

## NOTES.

50. *The Distribution of Quinol between Ether and Water.*

By R. A. ROBINSON.

THE distribution coefficient of quinol between ether and water does not seem to be known with certainty; thus, the International Critical Tables (1928, vol. III, p. 428) give 2.7 as the ratio at 15° of the volume concentration in the ethereal layer to that in the aqueous layer, a figure based on Pinnow's data (*Z. anal. Chem.*, 1911, **50**, 162) although Seidell ("Solubilities of Organic Compounds," 3rd Edn., 1941, vol. II, p. 400) remarks that "the terms in which the concentration is expressed (by Pinnow) are not stated." A graph given by Baumbach (*J. Soc. Motion Picture Engineers*, 1939, **33**, 517) indicates a coefficient of 1.6 at 22°, said to be independent of concentration, contrary to the finding of Pinnow. On the other hand, extrapolation of Walker, Collett, and Lazzell's data (*J. Phys. Chem.*, 1931 **35**, 3259) indicates a ratio not far from 0.45 at room temperature on a weight basis and 0.32 on a volume basis.

The matter is of more than academic interest because quinone is often used as an oxidising agent and ether is used to extract the quinol formed in the reaction. If the product is to be used in animal feeding experiments, it is important to be assured that ether is an efficient solvent for the extraction.

I have measured the distribution coefficient at 25°, in an atmosphere of nitrogen, titrating the quinol with ceric sulphate and using ferrous phenanthroline as indicator

(Kolthoff and Lee, *Ind. Eng. Chem., Anal.*, 1946, **18**, 452). The following results are expressed in terms of g. of quinol per 100 g. of solution :

Ether .....	1.450	2.093	4.207	6.251	8.811	21.54	22.98
Water .....	0.513	0.697	1.222	1.659	2.092	3.738	3.901
$K_{\text{obs.}}$ .....	2.83	3.01	3.44	3.77	4.21	5.77	5.89
$K_{\text{calc.}}$ .....	2.83	3.00	3.47	3.86	4.25	5.73	5.88

$K_{\text{calc.}}$  is obtained from the empirical equation :  $K_{\text{calc.}} = 2.37 (1 + 4.17[Q]_w)$ , where  $[Q]_w$  is the concentration, in moles per 1000 g. of solution, of the aqueous layer. (If  $K_{\text{calc.}}$  is expressed in terms of volume concentrations and  $[Q]_w$  in g. of quinol per 5 c.c. of aqueous layer, this equation becomes  $K_{\text{calc.}} = 1.68 + 12.7[Q]_w$ , which compares with an equation given by Pinnow,  $K_{\text{calc.}} = 1.885 + 12.6[Q]_w$ , and suggests that he used g. per 5 c.c. of solution as his unit of concentration.) This equation is consistent with dimerisation in the ethereal layer, with an equilibrium constant,  $K' = [Q]_E^2 / [(Q)_2]_E$ . If  $K^\circ$  is the distribution coefficient of the monomer, it is easy to show that  $K_{\text{calc.}} = K^\circ (1 + 2K^\circ [Q]_w / K')$ , and this conforms with the experimental findings if  $K^\circ = 2.37$  and  $K' = 1.14$  moles per 1000 g. of solution.

Facile as this explanation may be, there is little evidence for the presence of double molecules of quinol in ether; indeed, Beckmann's b. p. measurements (*Z. physikal. Chem.*, 1889, **3**, 603) can be interpreted to imply only a slight association, far from the amount required by the above equation. For practical purposes, however, the distribution coefficient under the conditions prevailing when ether is used for extraction may be taken to be of the order of 3 on a wt. concentration basis and 2 if volume concentrations are used.

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[Received, August 13th, 1951.]

### 51. *The Electrolytic Reductive Coupling of p-Dimethylaminoacetophenone and p-Methoxyacetophenone.*

By HAROLD A. LEVINE and MILTON J. ALLEN.

DURING an investigation of the mechanism of formation of pinacols from ketones at a mercury cathode surface by application of a controlled potential (Allen and Corwin, *J. Amer. Chem. Soc.*, 1950, **72**, 114; Allen, *Analyt. Chem.*, 1950, **22**, 804; *Trans. Electrochem. Soc.*, in the press) the reduction of a mixture of ketones was studied. Previous investigators (Laude and Wiemann, *Bull. Soc. chim.*, 1946, 256) have reported the formation of mixed pinacols when a mixture of ketones was reduced by metallic sodium. In extending these observations to pinacol formation by electrolytic reduction, a mixture of ketones was chosen such that a *quantitative* determination of the amount of mixed pinacol formation could be obtained. The reductive coupling of *p*-dimethylaminoacetophenone with *p*-methoxyacetophenone gave a product which could be completely separated from one of the starting materials and its neutral reduction products by solubility in dilute acid. Analysis of the basic fraction for methoxyl content afforded a direct measure of the yield of mixed pinacol. A check on these yields was obtained by comparing the analytical values found for nitrogen in the samples with values calculated for the appropriate mixture of mixed pinacol, 2-*p*-dimethylaminophenyl-3-*p*-methoxyphenylbutane-2 : 3-diol, and the symmetrical pinacol, 2 : 3-bis-(*p*-dimethylaminophenyl)butane-2 : 3-diol. These data, presented in the table, show satisfactory agreement. The presence of small amounts of basic products other than pinacols (cf. Allen and Corwin, *loc. cit.*) is, however, not excluded, but would not greatly affect the calculated end values.

*Experimental.*—The cell used was modified from that described by Allen and Corwin by addition of a 24/40 standard-taper joint for insertion of a reflux condenser. The anode chamber was a fine-porosity alundum crucible, 2.9 cm. in diameter and 8 cm. high, held in position by means of a carefully cut, tightly fitting rubber stopper. A cylindrical platinum anode was used. The cathode surface area was 23.5 cm.<sup>2</sup>.

An equimolecular mixture of *p*-methoxyacetophenone (3.00 g.) and *p*-dimethylaminoacetophenone (3.26 g.) was dissolved in the appropriate catholyte as illustrated in the table. The solu-



Standardised quantitative Dische tests were carried out with 2 : 3-dideoxyribose and derivatives thereof, and also with intermediates obtained from the syntheses. In their quantitative Dische tests, Deriaz, Stacey, Teece, and Wiggins (*J.*, 1949, 1222) heated the reactants together for 3.25 minutes. It has been shown, however, that if the heating is prolonged to 15 minutes no further development of colour results after this period, and that by heating for this time better controls can be maintained. Consequently we have adopted the latter conditions in preference to those described by Deriaz *et al.* (*loc. cit.*) (cf. Overend, *J.*, 1951, 1484; Woodhouse, *Brit. J. Cancer*, 1949, 3, 510). It was found that, although a blue colour is produced when Dische reagent is added to 2 : 3-dideoxyribose, and also to its acetate and 6- $\beta$ -ethylglycoside, this is very weak and in no way comparable in intensity with the colour developed with 2-deoxyribose. Intermediates having an ethylenic linkage between C<sub>(2)</sub> and C<sub>(3)</sub> behave similarly to arabinal and diacetyl arabinal and give strong positive Dische tests.

For comparative purposes  $\beta$ -methyl-3-deoxy-L-xyloside (riboside) was prepared from 2 : 3-anhydro- $\beta$ -methyl-L-riboside by essentially the method of Todd and Mukherjee (*J.*, 1947, 969). Hydrolysis afforded 3-deoxy-L-xylose (-L-ribose) which readily yielded a dibenzyl mercaptal. With the Dische reagent 3-deoxy-L-xylose and its glycoside gave blue colours similar to that obtained with 2 : 3-dideoxyribose.

In the preparation of 2-deoxyribose and 3-deoxyxylose derivatives from 2 : 3-anhydro-methylriboside, a negative Dische test has frequently been taken as indicative of the absence of 2-deoxyribose in the reaction products (cf. Stacey, Kent, and Wiggins, *J.*, 1949, 1232; Davoll, Lythgoe, and Trippett, *J.*, 1951, 2230). Although it is now shown that a blue colour can be obtained when Dische reagent is added to 3-deoxyxylose and its derivatives, it must be emphasized that to obtain this colour it is necessary to use a much higher concentration of the sugar than is usual with 2-deoxyribose, and to heat for a much longer time to ensure onset of formation of the colour. It can be concluded that the diphenylamine colour reaction for 2-deoxypentoses is relatively non-specific and needs careful control when used in quantitative estimations.

*Experimental.*—3-Deoxy-L-xylose (-L-ribose). Prepared essentially by the method of Todd and Mukherjee (*loc. cit.*), the deoxy-sugar (0.114 g.) was shaken with toluene- $\omega$ -thiol (0.22 c.c.) and concentrated hydrochloric acid (0.22 c.c.); isolation in the usual manner gave 3-deoxy-L-xylose dibenzyl mercaptal (0.21 g., 67%) as a yellow oil, b. p. 204—220°/0.008 mm.,  $[\alpha]_D^{25} +18.2^\circ$  (*c.* 0.77 in chloroform) (Found: C, 62.9; H, 6.5; S, 17.7. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>S<sub>2</sub> requires C, 62.7; H, 6.6; S, 17.6%).

1 : 4-Diacetyl 2 : 3-dideoxy-L-ribose. 1 : 4-Diacetyl 2 : 3-didehydro-2 : 3-dideoxy-L-arabinose (prepared by the method of Bergmann and Breuers, *Annalen*, 1929, 470, 51) (5.1 g.) was shaken in methanol (40 c.c.) containing palladium on charcoal (1 g.) at room temperature in an atmosphere of hydrogen. When the uptake of hydrogen was complete the solution was filtered and the residue was well washed with methanol. The washings were added to the filtrate which was then concentrated to afford a syrupy residue. Distillation yielded 1 : 4-diacetyl 2 : 3-dideoxy-L-ribose (4.14 g., 80.6%) as a colourless mobile liquid, b. p. 97—119°/0.01—0.03 mm.,  $n_D^{25} 1.4425$ ,  $[\alpha]_D^{17} +34.4^\circ$  (*c.* 0.69 in chloroform) (Found: C, 53.2; H, 6.8. C<sub>9</sub>H<sub>14</sub>O<sub>5</sub> requires C, 53.5; H, 6.9%).

2 : 3-Dideoxy-L-ribose. 1 : 4-Diacetyl 2 : 3-dideoxy-L-ribose (0.69 g.) was dissolved in methanol (30 c.c.) saturated at 0° with dry ammonia and the solution was kept at 0° for 4 days. The solution was then evaporated to dryness and ammonium acetate in the residue was removed by sublimation at 30—40°/0.005—0.01 mm. 2 : 3-Dideoxy-L-ribose (0.28 g., 65%) was obtained as a viscous syrup,  $[\alpha]_D^{19} +22.7^\circ$  (*c.* 3.97 in water) (Found: C, 50.6; H, 8.7. C<sub>5</sub>H<sub>10</sub>O<sub>3</sub> requires C, 50.9; H, 8.5%). The deoxy-sugar (0.14 g.) was shaken for 20 minutes at room temperature with toluene- $\omega$ -thiol (2.2 mols., 0.304 c.c.) and concentrated hydrochloric acid (0.3 c.c.). Isolation in the usual manner afforded 2 : 3-dideoxy-L-ribose dibenzyl mercaptal (0.22 g., 54.5%) as a yellow viscous liquid, b. p. 215—234°/0.009 mm. This crystallised after several days and was recrystallised from methanol-water; it then had m. p. 74°,  $[\alpha]_D^{21} +20.4^\circ$  (*c.* 0.88 in chloroform) (Found: C, 65.0; H, 6.9; S, 17.9. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>S<sub>2</sub> requires C, 65.5; H, 6.9; S, 18.4%).

4-Acetyl 2 : 3-dideoxy- $\alpha\beta$ -ethyl-L-riboside. 4-Acetyl 2 : 3-didehydro-2 : 3-dideoxy- $\alpha\beta$ -ethyl-L-arabinoside (prepared according to the method of Gehrke and Aichner, *loc. cit.*) (2.08 g.) was dissolved in methanol (50 c.c.) containing palladium on charcoal (*ca.* 2 g.), and the mixture was

shaken in an atmosphere of hydrogen at room temperature. When the uptake of hydrogen was complete the solution was filtered and the filtrate evaporated to dryness. Distillation of the residue yielded 4-acetyl 2 : 3-dideoxy- $\alpha\beta$ -ethyl-L-ribose (1.37 g., 65%) as a colourless liquid, b. p. 85—95°/0.1 mm.,  $n_D^{13}$  1.4435,  $[\alpha]_D^{17} +45.3^\circ$  (c, 0.53 in chloroform) (Found : OEt, 24.2. C<sub>9</sub>H<sub>16</sub>O<sub>4</sub> requires OEt, 23.9%).

*Quantitative Dische tests.* The Dische reagent was prepared as described by Deriaz *et al.* (*loc. cit.*). The general procedure was to dissolve the sugar derivative in water (3 c.c.) and add Dische reagent (6 c.c.). The solution was heated at 100° for 15 minutes, then cooled at 0° for 10 minutes, and the intensity of the colour developed was measured by use of the Spekker photoelectric absorptiometer.

*Intensity of Dische colours developed as shown by extinction coefficient ( $\epsilon$ ) at 5800 A.*

Sugar derivative	$\epsilon$	Sugar derivative	$\epsilon$
2-Deoxy-D-ribose .....	3660	3-Deoxy- $\beta$ -methyl-L-xyloside .....	125
$\beta$ -Methyl-2-deoxy-D-ribofuranoside ...	4100	3-Deoxy-L-xylose .....	126
Diacetyl-L-arabinal .....	2540	3-Deoxy-L-xylose (heated for 30 mins.)	149.5
4-Acetyl <i>pseudo</i> -L-arabinal .....	2920	4-Acetyl $\alpha\beta$ -ethyl- <i>pseudo</i> -L-arabinal	
Diacetyl <i>pseudo</i> -L-arabinal .....	2560	(heated for 3.25 mins.) .....	1090
1 : 4-Diacetyl 2 : 3-dideoxy-L-ribose ...	203	4-Acetyl 2 : 3-dideoxy- $\alpha\beta$ -ethyl-L-	
2 : 3-Dideoxy-L-ribose .....	107	ribose (heated for 10 mins.) .....	216

The authors thank the British Empire Cancer Campaign (Birmingham Branch) for financial assistance. One of them (R. A.) thanks the University of Birmingham for the award of a Research Scholarship.

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[Received, September 4th, 1951.]

### 53. 8-Methyl-3 : 4-benzopyrene.

By J. M. L. CAMERON, J. W. COOK, and (Miss) R. SCHOENTAL.

8-METHYL-3 : 4-BENZOPYRENE has been synthesised from an available intermediate, in order to extend the range of 3 : 4-benzopyrene derivatives tested for carcinogenic activity. 1 : 2 : 3 : 12-Tetrahydromesobenzanthrene-3- $\beta$ -propionic acid-A [prepared as described by Cook, Ludwiczak, and Schoental (*J.*, 1950, 1118)], was cyclised with anhydrous hydrogen fluoride. The product, purified by chromatography on alumina from benzene-light petroleum, gave not only the keto-octahydrobenzopyrene-A described by these authors, but also the more strongly adsorbed 8-*keto*-1 : 2 : 8 : 9 : 10 : 11-hexahydro-3 : 4-benzopyrene which formed canary-yellow leaflets (from benzene), m. p. 209—210° (Found : C, 87.9; H, 6.1. C<sub>20</sub>H<sub>16</sub>O requires C, 88.2; H, 5.9%). A solution of this ketone (0.5 g.) in benzene (15 c.c.) was added to a stirred Grignard solution, prepared from magnesium turnings (2 g.) and methyl iodide (10 c.c.) in dry ether (50 c.c.). The mixture was kept overnight, then boiled for an hour, and decomposed with ice and ammonium chloride. The product was purified by passage of its benzene solution through a column of alumina, and crystallised from benzene-light petroleum and then acetone. 8-Methyl-1 : 2 : 10 : 11-tetrahydro-3 : 4-benzopyrene formed yellowish needles, m. p. 162—163° (Found : C, 93.4; H, 7.0. C<sub>21</sub>H<sub>18</sub> requires C, 93.3; H, 6.7%). Dehydrogenation was effected by boiling a solution of this hydrocarbon (300 mg.) in 1-methylnaphthalene (5 c.c.) with palladium black (40 mg.) under nitrogen for 10 hours. The solution was diluted with light petroleum and passed through a column of alumina. The main, yellowish, band was cut and eluted with benzene, giving 8-methyl-3 : 4-benzopyrene as yellow prisms (from benzene), m. p. 192—193° (Found : C, 94.6; H, 5.3. C<sub>21</sub>H<sub>14</sub> requires C, 94.7; H, 5.3%). The *picrate* formed dark brown needles (from benzene), m. p. 205° (decomp.) (Found : C, 65.55; H, 3.5; N, 8.15. C<sub>21</sub>H<sub>14</sub>.C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub> requires C, 65.45; H, 3.5; N, 8.5%), and the *s*-trinitrobenzene complex crystallised from benzene in red needles, m. p. 233° (decomp.) (Found : N, 8.5. C<sub>21</sub>H<sub>14</sub>.C<sub>6</sub>H<sub>3</sub>O<sub>6</sub>N<sub>3</sub> requires N, 8.8%).

We are indebted to the British Empire Cancer Campaign for a grant which has supported this work.

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[Received, September 10th, 1951.]

## 54. Organic Fluorides. Part XI.\* Fluorination of Heterocyclic Compounds with Cobalt Trifluoride.

By R. MONTGOMERY and F. SMITH.

THE fluorination of heterocyclic compounds has received very little attention, and appears to lead to extensive degradation. Fluorination of pyridine by electrolysis in anhydrous hydrogen fluoride (Simons *et al.*, *J. Electrochem. Soc.*, 1949, **95**, 47) produced perfluoropentane and nitrogen trifluoride, and that of 2:6-lutidine (Haszeldine, *J.*, 1950, 1638), by means of either a catalytic or a cobalt trifluoride procedure, afforded a small amount of a compound believed to be perfluoro-2:6-dimethylpiperidine, the major portion of the products boiling below room temperature. Similar results have been obtained in the fluorination of quinoline, only a small amount of perfluorodecahydroquinoline being isolated (Haszeldine and Smith, unpublished). However, the nitrogen linkages in the chlorinated products of triphenylamine and *N*-phenylcarbazole were intact after treatment with both silver difluoride and antimony pentafluoride in the liquid phase (Stilmar, Struve, and Wirth, *Ind. Eng. Chem.*, 1947, **39**, 348), as also were those from the vapour-phase fluorination of several tertiary alkylamines with cobalt trifluoride (Haszeldine, *Research*, 1950, **3**, 430). A preliminary study of the fluorination of 2-methylindole with cobalt trifluoride in a rotating reactor (Massingham, Montgomery, Smith, and Thomas, *J. Appl. Chem.*, in the press) showed that, as with 2:6-lutidine and pyridine, the compound underwent extensive fragmentation; the main product was a mixture of perfluorohydrocarbons but a small amount of fully fluorinated material was obtained which still contained nitrogen. Fission of the oxygen-carbon linkage often, but not always, occurs on fluorination of diphenyl ether and its derivatives (Fowler *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 292; Stilmar *et al.*, *loc. cit.*).

We have now shown that fluorination of thionaphthen in the vapour phase with cobalt trifluoride leads to complete elimination of the sulphur. The principal product, perfluoroethylcyclohexane, was accompanied by a small amount of perfluorocyclohexane and a high-boiling polymeric material, probably similar to those high-boiling fluorocarbons produced when hydrocarbons are subjected to fluorination under similar conditions (Haszeldine and Smith, *J.*, 1940, 2689). In no fraction could sulphur be detected, and it seemed most probable that sulphur hexafluoride was formed but could not be isolated under the experimental conditions (cf. Neudorffer, *Compt. rend.*, 1950, **231**, 1070).

In general, therefore, it would seem that the principal reaction in the fluorination of compounds containing nitrogen, oxygen, or sulphur is one of fission with the elimination of these elements and the fluorination of the hydrocarbon fragments. The extent of this degradation is dependent upon the method of fluorination and appears to be capable of modification by a preliminary stabilisation by chlorination; it is also probable that certain perfluoroheterocyclic nitrogen compounds could be obtained by use of a mild fluorinating agent, such as cobalt trifluoride, since the bond energies for C-N and N-F are 48.6 and 68.8 kcal. per mole, respectively (Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, 1940). Similarly, the bond energies for C-S and S-F, being 50.1 and 84.8 kcal. per mole, respectively (Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645), will necessitate a new method of fluorination for the preparation of perfluoro-heterocyclic sulphur compounds.

*Experimental.*—Fluorination of thionaphthen with cobalt trifluoride. Thionaphthen (75 g.), in three portions, was passed at 10–15 g./hour over cobalt trifluoride in a vertical reactor heated to 330–390°. The effluent vapours were condensed in traps cooled in solid carbon dioxide-ethanol, and the product was washed with water. The crude product (94.2 g.) was extracted with absolute alcohol (Haszeldine and Smith, *J.*, 1950, 3617) and the alcohol-insoluble material (71.3 g.) was distilled, five fractions being collected (total weight 61.8 g.) with a total b. p. range up to 245°. Each of these fractions was found by sodium fusion to contain fluorine but in no case was sulphur detected. After treatment of each fraction with uranium hexa-

\* Part X, *J. Appl. Chem.*, in the press.

fluoride in the usual way in order to effect complete fluorination (*idem, ibid.*, p. 2689) further distillation yielded fractions: (i) 1.6 g., b. p. 48—55°, m. p. 51°; (ii) 2.8 g., b. p. 55—96°; (iii) 24.6 g., b. p. 98—100°,  $d_4^{25}$  1.827,  $d_4^{30}$  1.813,  $\eta^{25}$  17.19 millipoises,  $\eta^{30}$  15.70 millipoises,  $n_D^{18}$  1.289 (Found: F, 77.0. Calc. for  $C_8F_{16}$ : F, 76.0%); (iv) 9.1 g., b. p. 100—110°; (v) 2.0 g., b. p. 110—245°.

Fraction (i) was identified by m. p. and mixed m. p. as perfluoro*cyclohexane*. Fraction (iii) was identical in physical characteristics with perfluoroethyl*cyclohexane*, the constants for an authentic sample of which were: b. p. 101°;  $d_4^{25}$  1.826,  $d_4^{30}$  1.812;  $\eta^{25}$  17.42 millipoises,  $\eta^{30}$  15.76 millipoises;  $n_D^{18}$  1.286. [The viscosities were determined in an Ostwald viscometer with water as reference liquid, so the values obtained differ from those quoted (*idem, ibid.*), for which benzene was used as reference liquid.] Fractions (ii) and (iv) were mixtures and fraction (v) was a viscous oil.

*Fluorination of 2-methylindole.* 2-Methylindole (170 g.), in three aliquots, was passed at rates of 15—35 g./hour over cobalt trifluoride in a rotating reactor (Massingham *et al.*, *loc. cit.*) heated to 336—390°. The effluent vapours were treated as described above, yielding a crude product (129.4 g.) containing alcohol-insoluble material (106.4 g.). This crude fluorocarbon mixture was treated with uranium hexafluoride in the usual way and repeatedly fractionally distilled, the 11 fractions obtained having the properties shown below:

Fraction	Wt. (g.)	B. p.	$n_D^{21}$	$d_4^{25}$	Fraction	Wt. (g.)	B. p.	$n_D^{21}$	$d_4^{25}$
1	1.7	35—48°	<1.255	—	8	5.8	120—135°/ 12 mm.	1.3376	2.000
2	5.4	48—57	1.255	1.682	9	4.2	135—155°/ 12 mm.	1.3461	2.031
3	4.1	57—87	1.276	1.765	10	6.7	158—176°/ 12 mm.	1.3518	—
4	8.6	87—103	1.291	1.807 (20°)	11	12	Residue		
5	5.9	103—108	1.297	1.826					
6	4.2	137—148	1.3089	1.879 (20°)					
7	5.7	156—176	1.3171	1.920					

Only fractions (5) and (10) gave a positive test for nitrogen. Fraction (2) is probably perfluoro*cyclohexane* for which Bigelow (*J. Amer. Chem. Soc.*, 1940, **62**, 2792) reports b. p. 51°,  $d_4^{30}$  1.684,  $n_D^{30}$  1.2685. Fraction (3) appears to be perfluoromethyl*cyclohexane* which has b. p. 76.2°,  $d_4^{25}$  1.784,  $n_D^{25}$  1.276 (Haszeldine and Smith, *J.*, 1950, 2689).

From the above results it is also evident that the fluorination of 2-methylindole is extremely complicated but that the nitrogen shows some stability to cobalt trifluoride (fractions 5 and 10). Appreciable polymerisation of the fragments takes place (fractions 8—11) and this sometimes involves a nitrogen-containing monomer (fraction 10). Fractions (8)—(10) were viscous oils, and fraction (11) was a glassy solid sublimation of which produced a white powder having a softening point of about 75°.

The authors thank the late Sir Norman Haworth, F.R.S., for his interest and the Director of Scientific Research for permission to publish this work.

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[Received, September 17th, 1951.]

## 55. 1 : 2 : 5 : 6-Tetrachloronaphthalene.

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By nitration of 2 : 6-dichloronaphthalene Alén (*Bull. Soc. Chim.*, 1881, **36**, 435) obtained mono-, di-, and tri-nitro-compounds, and the dinitro-compound on fusion with phosphorus pentachloride gave a tetrachloronaphthalene, m. p. 159.5—160.5°. We have confirmed the preparation of the di- and the tri-nitro-compound, although the reaction conditions preferred by us are somewhat different from those recommended by Alén. Reduction of the dinitro-compound to the diamine, followed by a Sandmeyer reaction, gave a tetrachloronaphthalene, m. p. 164°, possibly identical with Alén's tetrachloro-compound.

Among the fifteen tetrachloronaphthalenes prepared by Turner and Wynne (*J.*, 1941, 247) was one of m. p. 164°, designated as a 1 : 2 : 5 : 6-tetrachloronaphthalene since it was obtained from 1 : 2 : 5-trichloronaphthalene by chlorosulphonation followed by fusion with phosphorus pentachloride. A sample of Turner and Wynne's preparation, now in our possession, has been identified with the tetrachloronaphthalene prepared

above, thereby establishing its constitution as 1:2:5:6-tetrachloronaphthalene. Accordingly the dinitro-compound from which we prepared this tetrachloronaphthalene is 2:6-dichloro-1:5-dinitronaphthalene.

*Experimental.*—2:6-Dichloro-1:5-dinitronaphthalene. 2:6-Dichloronaphthalene (12.0 g.) was added gradually to nitric acid (100 c.c.;  $d$  1.50) with stirring and ice-cooling to keep the temperature below 20°. After  $\frac{1}{2}$  hour's further stirring, the mixture was poured into water (1 l.), and the product filtered off, washed, and dried. The crude product (16.6 g.) was freed from a little trinitro-compound by extraction with hot acetic acid and was crystallised from *o*-dichlorobenzene as needles, m. p. 262—263° (11.5 g.) (Found: N, 9.7; Cl, 24.5. Calc. for  $C_{10}H_4O_4N_2Cl_2$ : N, 9.8; Cl, 24.8%). Alén gives m. p. 252—253°.

2:6-Dichloro-1:5:?:-trinitronaphthalene. To a solution of 2:6-dichloronaphthalene in sulphuric acid (20 c.c.;  $d$  1.84), nitric acid (2.6 c.c.;  $d$  1.50) was added and the temperature raised to 60° for 18 hours. The mixture was poured into water (200 c.c.), and the precipitated solid filtered off, washed with water and alcohol (to remove a brown by-product), dried, and crystallised from acetic acid. It formed stout prisms, m. p. 204—205° (1.5 g.) (Found: N, 12.7; Cl, 21.4. Calc. for  $C_{10}H_3O_6N_3Cl_2$ : N, 12.7; Cl, 21.4%) (Alén gives m. p. 198—200°). This compound was also obtained by nitrating 2:6-dichloro-1:5-dinitronaphthalene under the above conditions.

1:5-Diamino-2:6-dichloronaphthalene (plates, m. p. 202—203°, from alcohol) was obtained by reduction of 2:6-dichloro-1:5-dinitronaphthalene with iron filings and hydrochloric acid in ethylene glycol monoethyl ether (Found: N, 11.85. Calc. for  $C_{10}H_8N_2Cl_2$ : N, 12.2%). Alén gives m. p. 204—205°.

1:2:5:6-Tetrachloronaphthalene was prepared from 1:5-diamino-2:6-dichloronaphthalene by a modification of the Hodgson-Walker method (cf. *J.*, 1933, 1620). The diamine (1.0 g.) was dissolved in warm acetic acid (12 c.c.), and sulphuric acid (5 c.c.) was added, giving a fine suspension of the sulphate which was poured slowly into nitrosylsulphuric acid prepared from sodium nitrite (0.8 g.) and sulphuric acid (7 c.c.) at <20°. The resultant viscous liquid was poured into a solution of cuprous chloride (1.1 g.) in concentrated hydrochloric acid (10 c.c.) at 60°. Frothing occurred and, when reaction was complete, water was added to precipitate the product which was then filtered off and crystallised from 2-ethoxyethanol (carbon). White needles (0.6 g.) were obtained, having m. p. 164° alone or mixed with Turner and Wynne's 1:2:5:?:-tetrachloronaphthalene (Found: Cl, 53.0. Calc. for  $C_{10}H_4Cl_4$ : Cl, 53.4%).

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## 56. Crystalline 2:3-Dimethyl $\alpha$ -D-Xylose.

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BY the hydrolysis of methylated esparto xylan Hampton, Haworth, and Hirst (*J.*, 1929, 1739) isolated 2:3-dimethyl *D*-xylose as a syrup, and proved its constitution. This sugar has been isolated several times since (Robertson and Speedie, *J.*, 1934, 824; Chanda, Hirst, Jones, and Percival, *J.*, 1950, 1289; Chanda, Hirst, and Percival, *J.*, 1951, 1240) but invariably in a syrupy condition: it has now crystallised.

*Experimental.*—Purification of a specimen prepared from methylated esparto xylan (Chanda *et al.*, *loc. cit.*) by passage, in light petroleum (b. p. 100—120°)—*n*-butanol (7; 3), saturated with water, through a column of powdered cellulose in the usual way, isolation of the product, and repetition of the operation gave a colourless syrup which crystallised completely when kept for 2 years in a vacuum over phosphoric oxide. The crystals had m. p. 79—80°,  $[\alpha]_D^{25} +70^\circ$  (3 minutes),  $+68^\circ$  (5 minutes),  $+61^\circ$  (8 minutes),  $+48^\circ$  (20 minutes),  $+37^\circ$  (35 minutes),  $+23^\circ$  (14 hours, constant) ( $c$ , 1.0 in water) (Found: C, 47.2; H, 8.1. Calc. for  $C_7H_{14}O_5$ : C, 47.2; H, 8.9%).

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[Received, October 16th, 1951.]