J. D. Bu'Lock.

*Polyporus fumosus* (strain number 24A of the Forest Products Research Laboratory collection) grows well on a corn-steep (maize)–glucose medium, and methylene chloride extracts of the culture medium show characteristic strong ultra-violet absorption. From the extracts, a yellow crystalline solid has been isolated. After purification, this had m. p. *ca.* 250° (with sublimation and decomposition); elementary analysis indicated a formula

*Absorption spectra (maxima, in* Å, *followed by* log ε).

| | | |
|---|---|---|
| 3 : 4-Dimethoxy-2 : 5-toluquinone (cf. Vischer, J., 1953, 815) ... | 2650 (4·15) | — |
| 2 : 6-Dimethoxybenzoquinone ........................................ | 2860 (4·16) | 3800—3830 (2·75) |
| 2 : 5-Dimethoxybenzoquinone (natural and synth.) ........... | 2820 (4·13) | 3600—3700 (3·53) |

$C_8H_8O_4$, with two methoxyl groups. The absorption spectrum (Table) was similar to, but not identical with, that of 2 : 6-dimethoxybenzoquinone, m. p. *ca.* 250° (decomp.), from which it was also distinguished by giving a blood-red, rather than a magenta, colour in concentrated sulphuric acid. The isomeric 2 : 5-dimethoxybenzoquinone was accordingly prepared, and this was found to have the same ultra-violet absorption spectrum and m. p. as, and mixed m. p. with, the natural product. Since criteria of m. p. are inadequate in compounds of this nature, the identification was confirmed by measurements of the infra-red spectra (in Nujol mull) of the natural and the synthetic material and of 2 : 6-dimethoxybenzoquinone. The latter compound shows four bands in the region 1500—1700 cm.$^{-1}$ (at 1595, 1620, 1640, and 1690 cm.$^{-1}$), but the more symmetrical 2 : 5-isomer shows only two (at 1660 and 1695 cm.$^{-1}$).

The isolation of 2 : 5-dimethoxybenzoquinone from a natural source has not previously been recorded, but the 2 : 6-isomer was isolated from *Adonis vernalis* (Karrer, *Helv. Chim. Acta*, 1930, **13**, 1424), and then from fermented wheat germ (Vuataz, *ibid.*, 1950, **33**, 433; Cosgrove, Daniels, Whitehead, and Goulden, *J.*, 1952, 4821). In the latter it occurs together with methoxy-1 : 4-benzoquinone, which is known to be formed during the fermentation from a glucoside of the corresponding quinol (de Jong, *Nature*, 1953, **172**, 402). In the present work, corn-steep liquor has been used as a supplement in the culture

* Infrared spectra thus recorded have been deposited with the Society. Photocopies may be obtained, Price 3s. 0d. per copy, on application to the General Secretary.

† Part III, *J.*, 1953, 3719.

medium, and it is thus possible that the 2 : 5-dimethoxybenzoquinone is similarly formed from a simply related precursor in the liquor. The formation of a substance with a similar absorption spectrum has been observed when other *Polyporus* species were grown on this medium. The third isomer, 2 : 3-dimethoxybenzoquinone, is not known to occur naturally, but the related 2 : 3-dimethoxy-5 : 6-dimethylbenzoquinone is produced, together with the corresponding quinhydrone and β-quinol, by certain *Gliocladium* species (Vischer, *J.*, 1953, 815). In the case of *Polyporus fumosus* (and, apparently, of some other *Polyporus* species which have been examined), preliminary experiments are interpreted as showing that appreciable amounts of the quinone are produced only in the period of relatively rapid growth following inoculation.

*Experimental.*—The fungus was grown in penicillin flasks on a glucose–salts–corn-steep medium (Hervey, *Bull. Torrey Bot. Club*, 1947, 74, 476); after 3 weeks, when a full mat of mycelium had formed, the culture medium was drained off and extracted four times with methylene chloride (0·05 pt. by vol.). Evaporation of the combined extracts from 2 l. of medium gave *ca.* 0·1 g. of partly crystalline material. This was purified by vacuum-sublimation or by repeated recrystallisation from ethanol or acetic acid (charcoal). The product, heated on the Kofler block, began to sublime at *ca.* 200° and to melt with decomposition at *ca.* 250° (Found : C, 57·3; H, 5·15; OMe, 38·1. Calc. for $C_8H_8O_4$ : C, 57·15; H, 4·8; 2OMe, 37·0%). 2 : 5-Dimethoxybenzoquinone was prepared by the zinc chloride-catalysed addition of methanol to benzoquinone; its behaviour on heating was identical with that of the natural product.

Acknowledgments are made to Professor E. R. H. Jones, F.R.S., for his interest, to the Director of the Forest Products Research Laboratory, Princes Risborough, for the supply of fungus cultures, and to Mr. D. Buckley for a sample of 2 : 6-dimethoxybenzoquinone.
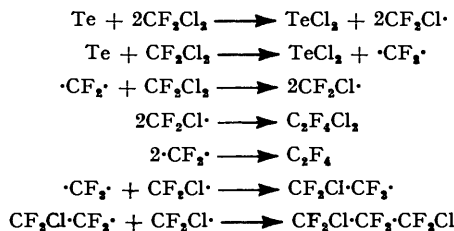
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## The Reaction between Tellurium and Dichlorodifluoromethane.

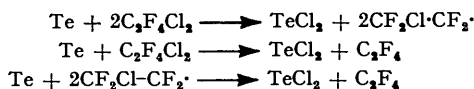By E. E. AYNSLEY and R. H. WATSON.

[Reprint Order No. 5791.]

A RECENT paper (Aynsley, *J.*, 1953, 3016) describes a convenient preparation of tellurium dichloride from dichlorodifluoromethane (Arcton 6) and molten tellurium. A first examination of the gaseous by-products of the reaction showed the presence in them of 1 : 2-dichlorotetrafluoroethane, indicating that the radical $CF_2Cl\cdot$ is involved in the reaction. This communication records a more detailed examination of the products formed at 500°. At this temperature the gaseous by-products contain 1 : 2-dichlorotetrafluoroethane (61·2%), tetrafluoroethylene (16·4%), and 1 : 3-dichlorohexafluoropropane (22·4%). In addition, a minute quantity of a volatile and foul-smelling substance containing tellurium is always formed at 500°, but never in sufficient quantity for identification.

If the radicals $CF_2Cl\cdot$ and $\cdot CF_2\cdot$ are involved then possible reactions which would lead to the by-products are :

$$Te + 2CF_2Cl_2 \longrightarrow TeCl_2 + 2CF_2Cl\cdot$$
$$Te + CF_2Cl_2 \longrightarrow TeCl_2 + \cdot CF_2\cdot$$
$$\cdot CF_2\cdot + CF_2Cl_2 \longrightarrow 2CF_2Cl\cdot$$
$$2CF_2Cl\cdot \longrightarrow C_2F_4Cl_2$$
$$2\cdot CF_2\cdot \longrightarrow C_2F_4$$
$$\cdot CF_2\cdot + CF_2Cl\cdot \longrightarrow CF_2Cl\cdot CF_2\cdot$$
$$CF_2Cl\cdot CF_2\cdot + CF_2Cl\cdot \longrightarrow CF_2Cl\cdot CF_2\cdot CF_2Cl$$

It is clear that the first reaction would explain the formation of $C_2F_4Cl_2$ but not that of the other two compounds, whereas if the second reaction is assumed to constitute the initiation then the presence of all three compounds can be accounted for. Moreover the reaction $CF_2Cl\cdot + CF_2Cl_2 \longrightarrow CF_3Cl + CFCl_2\cdot$ does not occur under these conditions since chlorotrifluoromethane was not found among the products.

An alternative scheme for the formation of tetrafluoroethylene and the $CF_2Cl\cdot CF_2\cdot$ radical is :

$$Te + 2C_2F_4Cl_2 \longrightarrow TeCl_2 + 2CF_2Cl\cdot CF_2\cdot$$
$$Te + C_2F_4Cl_2 \longrightarrow TeCl_2 + C_2F_4$$
$$Te + 2CF_2Cl-CF_2\cdot \longrightarrow TeCl_2 + C_2F_4$$

This avoids the assumption of the $\cdot CF_2\cdot$ radical but requires the further reaction of initial products with the tellurium. In the flow method used the chances of this are small. The further possibility that tetrafluoroethylene is formed by the pyrolysis of the dichloride is unlikely since the time spent by the vapours in the hot zone was short (~15 sec.). Furthermore the chlorine liberated would be likely to convert some tellurium dichloride into the tetrachloride, and this was absent from the solid product. It thus seems that the scheme involving $\cdot CF_2\cdot$ radicals is the more probable.

Not more than 0·2% of perfluoro*cyclo*butane was formed, this being the limit of detection in our process. Further the total weight of chlorine in the tellurium dichloride and in the three by-products equalled that lost by the dichlorodifluoromethane. The $C_3F_6Cl_2$ fraction, b. p. 35·5°, could be 1 : 2- or 1 : 3-dichlorohexafluoropropane, which are practically indistinguishable by boiling point, density, or refractive index. It is known that tetrafluoroethylene dimerises at 500° but that the formation of hexafluoropropylene, occurs only at higher temperatures (Atkinson and Trenwith, *J.*, 1953, 2082). Since this is the only likely compound from which the 1 : 2-dichloro-compound could be formed in our preparation, we have assumed that the $C_3F_6Cl_2$ is, in fact, the 1 : 3-dichloro-compound.

*Experimental.*—Arcton 6 (from Imperial Chemical Industries Limited), washed with potassium hydroxide solution and dried with concentrated sulphuric acid and with phosphoric oxide, was led over molten tellurium at 500° contained in the first section of a 25-mm. Pyrex tube, constricted at intervals of about 10 cm. to furnish six compartments. The tellurium dichloride was distilled forward in the gas stream from section to section and finally into a receiver. Beyond this was a 10-cm. tube containing glass wool and " Carbosorb " to remove small amounts of tellurium compounds carried forward in the gas stream. The unchanged Arcton 6 together with the gaseous by-products of the reaction then passed into a trap surrounded by liquid air. This trap was protected by a drying tube and a potassium hydroxide tube.

| Fraction | B. p. | $M$ (calc.) | $M$ (obs.) | Vol. % in distn. mixture | Vol. % of gaseous by-products | Weight (g.) |
|---|---|---|---|---|---|---|
| $C_2F_4$ ............ | −76·3° | 100 | 100·6 + 1·0 | 1·40 | 16·4 | 0·0876 |
| $CF_2Cl_2$ (un-decomp.) | −30·0 | 121 | — | 91·44 | — | 6·9296 |
| $C_2F_4Cl_2$ ...... | + 3·6 | 171 | 170·3 + 1·0 | 5·24 | 61·2 | 0·5617 |
| $C_3F_6Cl_2$ ...... | +35·5 | 221 | 222·0 + 3·0 | 1·92 | 22·4 | 0·2662 |

The contents of the trap were transferred to the bottom of a Podbielniak-type low-temperature fractionation column (Podbielniak, *Ind. Eng. Chem.*, 1931, 3, 177), and the amounts and molecular weights of the fractions were determined (see Table). Because the separation of the fractions was sharp, the apparatus was capable of detecting 1 pt. of a compound in 500 pt. of total material. 1·4750 g. of tellurium dichloride was collected, and the weight of chlorine in this together with the weights of carbon, fluorine, and chlorine in the by-products gave a C : F : Cl ratio of 1 : 2 : 2.

KING'S COLLEGE, NEWCASTLE-ON-TYNE, 1. *[Received, October 9th, 1954.]*

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# *Synthesis of Plant-growth Regulators. Part IV.\* Substituted α-2-Naphthyloxypropionic Acids.*

By (MRS.) P. M. POPE and D. WOODCOCK.

SUBSTITUTED β-naphthyloxyacetic acids (James and Woodcock, *J.*, 1951, 3418; 1953, 2089) have been examined for parthenocarpic activity, by using unpollinated tomato ovaries, and the effect of the position of the nuclear chlorine atoms on the activity of the molecule has been shown to be critical (Luckwill and Woodcock, unpublished). α-2-Naphthyloxy-

\* Part III, *J.*, 1954, 1721.

propionic acid has recently been found to be as effective as the corresponding acetic acid as a fruit-setting spray for outdoor tomatoes (Wain, *J. Hort. Sci.*, 1950, **25**, 249). Substituted α-2-naphthyloxypropionic acids, prepared for a similar investigation, are now described. Other members of this and similar series have already been tested for systemic fungicidal activity against chocolate spot of broad bean caused by *Botrytis fabae* (Byrde, Crowdy, and Woodcock, *Ann. Appl. Biol.*, 1953, **40**, 152).

Differences in the plant-growth regulating activity of optical isomers have been reported by several workers. Thus Kögl and Verkaaik (*Z. physiol. Chem.*, 1944, **280**, 167) found that (+)-α-3-indolylpropionic acid was some thirty times more active than the (−)-form in the Avena curvature test, and Smith and Wain (*Proc. Roy. Soc.*, 1951, *B*, **139**, 118) have shown that (+)-α-2-naphthyloxypropionic acid is similarly highly active in six different tests, whereas the (−)-form has little or no activity. Resolution of (±)-α-(3-chloro-2-naphthyloxy)propionic acid with cinchonine is described in the present paper. This acid provides yet another example of a racemic plant-growth substance providing a highly active (+)-form and a correspondingly inactive (−)-form on resolution.

*Experimental.*—α-2-*Naphthyloxypropionic acid.* The product, m. p. 114—115°, obtained on several occasions is interconvertible with that previously recorded by Bischoff (*Ber.*, 1900, **33**, 1390) as of m. p. 107—108°, and is probably identical with the modification reported by Fregda and Matell (*Arkiv Kemi*, 1951, **3**, 429). We are grateful to a referee for drawing our attention to the later paper. Each of the above forms gave the same *amide* and S-*benzylthiuronium salt*. The amide formed small rectangular prisms, m. p. 157—157·5°, from benzene (Found : C, 72·5; H, 6·0; N, 6·5. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·0; N, 6·5%). Fourneau and Balaceano (*Bull. Soc. chim.*, 1925, **37**, 1602) give m. p. 169° but no analytical results. The salt, prepared in aqueous solution, crystallised from 50% aqueous ethanol in rhombs, m. p. 159—159·5° (Found : C, 65·8; H, 5·7; N, 7·3; S, 8·2. $C_{21}H_{22}O_3N_2S$ requires C, 66·0; H, 5·8; N, 7·3; S, 8·4%).

*Substituted* α-2-*naphthyloxypropionic acids.* These were prepared by condensation of ethyl α-bromopropionate and the sodium salt of the appropriate naphthol, as described for the corresponding acetic acids in Part I, analytical details being tabulated below. Crystallisation from methanol or ethanol alone was avoided since esterification was rapid in hot solution. Thus, on one occasion *methyl* α-(3-*chloro*-2-*naphthyloxy*)*propionate* was isolated from the mother liquors, as large rhombs, m. p. 77—78° (Found : C, 63·4; H, 4·9; Cl, 13·5. $C_{13}H_{11}O_3Cl$ requires C, 63·5; H, 4·9; Cl, 13·4%).

*Resolution of* α-(3-*chloro*-2-*naphthyloxy*)*propionic acid.* A solution of the (±)-acid (5·0 g.) and cinchonine (5·8 g.) in boiling methanol (50 ml.) was diluted with hot water and allowed to cool. The *cinchonine salt* of the (−)-acid, which gradually separated, was twice recrystallised from aqueous methyl alcohol; monoclinic prismatic plates, which decomposed at 148—150° after softening *ca.* 125°, were obtained (Found : C, 68·2; H, 6·2; loss in vacuum at 110°, 3·2. $C_{13}H_{11}O_3Cl,C_{19}H_{22}ON_2,H_2O$ requires C, 68·2; H, 6·2; loss 3·2%); $[\alpha]_D^{21}$ +33·2° (*c*, 1·022 in MeOH). Concentration of the mother liquors yielded a little more of the same salt, and

*Substituted* α-2-*naphthyloxypropionic acids,* $RR'C_{10}H_6 \cdot O \cdot CH(Me \cdot)CO_2H.$

| | | Found, % | | | | Required, % | | |
|---|---|---|---|---|---|---|---|---|
| RR′ | M. p. | C | H | Cl or N | Formula | C | H | Cl or N |
| 3-Cl,H ......... | 175—176° | 62·1 | 4·4 | 14·1 | $C_{13}H_{11}O_3Cl$ | 62·3 | 4·4 | 14·2 |
| 4-Cl,H ......... | 123—124 | 62·3 | 4·3 | 14·2 | ,, | ,, | ,, | ,, |
| 5-Cl,H ......... | 173—174 | 62·2 | 4·4 | 14·2 | ,, | ,, | ,, | ,, |
| 6-Cl,H ......... | 157—158 | 62·3 | 4·2 | 14·1 | ,, | ,, | ,, | ,, |
| 8-Cl,H ......... | 132—133 | 62·3 | 4·2 | 14·2 | ,, | ,, | ,, | ,, |
| 5 : 6-Cl₂ ........ | 148—149 | 55·0 | 3·4 | 24·8 | $C_{13}H_{10}O_3Cl_2$ | 54·8 | 3·5 | 24·9 |
| 5-NO₂,H ...... | 200—201 | 60·5 | 4·3 | N, 5·1 | $C_{13}H_{11}O_5N$ | 59·8 | 4·2 | 5·4 |
| 8-NO₂,H ...... | 183—184 | 59·8 | 4·4 | N, 5·0 | ,, | ,, | ,, | ,, |

Solvent : aqueous methanol for the chloro-compounds, aqueous acetic acid for the nitro-compounds.

eventually the cinchonine salt of the (+)-acid was obtained as a gum. The two salts were separately dissolved in chloroform, the solutions shaken with dilute ammonia solution, and the acids recovered from the alkaline layers were crystallised twice from aqueous methanol. The (−)-*acid*, obtained as a matte of fine needles, m. p. 175—176° (Found : C, 62·5; H, 4·4; Cl, 13·8. $C_{13}H_{11}O_3Cl$ requires C, 62·3; H, 4·4; Cl, 14·2%), had $[\alpha]_D^{21}$ −56·8° (*c*, 1·012 in MeOH). The (+)-*acid* crystallised in fine needles, m. p. 175—176°, $[\alpha]_D^{20}$ +55·6° (*c*, 0·990 in MeOH)

(Found : C, 62·3; H, 4·4; Cl, 14·1%). Crystallisation of equimolecular proportions of the (+)- and the (−)-acid from aqueous methanol yielded the (±)-acid, m. p. 175—176°.

The authors thank Mr. J. F. Harris for the analytical results.

DEPARTMENT OF AGRICULTURE AND HORTICULTURE,
UNIVERSITY OF BRISTOL, RESEARCH STATION,
LONG ASHTON, BRISTOL. *[Received, October 8th, 1954.]*

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# Oxidation of Some Enediols with Selenium Dioxide.

## By J. R. HOLKER.

COMPOUNDS of the type HO·CR:CR'·OH are generally readily oxidised to R·CO·CO·R' with, *e.g.*, iodine, Tillmann's reagent (2 : 6-dichlorophenol–indophenol), and silver oxide. The first two reagents can be applied to the quantitative estimation of the enediol group (see, *e.g.*, von Euler, " Sammlung chemischer und chemisch-technischer Vorträge," Enke, Stuttgart, 1950, Heft 50), but are not always suitable for preparatory work. Silver oxide and other reagents are usually satisfactory only when the product is stable to further oxidation.

We have found that a number of enediols possessing an α-carbonyl group are rapidly and quantitatively oxidised in aqueous or alcoholic solution by selenium dioxide. The reaction is slightly exothermic. After removal of precipitated selenium, recovery of the oxidation product is extremely simple.

Mesoxaldehyde was obtained from reductone, and use of excess of selenium dioxide did not cause further oxidation to mesoxalic acid. The preparation of crystalline dehydro-L-ascorbic acid requires anhydrous conditions, and by using chlorine in dry methanol, Pecherer (*J. Amer. Chem. Soc.*, 1951, **73**, 3827) obtained a 39% yield; oxidation with selenium dioxide in anhydrous ethanol readily afforded a high yield of the crystalline dehydro-acid. Svirbely (*Biochem. J.*, 1938, **32**, 467) observed a low content of ascorbic acid in the organs of selenite-poisoned rats. Dihydroxymaleic acid in aqueous solution gave dihydroxytartaric acid, isolated as the sparingly soluble sodium salt. The deep red reduced form of perinaphthindanetrione is rapidly re-oxidised to the trione in alcoholic solution. The reaction will be extended to other enediols as these become available from another investigation.

This reaction has been extended to the use of selenium dioxide as a spray for paper chromatograms of reductone. Reddish-brown spots of selenium are produced in the cold and their stability to light and air make the reagent more suitable than silver nitrate or Tillmann's reagent. Aqueous solutions of reductone slowly decompose. Paper chromatograms of such solutions gave no other spot with selenium dioxide, indicating that the decomposition products are not enediols.

*Experimental.*—*Mesoxaldehyde.* Reductone (Cocker *et al.*, *J.*, 1950, 2052) was rapidly recrystallised from water (60°), with considerable loss, and dried (P₂O₅). This material [1·0 g.; m. p. 149° (decomp.)] in water (10 ml.) was shaken for 1 hr. with selenium dioxide (0·6 g.) in water (10 ml.). The mixture was kept overnight, selenium (0·45 g.) filtered off, and the filtrate treated with aqueous phenylhydrazine acetate. The precipitated mesoxaldehyde bisphenyl-hydrazone had m. p. 174—175° after recrystallisation. Moubasher (*J. Biol. Chem.*, 1948, **176**, 532) gives m. p. 176°.

Use of a large excess (2·0 g.) of selenium dioxide gave only 0·48 g. of selenium.

*Dehydro-L-ascorbic acid.* Dried selenium dioxide (0·55 g.) (1 hr. at 100°) was shaken for 1 hr. with L-ascorbic acid (1·74 g.) in freshly purified ethanol (20 ml.); the acid slowly dissolved and selenium was precipitated. The following day the solution, after removal of selenium (96%) by filtration, was evaporated and finally heated to 100° *in vacuo*. The syrup slowly yielded a semisolid which solidified completely when boiled with a few ml. of xylene. The powder had m. p. 222—224° (decomp.); Pecherer (*loc. cit.*) gives m. p. 220—225° (decomp.). It gave the bright orange 2 : 4-dinitrophenylosazone, m. p. 274—275°; Penney and Zilva (*Biochem. J.*, 1943, **37**, 404) give m. p. 280°. An aqueous solution of the dehydro-acid exhibited typical mutarotation; it also gave the characteristic pink colour, deepening with heat, with glycine (Pecherer, *loc. cit.*).

Oxidation was also carried out in methanol. The syrup produced crystallised when boiled with xylene for a few minutes.

*Dihydroxytartaric acid.* Selenium dioxide (0·6 g.) in water (20 ml.) was shaken with dihydroxymaleic acid (1·5 g.) for 2 hr. Selenium was filtered off and the filtrate neutralised with 10% sodium hydroxide solution. After 2 hr. at 0°, the insoluble sodium dihydroxytartrate was filtered off, washed, and dried ($P_2O_5$); the yield was 0·75 g. It gave diketosuccinic acid osazone, m. p. 200—201° (decomp.); Moubasher (*loc. cit.*) gives m. p. 200°. When this oxidation was carried out in 95% ethanol the product was an oil which did not crystallise after several days at 0°.

*Perinaphthindanetrione.* This was obtained from the reduced form (dihydroxyperinaphthindenone) in alcohol solution. After crystallisation from water it had m. p. and mixed m. p. 267—269° (decomp.).

*Paper chromatography of reductone.* Freshly prepared aqueous reductone (2·5%; 0·005 ml.) was chromatographed on Whatman No. 1 paper for 16 hr., the upper phase of a *n*-butanol–acetic acid–water mixture (100 : 20 : 50 v/v) being used. After being roughly dried at room temperature for 30 min. the paper was sprayed with 1% selenium dioxide solution. A red-brown spot ($R_F$ 0·58—0·59) appeared immediately. Weygand (*Arkiv Kemi*, 1951, **3**, 11) gives reductone $R_F$ 0·59—0·64. The same reductone solution, after 48 hours in a stoppered tube gave only one weak spot with selenium dioxide ($R_F$ 0·58).

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# Quantitative Analysis of Mixtures of Sodium, Potassium, Magnesium, and Calcium by Paper Chromatography.

By D. R. TRISTRAM and C. S. G. PHILLIPS.

FOR a number of purposes, especially the characterisation of certain minerals, a simple method is required for the estimation of sodium, potassium, calcium, and magnesium, in the form of their chlorides, in the presence of one another and of hydrochloric acid, and with an accuracy of 2—3%. This paper describes how such analyses may be effected by means of paper chromatography. After the chromatography, the chloride bands are converted on the paper into the equivalent amount of metallic silver. For quantitative analysis the silver bands are dissolved in nitric acid, and the silver titrated with ammonium thiocyanate. The method is suitable for 100 μg. to 10 mg. of the salts.

## EXPERIMENTAL

*Chromatography.*—The separation of the alkali metals and of the alkaline earths on cellulose as chlorides was first described by Burstall, Davies, Linstead, and Wells (*J.*, 1950, 516). We have found Whatman 540 (supplied in strips) the best paper. It gives a low background and retains its strength when wet. The best solvent found was laboratory ethyl alcohol containing an additional 6% of water. The solution to be analysed is run on to the strips from a micro-burette, by stroking the tip of the burette across the strip about 2 in. from the end. The strip is then dried for a few minutes, and placed in the normal paper chromatography apparatus. After chromatography for 12—20 hr. the strips are removed and the alcohol allowed to evaporate. The strip is dipped into 0·1N-silver nitrate, which causes all the chloride ion to be precipitated on the strip as silver chloride. The strip is then thoroughly washed with distilled water, soaked in a bath of photographic developer to reduce the silver chloride to metal, and finally washed again. At this stage the bands show up very clearly and enable a rough quantitative analysis to be made by inspection.

*Quantitative Determination.*—The silver bands are cut out and placed separately in small (2″) evaporating dishes. 2N-Nitric acid (5 ml.) is then added to each dish, and they are warmed until the bands are decolorised. When cool, crystals of ferric nitrate are added, and the solutions titrated with 0·1N-ammonium thiocyanate from a microburette (capacity 0·1 ml.) calibrated in thousandths of a ml. The paper remains in the dishes during the titrations.

<div align="center">RESULTS AND DISCUSSION</div>

*Accuracy.*—The accuracy of the conversion and titration procedure, tested by carrying out the above operations without any chromatography, is 1—2%. The overall accuracy thus depends upon the chromatography, the two main sources of error being the paper and incomplete separation. Traces of calcium, magnesium, and other metals on the paper give rise to diffuse bands. Anything which reacts with silver nitrate produces a background. For these reasons ordinary filter paper is not satisfactory. Incomplete separation of the sodium and the calcium bands occurs when insufficient time is allowed for the chromatography. Good results are obtained after 12—20 hours, the solvent front then having passed off the end of the paper.

The Table gives results of four runs on solutions made up by the senior and analysed by the junior author. The values quoted are in microequivalents (ml. of 0·1N-ammonium thiocyanate × 100).

| | K | Na | Ca | Mg | | K | Na | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|
| *Mixture A.* | | | | | *Mixture C.* | | | | |
| Correct .................. | 20·0 | 20·0 | 20·0 | 20·0 | Correct .................. | 22·8 | 17·1 | 28·6 | 11·4 |
| Estimated ............... | 18·5 | 19·0 | 20·0 | 20·8 | Estimated ............ | 20·6 | 16·3 | 27·6 | 12·7 |
| Error (% of total) ... | −2 | −1·2 | 0 | +1 | Error (% of total) ... | −2·8 | −1 | −1·3 | +1·6 |
| *Mixture B.* | | | | | *Mixture D.* | | | | |
| Correct .................. | 14·5 | 14·5 | 35·5 | 14·5 | Correct .................. | 16·0 | 8·0 | 16·0 | 4 ·0 |
| Estimated ............... | 13·9 | 14·3 | 34·9 | 15·3 | Estimated ............ | 15·0 | 8·7 | 14·6 | 38·4 |
| Error (% of total) ... | −0·8 | −0·3 | −0·8 | +1 | Error (% of total) ... | −1·3 | +0·9 | −1·8 | −2 |



*Amounts (microequivs.) in mixture*
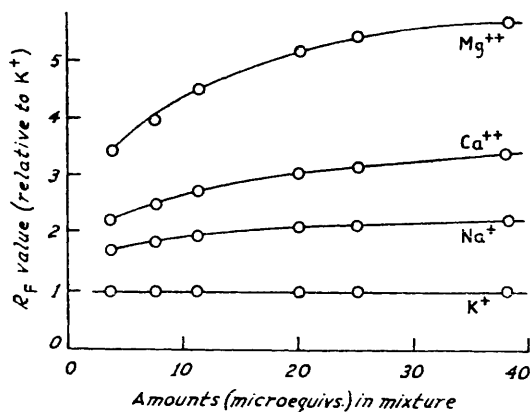
*Hydrochloric Acid.*—The presence of hydrochloric acid in concentrations of the same order as the metal ions leads to no appreciable error. The acid is carried down near the solvent front and runs off the end of the strip. This is an attractive feature of the method, if, for example, a dolomite has been brought into solution with hydrochloric acid.

*Ammonium, Lithium, Barium, and Strontium.*—Excellent separations of potassium, sodium, ammonium, and lithium, and of barium, strontium, and calcium have been obtained by the same methods, and we have made quantitative analyses of mixtures of potassium, sodium, calcium, magnesium, and lithium. In each of these mixtures the bands appear in the order written.

*Displacement.*—The fact that sodium and calcium are satisfactorily separated suggests that they must possess very different $R_F$ values. However, when the two ions are run separately there is little difference in $R_F$ value. This seems to indicate that displacement is involved in the early stages of the separations. The effect may also be illustrated by the results in the Figure, in which the $R_F$ values of sodium, calcium, and magnesium (relative to potassium) increase up to a limit with the concentration of the sample on the strip.

## Addendum : *Chemical Action of Ionizing Radiations in Aqueous Solutions. Part XIII.\* Absolute Yield of the Ferrous Sulphate Dosimeter.*

By F. T. FARMER, T. RIGG, and J. WEISS.

[Reprint Order No. 5819.]

SINCE the paper under the above title was submitted the National Physical Laboratory have made known (Wyckoff, Aston, and Smith, *Brit. J. Radiol.*, 1954, **27**, 325) that their standardisation of dosimeters is subject to a further correction of about 4% in the same direction as the 3% already referred to in our paper. This will further reduce the value of $G$ from 16·2 there quoted, and will bring the yield of the ferrous $\longrightarrow$ ferric reaction for $X$-rays (200 kv) to $G = 15·6 \pm 0·8$ moles per 100 ev.

KING'S COLLEGE, NEWCASTLE-ON-TYNE, 1.

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## An Improved Synthesis of D-Xylose 5-(Barium Phosphate).

By P. A. J. GORIN, L. HOUGH, and J. K. N. JONES.

[Reprint Order No. 5772.]

D-XYLOSE 5-(BARIUM PHOSPHATE) was synthesised by Levene and Raymond (*J. Biol. Chem.*, 1933, **102**, 347) in rather low yield (16—18%) by the reaction of phosphorus oxychloride with 1 : 2-O-*iso*propylidene-D-xylose (I) in pyridine followed by partial hydrolysis of the product. In a successful attempt to improve this yield, the derivative (I) was treated in pyridine with 1 mol. of diphenyl phosphorochloridate (Foster, Overend, and Stacey, *J.*, 1951, 980) to give a good yield of the crystalline 5-(diphenyl phosphate) (II). Catalytic hydrogenation then gave the 1 : 2-O-*iso*propylidene salt (III) which was partially hydrolysed with mineral acid to give D-xylose 5-(barium phosphate) (IV).
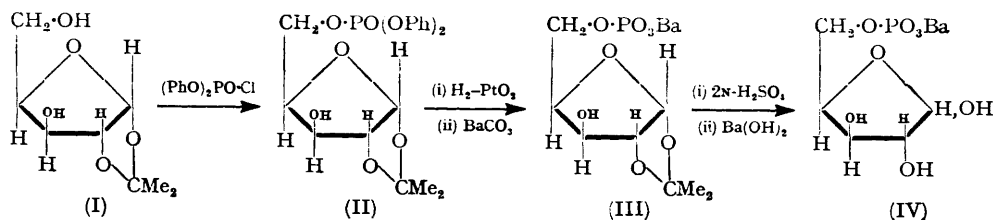


Like triphenylmethyl chloride and other activated chlorides, diphenyl phosphorochloridate reacts preferentially with the primary alcohol group giving, in this case, the 5- and not the 3-phosphate. The resistance of the phosphate ester (IV) to conditions of acid hydrolysis that would completely hydrolyse a 3-phosphate of xylose (Levene and Raymond, *J. Biol. Chem.*, 1934, **107**, 75) confirms the structure of the product.

It is interesting that the *iso*propylidene group in (III) is remarkably stable to acid hydrolysis, requiring 2N-sulphuric acid at 100° for 3 hours for complete removal. This stability is clearly attributable to the presence of the phosphate group, since in its absence, the *iso*propylidene group can be removed by 0·01N-sulphuric acid at 100° in 1 hour.

*Experimental.*—Determinations of carbon and hydrogen are by Mr. B. S. Noyes of Bristol.

1 : 2-O-iso*Propylidene*-D-*xylose* 5-(*diphenyl phosphate*) (II). Diphenyl phosphorochloridate (2·5 g.; 1·1 mol.) was added to 1 : 2-O-*iso*propylidene-D-xylose (1·74 g.) in dry ice-cold redistilled pyridine (3 c.c.). After 10 min. at 0° the solution was set aside at room temperature for 1 hr., then shaken with chloroform (25 c.c.) and aqueous sodium hydrogen carbonate (25 c.c.); the chloroform layer was separated, washed with water, dried ($MgSO_4$), filtered, and evaporated to a syrup (3·39 g.) which crystallised. Recrystallisation from light petroleum (b. p. 60—80°) gave the *ester* as needles, m. p. 99—100°, $[\alpha]_D^{20}$ +3° (*c*, 1·48 in $CHCl_3$) (Found : C, 56·7; H, 5·6; P, 7·6. $C_{20}H_{23}O_8P$ requires C, 56·9; H, 5·5; P, 7·3%).

* See *J.*, 1954, 3248.

1 : 2-O-iso*Propylidene*-D-*xylose* 5-(*barium phosphate*) (III). A solution of the ester (II) (810 mg.) in 32% aqueous methanol (66 c.c.) containing Adams platinic oxide (75 mg.) was shaken in hydrogen at slightly more than 1 atm. After 8 hr., when uptake of hydrogen had ceased, the catalyst was filtered off and the solution neutralised with barium carbonate. Insoluble material was filtered off and the filtrate evaporated under reduced pressure to a white solid (610 mg.), $[\alpha]_D^{20}$ $-2 \cdot 5°$ (*c*, 3·0 in MeOH).

D-*Xylose* 5-(*barium phosphate*) (IV). The *iso*propylidene salt (434 mg.) in 2N-sulphuric acid (8 c.c.) was heated at 100° for 3 hr. The solution was adjusted to pH 8 by aqueous barium hydroxide solution and filtered. The precipitate was washed and the filtrate evaporated under reduced pressure to a small volume. Paper chromatography showed the presence of unchanged (III) and xylose in addition to (IV). An excess of acetone was added to the aqueous solution, and the precipitate filtered and then triturated with a little ethanol to remove traces of impurities. The product [220 mg.; 47% overall yield from (I)] had $[\alpha]_D^{20}$ $+8°$ (*c*, 0·85 in $H_2O$) [Found : C, 19·9; H, 3·2. Calc. for $(C_5H_{10}O_8P)_2Ba$: C, 20·2; H, 3·4%]. Levene and Raymond (*loc. cit.*, 1933) record $[\alpha]_D^{22}$ $+5°$ (*c*, 2·0 in $H_2O$). It gave on paper chromatograms (Whatman No. 542 filter paper; ethyl acetate–acetic acid–formic acid–water, 18 : 3 : 1 : 4 v/v) one discrete spot (rate 0·3 relative to galactose) which was pink with the *p*-anisidine hydrochloride spray (Hough, Jones, and Wadman, *J.*, 1950, 1702) and blue with the ammonium molybdate–perchloric acid–phosphate spray (Hanes and Isherwood, *Nature*, 1949, **164**, 1107).

To a solution of D-xylose 5-(barium phosphate) (40·32 mg.) in water (25 c.c.) was added 6·13N-sulphuric acid (5 c.c.), the precipitate filtered off, and the filtrate heated at 100°. The liberation of inorganic phosphate was followed by the method of Foster, Overend, and Stacey (*J.*, 1951, 987); 50% hydrolysis was observed after 270 min. This result is similar to that observed by Levene and Raymond (*loc. cit.*, 1934) when they hydrolysed their product with N-hydrochloric acid.

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# *The Isolation of Oligosaccharides from Gums and Mucilages.  Part IV.\* The Isolation of* 3-O-β-L-*Arabopyranosyl*-L-*arabinose from Lemon Gum.*

By P. ANDREWS and J. K. N. JONES.

PARTIAL hydrolysis of lemon gum yields a mixture of neutral and acidic mono- and oligo-saccharides. So far L-arabinose, D-galactose, D-glucuronic acid, a compound that was probably 4-(4-O-methyl-D-glucuronopyranosyl)-D-galactose (Connel, Hainsworth, Hirst, and Jones, *J.*, 1950, 1696), and 4-(4-O-methyl-α-D-glucuronopyranosyl)-L-arabinose have been separated and characterised (Andrews and Jones, *J.*, 1954, 1724). This publication records the isolation from lemon gum of 3-O-β-L-arabopyranosyl-L-arabinose, which was identified by its rate of movement on the paper chromatogram, by its high positive optical rotation, and by the fact that its phenylosazone was indistinguishable by *X*-ray diffraction analysis from the osazone of an authentic specimen of the disaccharide prepared from larch ε-galactan (Jones, *J.*, 1953, 1672). This arabopyranose-containing disaccharide is thus a constituent of larch ε-galactan, peach gum, cherry gum (Andrews, Ball, and Jones, *J.*, 1953, 4090), golden apple gum, and lemon gum. It is also present in the oligosaccharides produced when some commercial samples of gum acacia are hydrolysed but not in those from gum ghatti (unpublished results).

When arabinose is kept in 6N-hydrochloric acid for some days condensation occurs, giving a complex mixture of di- and oligo-saccharides in about 10% yield. Lemon gum on autohydrolysis yields, first, a mixture of arabinose and a neutral pentose-containing disaccharide, 3-O-β-L-arabopyranosyl-L-arabinose. On prolonged autohydrolysis the

\* Part III, *J.*, 1954, 4134.

latter sugar disappears because it is hydrolysed to arabinose. Similar results are observed when lemon gum is hydrolysed with cold dilute hydrochloric acid. However, when arabinose undergoes reversion in the presence of an acid catalyst, the concentration of di- and oligo-saccharides increases until an equilibrium mixture is reached. It is inferred that the neutral arabinose-containing disaccharide isolated from lemon gum is a true component of the polysaccharide and that it is not an artefact produced by reversion. Nevertheless when the hydrolysis of gums or mucilages is carried out in concentrated solution in the presence of hydrochloric or sulphuric acid, reversion products may be formed in considerable quantity and their isolation may lead to incorrect conclusions as to structure. Further details will be published later.

## EXPERIMENTAL

Chromatographic separations were carried out on Whatman No. 1 paper with (a) ethyl acetate–acetic acid–formic acid–water (18 : 3 : 1 : 4), and (b) *n*-butanol–pyridine–water (10 : 3 : 3). *p*-Anisidine hydrochloride was used as spray. Optical rotations were determined at 20° ± 2° in $H_2O$. Evaporation of solutions was carried out under reduced pressure.

*Hydrolysis of Lemon Gum with Cold Dilute Sulphuric Acid.*—Lemon gum (15 g.) was dissolved in cold N-sulphuric acid (150 c.c.), and the solution set aside at 20° ± 5°. Samples were examined at intervals on the paper chromatogram. After 24 weeks (cf. Andrews and Jones, *J.*, 1954, 1724) the solution was brought to pH 5 with barium hydroxide, concentrated to 40 c.c., and poured into alcohol. The precipitated barium salt of the degraded gum was collected, dried, and exhaustively extracted with methanol. The filtrate and alcoholic extracts were combined and evaporated to a syrupy mixture (6·5 g.). A portion (6·0 g.) of this was fractionated on a column of cellulose with ethyl acetate–acetic acid–water (9 : 2 : 2 v/v) as eluant. Those fractions of the effluent containing arabinose and galactose were discarded. Those containing the disaccharide, which was chromatographically pure, were combined and the solvent was evaporated. There remained a syrupy sugar which was purified by dissolution in water and filtration through a bed of charcoal. The solvent was removed from the filtrate and the residual syrup (98 mg.) examined chromatographically. It appeared homogeneous in solvents (a) and (b), and was indistinguishable from 3-*O*-β-L-arabopyranosyl-L-arabinose, prepared from cherry gum and larch ε-galactan. Its rate of movement relative to sucrose was 1·5 in solvent (a) and 1·0 in solvent (b), and it had $[\alpha]_D$ +196° ± 10° (c, 4·2). On acidic hydrolysis arabinose was the only sugar detectable on the chromatogram. Warming it with phenylhydrazine acetate solution gave an osazone in good yield, having m. p. 240° (block) after recrystallisation from aqueous alcohol (Found : C, 57·1; H, 6·1; N, 12·4. Calc. for $C_{22}H_{28}O_7N_4$ : C, 57·4; H, 6·1; N, 12·2%). Its m. p., which depends upon the rate of heating, was not depressed on admixture with an authentic sample. The *X*-ray diffraction pictures of this osazone and of an authentic sample were identical.

*Autohydrolysis of the Gum.*—Ash-free lemon gum (1·27 g.) was heated in water (10 c.c.) at 90°. At intervals samples were examined on the paper chromatogram. After 12 hours' heating arabinose and a trace of a pentose-containing disaccharide were detected. Thereafter the concentration of arabinose and the disaccharide increased until after 48 hr. the concentration of disaccharide appeared to reach a maximum, and at about this time galactose was detected on the chromatogram. After 60 hr. the galactose and arabinose concentrations had increased considerably while that of the disaccharide had diminished. At this stage the cooled solution was poured into alcohol, the precipitate of degraded gum filtered off, and the alcoholic solution evaporated to a syrup. Chromatography of this syrup (solvent b) indicated the presence of arabinose, galactose, and 3-*O*-β-L-arabopyranosyl-L-arabinose. When solvent (a) was used additional spots corresponding to the presence of acidic disaccharides appeared.

THE UNIVERSITY, BRISTOL.
QUEEN'S UNIVERSITY, KINGSTON, ONTARIO, CANADA.