Deoxy-sugars. Part XXVII. The Catalytic Oxidation of Some Derivatives of 2-Deoxy-D-hexoses.*

By W. G. Overend, F. Shafizadeh, M. Stacey, and G. Vaughan.

[Reprint Order No. 5245.]

Overend, Shafizadeh, and Stacey (*J.*, 1951, 1487) described the preparation of some derivatives of 2-deoxy-D-galacturonic acid from methyl 2-deoxy-3 : 4-*O*-*iso*propylidene-α-D-galactoside by oxidation with alkaline potassium permanganate. We now describe the selective oxidation of 2-deoxy-sugars in alkaline solution by gaseous oxygen in the presence of platinum black (cf. Fernández-Garcia, Amarós, Blay, Santiago, Soltero-Diaz, and Colón, *El Crisol* (*Puerto Rico*), 1950, **4**, 40; *Chem. Abs.*, 1951, **45**, 555; Barker, Bourne, and Stacey, *Chem. and Ind.*, 1951, 970; Marsh, *Nature*, 1951, **168**, 602; Mehltretter, Alexander, Mellies, and Rist, *J. Amer. Chem. Soc.*, 1951, **73**, 2424).

Methyl 2-deoxy-α-D-glucopyranoside thus afforded methyl 2-deoxy-α-D-glucosiduronic acid which was converted through the methyl ester into the crystalline amide. Likewise, crystalline methyl 2-deoxy-α-D-galactosiduronamide was prepared from methyl 2-deoxy-α-D-galactopyranoside. Attempts to oxidise methyl 2-deoxy-αβ-D-ribofuranoside by this method were inconclusive : oxidation occurred, but the labile sugar also partly decomposed and the product was impure. 2-Deoxy-D-glucose gave a crystalline 2-deoxy-D-glucarodilactone (cf. Overend *et al.*, *loc. cit.*, for the oxidation of 2-deoxy-D-galactose with dinitrogen tetroxide, and of 2-deoxy-D-galacturonic acid with bromine, procedures which afford a monolactone of 2-deoxy-D-galactaric acid). This dilactone, presumably the 1 : 4-3 : 6-dilactone, reduced Fehling's solution and in alkaline solution had a strong absorption band at 212 mμ., which was modified on acidification. In these respects it resembles the dilactones of D-glucaric and D-mannaric acid (Smith, *J.*, 1944, 510, 571, 634; Heslop and Smith, *J.*, 1944, 575, 638; Haworth, Heslop, Salt, and Smith, *J.*, 1944, 217) and so presumably undergoes the same type of isomerization.

Experimental.—Methyl 2-deoxy-α-D-glucosiduronamide. A gentle stream of pure oxygen was passed through a solution of methyl 2-deoxy-α-D-glucopyranoside (2 g.) and potassium hydrogen carbonate (3 g.) in water (250 c.c.) at 55°. Platinised charcoal (1·4 g.; 13% of Pt) was added and the solution was stirred mechanically. After one week when reaction was complete as indicated by passing the excess of oxygen through barium hydroxide solution (no more carbon dioxide), the mixture was filtered and evaporated to dryness. The residue was extracted with dry methanol, and after concentration of the extract to 10 c.c., methyl iodide (10 c.c.) was added, and the whole was heated under reflux for 7 hr. After evaporation, the product was extracted with ethyl acetate. The residue from this extraction was re-treated with methyl iodide, and the above procedure was repeated thrice, until a residue was obtained which gave only a very weak Tollens test for uronic acids. The combined ethyl acetate extracts were evaporated and the crude product was dissolved in dry methanol which had been saturated at 0° with ammonia. After being kept at 0° for 18 hr., the mixture was evaporated and afforded a crystalline residue, which was recrystallised from methanol. *Methyl 2-deoxy-α-D-glucopyranosiduronamide* (0·74 g., 34·4%) was obtained as colourless prisms, m. p. 192°, $[\alpha]_D^{19}$ +119·6° (*c*, 0·81 in MeOH) (Found : C, 44·1; H, 6·8; N, 7·4. $C_7H_{13}O_5N$ requires C, 44·0; H, 6·8; N, 7·3%). It gave a strong positive test for uronic acid with Tollens naphtharesorcinol reagent. Hydrolysis afforded only a syrup.

Methyl 2-Deoxy-α-D-galactosiduronamide. Methyl 2-deoxy-α-D-galactopyranoside (1·2 g.) and potassium hydrogen carbonate (1·6 g.) and 13% platinised charcoal (0·7 g.) in water (200 c.c.) were treated with pure oxygen for 8 days at 60°. Reaction was then complete and the mixture was worked up as described above. Methyl 2-deoxy-α-D-galactosiduronamide (0·3 g., 26·7%) had m. p. 202°, $[\alpha]_D^{16}$ +104° (*c*, 1·01 in MeOH) (Found : C, 44·1; H, 6·6; N, 7·2. Calc. for $C_7H_{13}O_5N$: C, 44·0; H, 6·8; N, 7·3%). Overend *et al.* (*loc. cit.*) report m. p. 203°, $[\alpha]_D$ +105·4° in MeOH.

2-Deoxy-D-glucosaccharodilactone (*2-deoxy-D-glucaric dilactone*). 2-Deoxy-D-glucose (2·5 g.) and potassium hydrogen carbonate (3·5 g.) in water (250 c.c.) were oxidised in the presence of platinum black as above. The filtered mixture was then passed through Amberlite IR–120

* Part XXVI, preceding paper.

(H), the effluent evaporated to dryness, and the residue extracted with hot ethyl acetate (300 c.c.). Evaporation of the extract afforded a syrup which crystallised on trituration with methanol. On recrystallisation from ethyl acetate *2-deoxy-D-glucarodilactone* (0·71 g., 29·6%) formed colourless needles, m. p. 139·5°, $[\alpha]_D^{25}$ +170° (*c*, 0·48 in MeOH) (Found: C, 45·9; H, 4·0. $C_6H_6O_5$ requires C, 45·6; H, 3·8%). It strongly reduced Fehling's solution and in 0·1N-sodium hydroxide exhibited absorption at 212 mμ. (ε 10,000) which was modified on acidification.

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Solubility and Chromatography of Hydroxybenzoic Acids.

By P. A. ONGLEY.

[Reprint Order No. 5272.]

MANY physiologically active compounds are chelated (cf. Davies, *Chem. and Ind.*, 1953, 614),* and because of the far greater antirheumatoid activity of 2 : 6-dihydroxybenzoic acid, than of the 2-mono- and of the 2 : 5-di-hydroxy-acid (Reid, Watson, Cochran, and Sproull, *Brit. Med. J.*, 1951, II, 321), the state of the 2 : 6-acid was studied. Since 2-nitroresorcinol (Baker, *J.*, 1933, 687; Hilbert, Wulf, Hendricks, and Liddell, *J. Amer. Chem. Soc.*, 1936, **58**, 548), 1 : 8-dihydroxyanthraquinone, and 2 : 2′-dihydroxybenzophenone are all dichelated (Hilbert, Wulf, Hendricks, and Liddell, *loc. cit.*), dichelation in 2 : 6-dihydroxybenzoic acid would not be surprising. Although Baker (*Nature*, 1936, **137**, 236) suggested that the very low pK_a of the acid may well be due to dichelation, the problem has never been thoroughly investigated.

The low solubility of hydroxybenzoic acids in non-polar solvents precludes any comparative examination of spectra, either of different acids in these solvents or of the same acid in polar and non-polar solvents, (cf. the work of Morton and Stubbs, *J.*, 1940, 1347) on the hydroxy-benzaldehydes and -acetophenones. Comparison of partition ratios (from which may be deduced data on the dissociation of the dimeric to the monomeric acids, cf. Moelwyn-Hughes, *J.*, 1940, 850) is likewise impossible. It was therefore decided to compare the solubilities of benzoic acid and various hydroxy- and methoxy-derivatives in several solvents. Although these data can only give a summation of the variations in ΔS and ΔH, and more information would be obtainable by calculating H from solubilities at several temperatures, the results so far obtained are sufficiently significant to merit being recorded.

p*S values of substituted benzoic acids in various solvents.*

	H_2O	N-NaCl	N-Salt *	C_6H_6	$CHCl_3$	CCl_4	*cyclo*Hexane
Benzoic acid	1·556	1·714	1·372	0·118	−0·188	0·291	1·038
o-Hydroxy-	1·793	1·991	1·413	1·239	0·680	1·644	2·192
m-Hydroxy-	1·275	1·422	—	3·198	2·629	4·699	>6·000
p-Hydroxy-	1·370	1·530	—	3·432	2·991	5·000	4·398
2 : 4-Dihydroxy-...	1·493	1·517	—	2·412	1·897	5·301	5·000
2 : 5-Dihydroxy-...	0·845	0·991	—	3·403	1·900	>6·000	>6·000
2 : 6-Dihydroxy-...	1·261	1·714	1·085	1·896	0·539	2·556	3·627
3 : 4-Dihydroxy-...	1·068	1·188	—	>6·000	3·311	4·398	>6·000
o-Methoxy-	1·507	1·672	—	0·674	−0·225	1·605	1·241
m-Methoxy-.....	1·028	1·195	—	0·398	−0·049	0·737	1·851
p-Methoxy-	2·620	2·979	—	1·714	1·130	—	—
2 : 6-Dimethoxy-	1·638	1·695	—	1·796	0·697	—	4·000

* N-Solution of the sodium salt of the benzoic acid.

Experimental.—The acids were either of "AnalaR" standard or were recrystallized before use. Solubilities were measured by rotating tubes of solvent and solute for at least 8 hr. at

* In this communication the term "chelation" is used in the restricted sense of intramolecular hydrogen bonding and not in the wider sense suggested by Rolla (*Gazzetta*, 1948, **78**, 316).

25° (preliminary experiments showed that saturation is reached in 2 hr.). The solutions were concentrated, if necessary, and were titrated with standard alkali, bromothymol-blue–neutral-red being used as mixed indicator.

Experimental values of solubilities are recorded in the Table. A new method of reporting them has been adopted. They are expressed as the negative logarithms (pS values) of the concentrations in the saturated solutions in moles per litre, by analogy with pH values.

Discussion.—Consideration of these results indicate that: 1. Values for the methoxy-acids show that there is no significant difference between the 2- and the 2 : 6-acid on the one hand and the 3- and the 4-acid on the other. From this it is evident that there is no steric effect, nor has the weak chelation of the former acids any effect. 2. The solubility in water, N-sodium chloride solution, and a normal solution of the salt of the particular acid is virtually uninfluenced by chelation. 3. In the non-polar solvents an acid containing an intermolecular bonded ("free") hydroxy-group is far less soluble than either the chelated isomer or the corresponding methoxy-acid. 4. 2 : 6-Dihydroxybenzoic acid behaves as an acid containing no free hydroxyl group. This is in agreement not only with the pK evidence cited by Baker (*loc. cit.*), but also with that from chromatographic adsorption (see below) and from infra-red spectra (Davies, private communication).

Chromatography of Hydroxybenzoic Acids.—Hoyer (*Kolloid Zeit.*, 1950, **116**, 121) stated that if a substance containing a hydroxy-group is passed in solution through such an adsorbent as silica, whether or not the substance is adsorbed on the column depends on whether the hydroxy-group is free or chelated. Although chelation prevents adsorption, intermolecular hydrogen bonding does not.

Solutions of the hydroxybenzoic acids in chloroform (0·0100M for benzoic, and 2-mono- and 2 : 6-dihydroxybenzoic acids, and saturated for the other acids) were passed down columns of activated silica. To obtain conditions as uniform as possible (*a*) the same batch of activated silica was used throughout; (*b*) 1·00 g. of silica was always used and was always packed in glass tubing of the same bore; (*c*) the amount of acid adsorbed was estimated by titrating the first 10·0-ml. sample; and (*d*) the time of flow was approximately constant. All determinations were carried out in quadruplicate, and the results were quite concordant. % Adsorptions are: benzoic acid, 55·0; *o*-hydroxy-, 28·0; *m*-hydroxy-94·2; *p*-hydroxy-, 97·8; 2 : 4-dihydroxy-, 87·2; 2 : 6-dihydroxy-, 61·0; and 3 : 4-dihydroxy-benzoic acid, 78·6.

If allowance is made for adsorption due to the carboxyl-group, these results clearly corroborate Hoyer's assertion. The somewhat low value for the 3 : 4-acid is possibly due to the weak chelation between the hydroxyl groups lessening but not abolishing hydroxyl-adsorption. The value for the 2 : 6-acid confirms its dichelation. It would seem, however, that the chelation of the second hydroxy-group is somewhat weaker.

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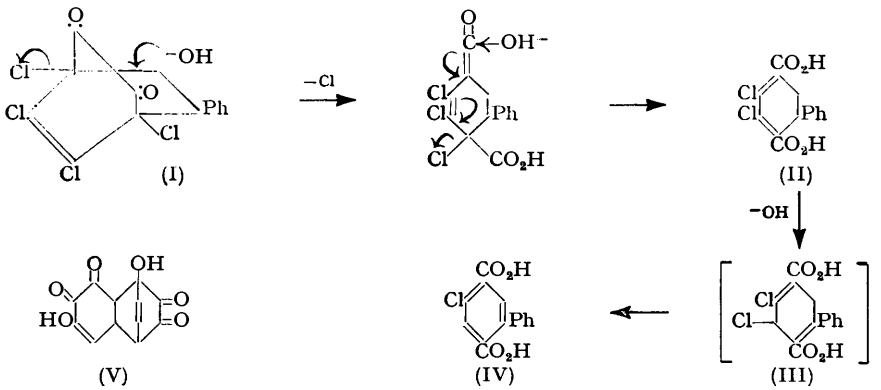
A Base-catalysed Rearrangement, of Non-benzilic Acid Type, of a Bridged α-Diketone.

By R. H. BURNELL and W. I. TAYLOR.

[Reprint Order No. 5355.]

HORNER and MERZ (*Annalen*, 1950, **570**, 89) showed that the adduct (I), formed from tetrachloro-*o*-benzoquinone by a Diels–Alder reaction, is smoothly converted by warm 2N-sodium hydroxide into a dicarboxylic acid to which structure (III) was assigned, and by more vigorous treatment into the diphenyl derivative (IV) which with concentrated sulphuric acid yielded the known 3-carboxy-2-chlorofluorenone. Although Horner and Merz stated that there was no known analogy for this isomerisation and although the ultra-violet absorption spectrum of the acid (III) (see curve 3) did not, as it should, resemble that of *cis*-cinnamic acid (curve 1), these authors made no further comment. Consideration of the stereochemistry of the adduct (I) led us to conclude that the action of alkali would lead to the acid (II) rather than to (III), according to the annexed scheme. This structure, containing vinyl chloride groups, is in better agreement with the known stability to alkali, for formation of the diphenyl (IV) is slow. The ultra-violet absorption spectrum of (II), either as the acid or its dimethyl ester (curve 3), shows a maximum almost identical with



that of dimethyl *cyclo*hexa-1 : 3-diene-1 : 4-dicarboxylate (curve 2), the lower value for ε being ascribed to steric inhibition of resonance between the homoannular diene and the 4-carboxy-group between the 3-chloro- and the 5-phenyl substituent (cf., for example, steric inhibition of resonance in substituted diphenyls). The conversion of the dichloro-acid (II) by strong alkali into the diphenyl (IV) is thought to proceed *via* (III) although we have been unable to isolate this, probably owing to its ready conversion into (IV). Baeyer (*Annalen*, 1889, **251**, 257; 1890, **258**, 1) showed that alkaline isomerisation of *cyclo*hexadiene-1 : 4-dicarboxylic acid yielded finally *cyclo*hexa-1 : 4-diene-1 : 4-dicarboxylic acid, which further supports the postulated intermediacy of (III) in the above scheme.

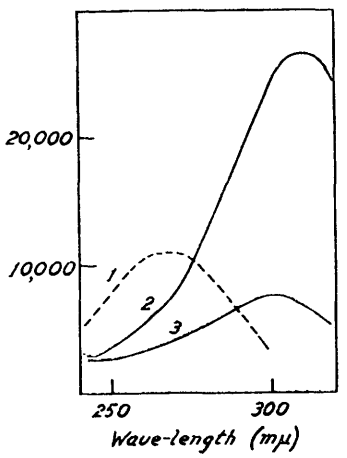
The adduct from tetrabromo-*o*-benzoquinone and phenylacetylene gave no homogeneous material on treatment with alkali. The results of this work support criticisms made by Cook and Loudon (*Quart. Reviews*, 1951, **5**, 99) against a suggestion that (V) was a precursor of purpurogallin, formed by a Diels–Alder reaction between two molecules of 3-hydroxy-*o*-benzoquinone. We were unable to add isoprene to 3-hydroxy-*o*-benzoquinone.

Experimental.—Adducts were prepared according to Horner and Merz's procedure (*loc. cit.*).

2 : 3-*Dichloro*-5-*phenyl*cyclo*hexa*-1 : 3-*diene*-1 : 4-*dicarboxylic acid* (II). The adduct prepared from styrene and tetrachloro-*o*-benzoquinone was warmed at 40° with 2N-sodium hydroxide for 1 hr., then acidified to furnish the *cyclo*hexadiene acid, m. p. 235° (from methanol–water) (Found : C, 53·7; H, 3·3. Calc. for $C_{14}H_{10}O_4Cl_2$: C, 53·7; H, 3·2%); absorption max. (curve 3) 302 mμ (ε = 7400 in EtOH), and 1705 (C=O) and 1685 cm.$^{-1}$. The dimethyl ester had m. p. 78° (from methanol–water) (Found : C, 56·4; H, 4·2. Calc. for $C_{16}H_{14}O_4Cl_2$: C, 56·3;

H, 4·1%); the absorption in EtOH was identical with that of the parent acid; infra-red max. were at 1728 (C=O) and 1710 cm.$^{-1}$. The adduct was also converted into (II) during 2 hr. at 60° in sodium carbonate solution. Sodium hydrogen carbonate was also effective but required more than a day at 60°. The adduct was recovered largely unchanged after being heated with sodium acetate or dilute sulphuric acid although small amounts of highly coloured material were slowly formed.

*Dimethyl*cyclo*hexa*-1 : 3-*diene*-1 : 4-*dicarboxylate*. *cyclo*Hexa-1 : 3-diene-1 : 4-dicarboxylic acid (Baeyer, *Annalen*, 1889, **261**, 301) with diazomethane furnished the pure ester, m. p. 81° (from methanol) (Found: C, 60·5; H, 6·3. Calc. for $C_{10}H_{12}O_4$: C, 61·2; H, 6·2%); absorption max. 309 mμ (ε = 27,300 in EtOH) (curve 2) and 1715 cm.$^{-1}$ (C=O).



1, cis-*Cinnamic acid*.
2, *Dimethyl* cyclo*hexa*-1 : 3-*diene*-1 : 4-*dicarboxylate*.
3, 2 : 3-*Dichloro*-5-*phenyl*cyclo*hexa*-1 : 3-*diene*-1 : 4-*dicarboxylic acid or its dimethyl ester*.

1 : 2 : 3 : 4-*Tetrabromo*-5 : 6-*dioxo*-8-*phenyl*bicyclo(2 : 2 : 2)*octa*-2 : 7-*diene*. Prepared from tetrabromo-*o*-benzoquinone and phenylacetylene, the adduct melted at 172° (from methanol). Even after many crystallisations we were unable to prepare an analytically pure sample (Found: C, 34·3; H, 1·3. Calc. for $C_{14}H_6O_2Br_4$: C, 32·0; H, 1·2%). The adduct was stable in water or dilute sulphuric acid but readily decomposed in hot sodium acetate, warm sodium carbonate, or sodium hydroxide solution.

We are indebted to the National Research Council of Canada for a grant and to Mr. W. Fulmor and staff, American Cyanamide Co., Lederle Laboratories Division, for determination of the infra-red spectra.

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The Compound of Antimony Pentachloride with Nitric Oxide.

By H. J. M. BOWEN.

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A COMPOUND of antimony pentachloride with nitric oxide was originally described by Besson (*Compt. rend.*, 1889, **108**, 1012) and given the formula $(SbCl_5)_2NO_2$. It is clear that Besson was using the wrong equivalent for oxygen (his formula for nitrogen dioxide is NO_4), but if the compound is correctly designated by $(SbCl_5)_2NO$ it should be paramagnetic. This deduction has now been tested.

Experimental.—Commercial antimony pentachloride was vacuum-distilled into Pyrex reaction vessels immediately before each run: distilled specimens melted at 1·8—2·2°. Nitric oxide, prepared by Johnston and Giauque's method (*J. Amer. Chem. Soc.*, 1929, **51**, 3194), was stored over phosphoric oxide in a reservoir flask. When it was condensed on to the solid antimony pentachloride at —196°, an intense purple colour, which vanished above —140°, developed at the interface. The mixture was allowed to warm to room temperature and

then further warmed to break up the surface crust of solid adduct formed. Several condensations were necessary before the reaction was tolerably complete. Excess of the reactants was then removed by continued pumping at room temperature, and the product was finally sealed off *in vacuo*. When the sealed tubes were heated at 100° for some time the compound crystallised in lemon-yellow plates, as observed by Besson (*loc. cit.*). Analysis was carried out by breaking a weighed tube of the sample, sealed *in vacuo*, under mercury, and heating it to approx. 240° until no more nitric oxide was evolved. The volume of the nitric oxide was measured and the chloride in the residue was determined by Volhard's method [Found : NO, 4·74; Cl, 55·9. $(SbCl_5)_2NO$ requires NO, 4·77; Cl, 56·4%. Calc. for $SbCl_5,NO$: NO, 9·11; Cl, 53·9%].

The magnetic susceptibility of the *compound* was measured at room temperature by Dr. J. K. Dawson and found to be less than 3×10^{-7} c.g.s. units/g. Hence the true formula of the compound must be some even multiple of $(SbCl_5)_2NO$. The substance sublimes at 100° *in vacuo*, but an attempt to measure the molecular weight by Victor Meyer's method gave a low value, indicating decomposition, which was in fact observed. The substance was insoluble in liquid nitric oxide, antimony pentachloride, and carbon tetrachloride, and reacted more or less violently with water, alcohol, acetone, ether, *iso*pentane, benzene, and chloroform. Sodium-dried ether gave a white precipitate, presumably of $SbCl_5,Et_2O$ (cf. Williams, *Ber.*, 1876, **9**, 1135), and sodium-dried benzene gave red and violet precipitates, soluble in excess of the solvent, in the same manner as antimony pentachloride itself (Hilpert and Wolf, *Ber.*, 1913, **46**, 2215).

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A.E.R.E., HARWELL, BERKS. [*Received, May 5th*, 1954.]

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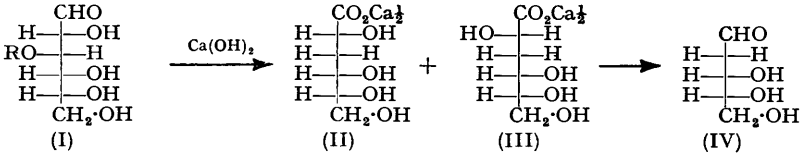
*The Preparation of 2-Deoxy-*D*-ribose.*

By G. N. RICHARDS.

[Reprint Order No. 5364.]

THE preparation of 2-deoxy-D-ribose has received much attention (see, *e.g.*, Overend and Stacey, *J. Sci. Food Agric.*, 1950, **1**, 168) but the glycal method, as modified by Deriaz, Overend, Stacey, Teece, and Wiggins (*J.*, 1949, 1879), remained the most satisfactory, affording 10% yields from D-arabinose. Now, however, the calcium salts of Nef's mixed glucometasaccharinic acids (*Annalen*, 1910, **376**, 1) are conveniently accessible by the action of lime-water on, *e.g.*, 3-*O*-methyl-D-glucose (I; R = Me) (Kenner and Richards, *J.*, 1954, 278), itself readily prepared in 60% yield (Glen, Myers, and Grant, *J.*, 1951, 2568) from D-glucose. These salts may be prepared from the 1 : 3-linked polysaccharide laminarin (Corbett, Kenner, and Richards, *Chem. and Ind.*, 1953, 462; Corbett and Kenner, *J.*, 1954, 3274), or from any other 3-*O*-substituted glucose, mannose, or fructose derivative (patent pending).



The structure suggested by Nef (*loc. cit.*) for the acids indicated that application of Ruff's method of degradation (*Ber.*, 1901, **34**, 1362) of either of the calcium glucometasaccharinates (II, III) should yield 2-deoxy-D-ribose (IV), and in fact by this procedure, as modified by Fletcher, Diehl, and Hudson (*J. Amer. Chem. Soc.*, 1950, **72**, 4546), either salt or the mixture of the two obtained directly by lime-water degradation of 3-*O*-methyl-D-glucose, afforded 2-deoxy-D-ribose in 30—35% yield. The amorphous product was found by paper chromatography to contain only traces of impurities and corresponded to authentic samples of 2-deoxy-D- and -L-ribose kindly supplied by Professor M. Stacey and by Dr. G. W. Kenner. Crystallisation occurred slowly on trituration with *iso*propanol, and the product was readily characterised as its aniline derivative. Other derivatives,

described in the Experimental section, were readily prepared from either amorphous or recrystallised 2-deoxy-D-ribose and it is suggested that the syrupy product obtained directly from the degradation is sufficiently pure for most synthetic work.

The fact that the isomeric glucometasaccharinic acids differ only in their configuration about $C_{(2)}$ was thereby confirmed, but the definite assignment of configuration to the α- and β-isomerides (II, III) requires knowledge of the orientation of the 2-hydroxyl group. The suggestion made previously (Kenner and Richards, *loc. cit.*) has been confirmed by the demonstration of the identity of β-glucometasaccharinolactone with 3-deoxy-γ-D-mannonolactone (from III), which was obtained by hydrolysis, and subsequent oxidation with bromine, of authentic methyl 3-deoxy-α-D-mannoside. The γ-lactone structure is proposed on the basis of the absence of mutarotation in an aqueous solution of the compound. It is reasonable to assume from the mechanism of saccharinic acid formation (Kenner *et al.*, *J.*, 1954, 278; 1953, 2245) that the corresponding α-isomer is the lactone of 3-deoxy-D-gluconic acid (from II).

Almost simultaneously with our earlier announcement (*Chem. and Ind.*, 1953, 1035), Sowden (Amer. Chem. Soc., 124th Meeting, 1953, Sept., 15D) reported that, from the crude mixture of saccharinic acids obtained directly by action of sodium hydroxide on glucose (Nef, *loc. cit.*), he had isolated an amorphous product which required purification through the benzylphenylhydrazone before crystallisation of the 2-deoxy-D-ribose was effected.

Experimental.—*2-Deoxy-D-ribose.* Barium acetate (1·15 g.) and ferric sulphate (0·60 g.) were added to a warm solution of the mixed calcium salts of 3-deoxy-D-mannonic and 3-deoxy-D-gluconic acids (10·01 g.; obtained by the action of lime-water on 3-*O*-methyl-D-glucose; Kenner and Richards, *loc. cit.*). The solution was heated to boiling and filtered, the precipitate being washed with boiling water (2 × 10 ml.). The combined filtrate and washings were cooled to 40° and hydrogen peroxide (7 ml.; 30%) added. After a short induction period the temperature of the solution rose to 70° and gas evolution occurred. The mixture was left to cool to 40°, then more hydrogen peroxide (7 ml.; 30%) was added, the temperature subsequently rising to 50°. The pressure in the flask was next reduced to 25 mm. and a slow stream of air drawn through the solution to decompose bicarbonates. After cooling to room temperature under these conditions the solution was filtered and stirred successively with Amberlite resins IR-120 (20 g.) for 15 min. and IR-4B (50 g.) for 1 hour. Deionisation of the solution was completed by standing over a mixture of the above resins (10 and 20 g. respectively) overnight. Evaporation of the solution then yielded a colourless syrup (2·12 g., 31·6%) which was shown by paper chromatography (alkaline silver nitrate spray; Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444) to be almost pure 2-deoxy-D-ribose (R_F 0·525; in butanol–pyridine–water, 3 : 2 : 1·5). The syrup crystallised slowly on trituration with dry *iso*propanol, and when repeatedly recrystallised from the same solvent mixed with ether, showed m. p. 90—92°, $[\alpha]_D^{21}$ −80° (5 min.) ⟶ −44° (24 hr., equil.) (*c*, 2 in MeOH) (Found: C, 44·6; H, 7·6. Calc. for $C_5H_{10}O_4$: C, 44·8; H, 7·5%). Deriaz *et al.* (*loc. cit.*) report m. p. 96—98°, $[\alpha]_D^{20}$ −93° (4 min.) ⟶ −46° (24 hr., equil.) (*c*, 6 in MeOH), for 2-deoxy-β-D-ribose.

Derivatives of 2-deoxy-D-ribose. 2-Deoxy-D-ribose (amorphous or crystalline) yielded in the usual manner colourless needles of the aniline derivative (60—70%), m. p. 171·5—173°, $[\alpha]_D^{20}$ +17·4° (*c*, 0·4 in EtOH) (Found: C, 62·9; H, 7·4; N, 6·8. Calc. for $C_{11}H_{15}O_3N$: C, 63·1; H, 7·2; N, 6·7%). Overend, Stacey, and Wiggins (*J.*, 1949, 1358) reported m. p. 174—175°, $[\alpha]_D^{22}$ +19·5°.

2-Deoxy-D-ribose (0·15 g.) and *p*-toluidine (0·12 g.) were dissolved, with warming, in ethanol (2 ml.) and the solution kept at room temperature overnight. White needles of N-*2-deoxy-D-ribosyl-p-toluidine* (0·20 g.) separated and after recrystallisation from ethanol had m. p. 167—168° (Found: N, 6·1. $C_{12}H_{17}O_3N$ requires N, 6·3%).

2-Deoxy-D-ribose (0·10 g.) in ethanol (2 ml.) was heated under reflux for 1½ hr. with 2 : 4-dinitrophenylhydrazine (0·14 g.). Addition of water then precipitated the *2 : 4-dinitrophenylhydrazone* as a yellow powder, m. p. 127—128° after crystallisation from ethanol–water (Found: N, 18·2. $C_{11}H_{14}O_7N_4$ requires N, 17·8%).

3-Deoxy-D-mannonolactone. A solution of methyl 3-deoxy-α-D-mannoside (0·65 g.; prepared according to Bollinger and Prins, *Helv. Chim. Acta*, 1946, **29**, 1061) in N-sulphuric acid (10 ml.) was heated on the boiling-water bath to constant rotation (3 hr.; $[\alpha]_D^{20}$ −12·4°). After neutralisation with barium carbonate, 3-deoxy-D-mannose was isolated in the usual way as a colourless

syrup (0·522 g., 87%), $[\alpha]_D^{20}$ −13·5° (*c*, 5 in H_2O) (Found: C, 44·3; H, 7·3. Calc. for $C_6H_{12}O_5$: C, 43·9; H, 7·4%). Bollinger and Prins (*loc. cit.*) reported $[\alpha]_D^{14}$ +17·7° for this compound, and it is intended to discuss this discrepancy in a later paper.

A solution of the amorphous product (0·502 g.) in water (5 ml.) was treated with bromine (0·5 ml.) at room temperature for 3 days and 3-deoxy-D-mannonic acid was isolated in the usual way as a pale yellow syrup (0·417 g.). When dried for several days over phosphoric oxide, 3-deoxy-γ-D-mannonolactone crystallised slowly, and when recrystallised from acetone showed m. p. 89—90°, alone or on admixture with β-D-glucometasaccharinolactone obtained from 3-*O*-methyl-D-glucose (Kenner and Richards, *loc. cit.*), $[\alpha]_D^{20}$ +8·0° (*c*, 2 in H_2O) unchanged after 24 hr. at room temperature (Found: C, 44·6; H, 6·3. Calc. for $C_6H_{10}O_5$: C, 44·4; H, 6·2%). Bollinger and Prins (*loc. cit.*) describe this compound as amorphous.

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Preparation of neo*Pentyl Chloride.*

By W. GERRARD and P. TOLCHER.

[Reprint Order No. 5400.]

*neo*PENTYL CHLOROSULPHINATE is readily prepared by the interaction of the alcohol and thionyl chloride (Gerrard, Nechvatal, and Wilson, *J.*, 1950, 2088) but, compared with chlorosulphinates of ordinary alcohols such as butan-1-ol or octan-2-ol, has remarkable thermal stability. Earlier attempts to catalyse the decomposition by means of pyridine hydrochloride were only partly successful, because the requirements of time and temperature were inadequately met. By heating the chlorosulphinate at 115° for 24 hr. in the presence of quinoline hydrochloride we have obtained *neo*pentyl chloride in 47% yield.

Our observation is relevant to a recent paper by Sommer, Blankman, and Miller (*J. Amer. Chem. Soc.*, 1954, **76**, 803), in which is described the formation of *neo*pentyl chloride from a mixture of *neo*pentyloxytriethylsilane, thionyl chloride, and quinoline hydrochloride heated at 115° for 23 hr. However, in the course of other work we found that *neo*pentyloxytrimethylsilane reacted readily with thionyl chloride alone to give *neo*pentyl chlorosulphinate.

$$Me_3Si{\cdot}O{\cdot}C_5H_{11} + SOCl_2 \longrightarrow Me_3SiCl + C_5H_{11}O{\cdot}SOCl$$

From this it appears that in the experiment of Sommer *et al.* the alkyl chloride was really coming from the chlorosulphinate.

Experimental.—neo*Pentyloxytrimethylsilane*, b. p. 121—122°, n_D^{20} 1·3934, d_4^{20} 0·7632 (Found: C, 60·7; H, 12·9. $C_8H_{20}OSi$ requires C, 60·0; H, 12·5%), was prepared by the addition of trimethylchlorosilane (1 mol.) to *neo*pentyl alcohol (1 mol.) and pyridine (1 mol.) in ether (160 c.c.) at −10°. Thionyl chloride (12·8 g., 1 mol.) was added to the silane (8·6 g., 0·5 mol.) at 15°, and after 10 min. excess of thionyl chloride was removed at 15°/20 mm. *neo*Pentyl chlorosulphinate (6·9 g., 75%), b. p. 62—66°/20 mm., n_D^{20} 1·4520 (Found: Cl, 20·5. Calc. for $C_5H_{11}O_2ClS$: Cl, 20·8%), and di*neo*pentyl sulphite (1·1 g., 18·6%), b. p. 110°/19 mm., n_D^{20} 1·4316, were obtained. When thionyl chloride (6·61 g., 1 mol. instead of 2 mols.) was used with the silane (8·9 g., 1 mol.) trimethylchlorosilane (5·6 g., 92%), b. p. 55—58° (Found: Cl, 33·7. Calc. for C_3H_9ClSi: Cl, 32·7%), was also isolated; but the yield of chlorosulphinate (2·2 g., 23%) b. p. 66—74°/20 mm., n_D^{20} 1·4501, was reduced, whereas that of the sulphite (3·5 g., 56%), b. p. 98—100°/12 mm., n_D^{20} 1·4300, increased.

Decomposition of neo*pentyl chlorosulphinate in the presence of quinoline hydrochloride.* The chlorosulphinate (prepared from alcohol and thionyl chloride) (15·0 g., 1 mol.) was mixed with the hydrochloride (0·3 g., 0·03 mol.) and heated at 115° for 24 hr. Volatile products were removed at 15°/15 mm. and collected at −80°. The condensate (6·2 g.) contained easily

hydrolysable chlorine (5·6%) representing 17% of *tert.*-amyl chloride, and the latter was removed by 2N-nitric acid (3 × 20 c.c.). After being washed with water and dried, the product afforded *neo*pentyl chloride (4·4 g., 47%), b. p. 82·5°, n_D^{20} 1·4048 (Found: C, 56·6; H, 10·25; Cl, 33·25. Calc. for $C_5H_{11}Cl$: C, 56·35; H, 10·3; Cl, 33·3%). The product did not contain easily hydrolysable chlorine.

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Crystalline 1-*Benzoyl*-1 : 2-*dihydroquinoline.*

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DURING an investigation requiring the preparation of derivatives related to the Reissert compound, which is considered to be 1-benzoyl-2-cyano-1 : 2-dihydroquinoline, a pure sample of 1-benzoyl-1 : 2-dihydroquinoline was required. This compound has been described as an oil by Johnson and Buell (*J. Amer. Chem. Soc.*, 1952, **74**, 4517) and by Rosenmund and Zymalkowski (*Chem. Ber.*, 1953, **86**, 37). It has now been obtained crystalline, is quite stable, and provides a useful reference derivative for the unstable 1 : 2-dihydroquinoline. A sample of freshly prepared 1 : 2-dihydroquinoline was observed to change to a brown oil when stored in a vacuum-desiccator over silica gel.

The structure of the crystalline benzoyl derivative was confirmed by hydrogenation over platinum to the known 1-benzoyl-1 : 2 : 3 : 4-tetrahydroquinoline (Johnson and Buell, *loc. cit.*). Acid hydrolysis of 1-benzoyl-1 : 2-dihydroquinoline yielded 67% of benzoic acid and a basic brown oil with the characteristic odour of 1 : 2-dihydroquinoline. This is in contrast to 1-benzoyl-2-cyano-1 : 2-dihydroquinoline which yields benzaldehyde on acid hydrolysis.

Experimental.—For 1 : 2-dihydroquinoline Bohlmann (*Chem. Ber.*, 1952, **85**, 390) gives m. p. 40—41°. Our specimen, prepared by his method but extracted with light petroleum (b. p. 40—60°) and crystallised at −80°, had m. p. 62—65°.

1 : 2-Dihydroquinoline (4 g.), freshly isolated and purified, in freshly distilled pyridine (15 ml.) was treated slowly with benzoyl chloride (5 ml.) in pyridine (5 ml.) at <10°, then with more benzoyl chloride (5 ml.) at <15°. The mixture was then left for 24 hr. at room temperature. Addition of water, extraction with ether, washing with dilute hydrochloric acid, water, and aqueous sodium hydroxide, drying, and evaporation gave an oil which was repeatedly extracted with light petroleum (b. p. 40—60°). The product (4·8 g.), m. p. 84—87°, crystallised on concentration and cooling to −80°. Recrystallisation from ethyl alcohol yielded pure 1-benzoyl-1 : 2-dihydroquinoline (3·1 g.), m. p. 89° (Found: C, 81·8; H, 5·7; N, 5·9. Calc. for $C_{16}H_{13}ON$: C, 81·7; H, 5·5; N, 5·95%).

Hydrogenation of this (0·6 g.) in ethyl alcohol (20 ml.) over platinum oxide (0·05 g.) gave 1-benzoyl-1 : 2 : 3 : 4-tetrahydroquinoline (0·45 g.), m. p. 74—75° (cf. Johnson and Buell, *loc. cit.*) (Found: C, 80·8; H, 6·37; N, 6·0. Calc. for $C_{16}H_{15}ON$: C, 81·0; H, 6·3; N, 5·9%). The quantity of hydrogen taken up was 71 ml. (20°/759 mm.) pressure, which, after allowance for the catalyst, corresponds to 1 approx. mol.

Hydrolysis of 1-benzoyl-1 : 2-dihydroquinoline (0·2 g.) with boiling 15% w/v hydrochloric acid (10 ml.) was complete after 1·5 hr. After cooling, benzoic acid (0·07 g.), m. p. and mixed m. p. 121—122°, crystallised. The filtrate was made alkaline with aqueous sodium hydroxide and extracted with ether. Evaporation of the ether yielded a small quantity of brown oil with an odour resembling that of 1 : 2-dihydroquinoline. No odour of benzaldehyde was detected.

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Preparation of ωω'-Diphenylpolymethylenes by Anodic Syntheses.

By E. A. Evans and Margaret Whalley.

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Few applications of the Kolbe reaction to the preparation of ωω'-diphenylpolymethylenes, $Ph\cdot[CH_2]_n\cdot Ph$, have been reported. Electrolysis of phenylacetic acid in methanol (Linstead, Shephard, and Weedon, *J.*, 1952, 3624) or in methanol and pyridine (Fichter and Stenzl, *Helv. Chim. Acta*, 1939, **22**, 976) gave dibenzyl in 50% yield. The latter workers also obtained 1 : 4-diphenylbutane in 25% yield from β-phenylpropionic acid.

In the present experiments, the conditions employed were essentially Fichter and Stenzl's. β-Phenylpropionic, γ-phenylbutyric, and δ-phenylvaleric acid yielded respectively 1 : 4-diphenylbutane (34%), 1 : 6-diphenylhexane (37%), and 1 : 8-diphenyloctane (47%). The yields thus increase slightly as the series is ascended.

Greaves, Linstead, Shephard, Thomas, and Weedon (*J.*, 1950, 3326) showed that the yield of decanoic acid obtained by electrolysis of mixtures of methyl hydrogen adipate and hexanoic acid increased from 36% when the ratio was 1 : 1 to 58% for a 1 : 6 ratio. In our work electrolysis of a 2 : 1 mixture of β-phenylpropionic acid and γ-phenylbutyric acid gave 1 : 5-diphenylpentane as principal neutral product, and only a small amount of 1 : 6-diphenylhexane; γ-phenylbutyric acid and δ-phenylvaleric acid (2 : 1) gave 1 : 7-diphenylheptane as sole neutral product.

The diphenylpolymethylenes were recovered unchanged after 6 hours' treatment with boiling alkaline potassium permanganate or chromic acid in acetic acid. With nitrating mixture, only 1 : 4-diphenylbutane yielded a crystalline nitro-compound (cf. Fichter and Stenzl, *loc. cit.*).

Experimental.—The electrolysis cell consisted of a cylindrical glass vessel (20 cm. × 3 cm. diam.) containing two parallel platinum electrode plates (2·5 × 2·5 cm.) placed 1—2 mm. apart. The acids were electrolysed at 30—40° for 5—6 hr. in methanol–pyridine (2 : 1) containing a trace of sodium methoxide to act as conductor. Electrolyses using ethanol instead of methanol failed owing to the high resistance of the solution.

1 : 4-*Diphenylbutane.* A solution of β-phenylpropionic acid (20 g.) in technical methanol (50 c.c.) and dry pyridine (25 c.c.) containing sodium methoxide (0·3 g.) was electrolysed until the electrolyte became slightly alkaline [5 hr.; 1 amp.; 120 v (D.C.)], the temperature being kept at 30—40° by cooling the cell in ice-water. The anode slime (1·0 g.) was filtered off and the filtrate concentrated under reduced pressure. Unchanged β-phenylpropionic acid (6 g., 30%), m. p. 47—48°, was recovered. The neutral product was 1 : 4-diphenylbutane (4·8 g., 34%), b. p. 108—109°/0·1 mm., m. p. 51° (Found : C, 91·4; H, 8·7. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%) (Fichter and Stenzl, *loc. cit.*, give m. p. 52°). Nitration yielded the tetranitro-derivative, m. p. 204—205°, described by Fichter and Stenzl (*loc. cit.*).

1 : 6-*Diphenylhexane.* γ-Phenylbutyric acid (20 g.), electrolysed as above, gave unchanged acid (6·3 g., 31%), m. p. 46—48°, and 1 : 6-diphenylhexane (5·3 g., 37%), b. p. 130—132°/0·1—0·2 mm., n_D^{24} 1·5574 (Found : C, 90·5; H, 9·5. Calc. for $C_{18}H_{22}$: C, 90·7; H, 9·3%) (Braun and Deutsch, *Ber.*, 1912, **45**, 1273, give b. p. 206—208°/20 mm.).

1 : 8-*Diphenyloctane.* δ-Phenylvaleric acid (Plati, *J. Amer. Chem. Soc.*, 1943, **65**, 1275) (20 g.) similarly gave unchanged acid (0·9 g., 5%) and 1 : 8-diphenyloctane (7·0 g., 47%), b. p. 138—142°/0·1—0·2 mm., n_D^{23} 1·5290 (Found : C, 89·9; H, 10·0. Calc. for $C_{20}H_{26}$: C, 90·2; H, 9·8%) (Braun and Deutsch, *loc. cit.*, give b. p. 208—210°/8 mm.; Borsche and Wollemann, *Ber.*, 1911, **44**, 3185, and 1912, **45**, 3713, give b. p. 215°/12 mm.).

1 : 5-*Diphenylpentane.* γ-Phenylbutyric acid (14 g.) and β-phenylpropionic acid (7 g.) were electrolysed as before, giving a small amount of 1 : 6-diphenylhexane, b. p. 130—132°/0·1—0·2 mm., and 1 : 5-diphenylpentane, b. p. 114°/0·1—0·2 mm., n_D^{23} 1·5510 (Found : C, 91·3; H, 8·9. Calc. for $C_{17}H_{20}$: C, 91·1; H, 8·9%) (Braun and Deutsch, *loc. cit.*, b. p. 187—189°/10 mm.; Borsche and Wollemann, *loc. cit.*, 190—200°/12 mm.).

1 : 7-*Diphenylheptane.* Electrolysis of a mixture of γ-phenylbutyric acid (8·2 g.) and δ-phenylvaleric acid (17·8 g.) yielded 1 : 7-diphenylheptane (4·5 g., 36%), b. p. 141°/0·6—

0·7 mm., n_D^{23} 1·5445 (Found : C, 90·2; H, 9·4. Calc. for $C_{19}H_{34}$: C, 90·5; H, 9·5%) (Borsche and Wollemann, *loc. cit.*, b. p. 207—208°/12 mm.).

Analyses were carried out in the microanalytical laboratory (Mr. F. H. Oliver) of this Department.

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The Synthesis of Sugars from Smaller Fragments. Part VIII. The Synthesis of* D-ido*Heptulosan from* D-*Xylose.*

By J. K. N. JONES.

[Reprint Order No. 5454.]

SOWDEN (*J. Amer. Chem. Soc.*, 1950, **72**, 3325) described how heptuloses may be synthesized from pentoses by condensation with nitroethanol, the resulting heptitol being converted into a heptulose by the Nef reaction (*Annalen*, 1894, **280**, 263). Difficulties in this method are the preparation of the unstable nitroethanol and the isolation of the heptulose. The synthesis has now been simplified and D-*ido*heptulosan isolated in *ca.* 10% yield from D-xylose by the following procedure. D-Xylose was condensed with nitromethane in the presence of sodium methoxide, and the resulting deoxynitrohexitol condensed with formaldehyde. Aldose sugars were then converted by bromine water into aldonic acids, which with the hydrogen bromide were removed on Amberlite resin IR-4B. The resulting mixture of ketoses was fractionated on cellulose (Hough, Jones, and Wadman, *J.*, 1949, 2511), and D-*ido*heptulosan isolated in the usual way (Pratt, Richtmyer, and Hudson, *J. Amer. Chem. Soc.*, 1952, **74**, 2210). D-Sorbose was obtained as a by-product. Other aldehydes may be used in place of formaldehyde and new sugar derivatives produced (unpublished results) (cf. Sowden, *Adv. Carbohydrate Chem.*, 1951, **6**, 318).

Experimental.—Chromatography was carried out on Whatman No. 1 filter paper sheets by the descending method (Partridge, *Biochem. J.*, 1948, **42**, 238), with the solvent systems, (*a*) ethyl acetate–acetic acid–water (9 : 2 : 2), (*b*) butanol–pyridine–water (10 : 3 : 3), and (*c*) butanol–ethanol–water (40 : 11 : 19) (all v/v). Sugars were detected on the chromatogram with *p*-anisidine hydrochloride, ketohexoses with resorcinol in alcoholic hydrogen chloride, and heptuloses with orcinol in a solution of butanol–trichloroacetic acid (Klevstrand and Nordal, *Acta Chem. Scand.*, 1950, **4**, 1320). Evaporation was under reduced pressure. Optical rotations were determined in water at 20° ± 2°.

Condensation of D-*xylose with nitromethane and paraformaldehyde.* D-Xylose (20 g.), methanol (40 c.c.), and nitromethane (72 c.c.) were mixed, a solution of sodium methoxide (6·5 g.) in methanol (140 c.c.) was added, and the whole was shaken for 12 hr. Ether (50 c.c.) was then added and the pale yellow precipitate collected, washed with ether and light petroleum (b. p. 40—60°), and dissolved in water (30 c.c.). Paraformaldehyde (4 g.) was added. When a clear solution had resulted (*ca.* 10 min.) the mixture was poured into sulphuric acid (70 c.c.) [ice (41 g.) plus concentrated sulphuric acid (31 c.c.)]. The solution was then neutralised with barium hydroxide, filtered, and concentrated to *ca.* 250 c.c. Paper chromatography of the solution (solvent *c*) revealed xylose, a hexose moving slightly faster than xylose, heptuloses moving at the rate of xylose and galactose, and a ketohexose moving at about the speed of glucose. Bromine was added to the solution, and oxidation was allowed to proceed for 48 hr. Excess of bromine was then eliminated by aeration and the solution heated at 100° for 1 hr. in order to convert D-*ido*heptulose into the equilibrium mixture of D-*ido*heptulose and D-*ido*-heptulosan. The solution was then cooled and hydrogen bromide and aldonic acids were removed on Amberlite resin IR-4B. The neutral solution was then passed down a column of Amberlite resin IR-120 to remove sodium ions and then down a column of Amberlite resin IR-4B to remove the last traces of acids. The neutral solution was concentrated to a syrup and fractionated on a column of hydrocellulose (24 × 3 cm.) (Hough *et al.*, *loc. cit.*) with butanol, half saturated with water, as mobile phase. Concentration of the appropriate fractions gave

* Part VII, *J.*, 1953, 2140.

fraction I, a syrup (0·1 g.), which gave the reactions of a heptulose sugar and moved at the speed of xylose; it was not further examined. Fraction II (2·75 g.) moved at the speed of arabinose, gave colour tests identical with those of D-*ido*heptulosan, and gradually crystallised. Trituration with methanol gave the crude sugar which was recrystallised from methanol to m. p. and mixed m. p. 174° (2·0 g.), $[\alpha]_D$ −42° (*c*, 2·1). It was chromatographically indistinguishable from D-*ido*heptulosan (solvent *a*, *b*, or *c*). Fraction III (2·7 g.) crystallised; trituration with methanol gave crude D-sorbose. Recrystallisation from methanol gave the pure product (0·9 g.), m. p. and mixed m. p. 164°, indistinguishable chromatographically from an authentic specimen in solvent mixture *a*, *b*, or *c*. Fraction IV (2·2 g.) was a brown syrup, which moved at the rate of galactose (solvent *c*) and gave the colour reactions of a heptulose; it was probably D-*ido*heptulose, which moves at this rate in this solvent.

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The Kinetics of the Oxidation of Propylene by Nitrogen Dioxide.

By T. L. COTTRELL and T. E. GRAHAM.

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THE kinetics of the reaction between nitrogen dioxide and ethylene have been investigated in some detail (Cottrell and Graham, *J.*, 1953, 556). The present note records a similar but less detailed study of the reaction with propylene in the temperature range 160—260° C.

The experimental technique was much the same as before, except for the determination of the nitrogen dioxide concentration as a function of time. The output from the photocell was connected to a rapidly recording potentiometer; the change in photocell output corresponding to the introduction of 12 cm. Hg of nitrogen dioxide caused approximately two thirds full-scale deflection. By this means quite rapid reactions could be followed because the instrument had a response time of about 2 sec., and the chart could be run at about 2 in./min. The recording system was calibrated at the beginning of each run by admitting the nitrogen dioxide stepwise in known amounts until the required pressure was obtained.

The nitrogen dioxide concentration and total pressure were both followed. The nitrogen dioxide concentration falls throughout the reaction, and kinetic analysis was confined to the initial slopes of the curves of nitrogen dioxide against time. The initial rate of disappearance of nitrogen dioxide was nearly proportional to the second power of its concentration and the first power of the propylene concentration, the more accurate exponents being 1·8 and 1·2. An Arrhenius plot of the third-order rate constant (k_3) against temperature gave $k_3 = 10^{9\cdot7} \exp(-13{,}600/\boldsymbol{R}T)$ $1.^2$ mole^{-2} sec.$^{-1}$ (160—260°). Below 160° there was an apparent decrease in the activation energy. Surface effects were found to be negligible in the range 190—260°.

At high temperatures there was a pressure rise, while at lower temperatures there was an initial pressure drop followed by a rise, much as in the reaction with ethylene. At the higher temperatures, when there was no apparent initial pressure decrease, the ratio of the pressure increase to the initial pressure of nitrogen dioxide was 0·48. This is to be compared with 0·55 for the reaction:

$$C_3H_6 + 9NO_2 \longrightarrow 3CO_2 + 3H_2O + 9NO$$

The reaction is very similar to that with ethylene, but about 3—4 times faster. This result is in line with the correlation proposed by Walsh (*Fuel*, 1954, **33**, 243) between the ionisation potential of a substrate and the activation energy of its reaction with nitrogen dioxide.

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