

## NOTES.

**361. 4 : 5- and 3 : 6-Dinitronaphthalic Anhydrides.**

By F. BELL.

4 : 5-DINITRONAPHTHALIC ANHYDRIDE has been prepared by (a) oxidation of dinitroacenaphthene (Mayer and Kaufmann, *Ber.*, 1920, **53**, 296), (b) oxidation of dinitroacenaphthenequinone (Rowe and Davies, *J.*, 1920, **117**, 1344), and (c) nitration of 4-nitronaphthalic anhydride (Rule and Thompson, *J.*, 1937, 1766). It was oriented by Rule and Brown (*J.*, 1934, 171). Rule and Thompson (*loc. cit.*) showed that the m. p. of the anhydride could be raised to 327—329° by repeated crystallisation from nitric acid and that it was best characterised by interaction with *o*-phenylenediamine to give a benziminazole derivative, m. p. 370°. 4 : 5-Dinitronaphthalic acid does not appear to have been described. If hydrochloric acid is added to a solution of the anhydride in aqueous sodium carbonate the resulting precipitate, which after drying darkens at 260° and melts indefinitely, is insoluble in boiling water and yields the anhydride when crystallised from other solvents.

The nitration of naphthalic anhydride was described by Anselm and Zuckmayer (*Ber.*, 1899, **32**, 3284) and, independently, by Francesconi and Bargellini (*Gazzetta*, 1902, (2), **32**, 94). The former authors by crystallisation of the nitration product from benzene obtained yellow-brown needles, m. p. 214°, of the dinitro-anhydride whereas the latter authors crystallised the product from water and obtained a dinitro-acid in silvery-white leaflets, m. p. 208—210°. Francesconi and Bargellini record that the acid dissolves in concentrated nitric acid to give a small yield of a compound, m. p. 266°, which was not analysed or examined further. Mihailescu and Steopoe (*Bull. Sect. Scient. Acad. Roumaine*, 1923, **8**, 102) describe the conversion of naphthalic anhydride into dinitronaphthalic anhydride, m. p. 207—208°, but state that their compound is much more soluble than would be gathered from Anselm and Zuckmayer's description. Rule and Brown (*loc. cit.*) first established that the acid was 3 : 6-dinitronaphthalic acid by decarboxylation to 2 : 7-dinitronaphthalene. Rule and Thompson (*loc. cit.*) state that the dinitro-acid can be

recrystallised unchanged from boiling nitrobenzene but is converted into the anhydride, m. p. 330°, by recrystallisation from boiling nitric acid. Francesconi and Bargellini's compound, m. p. 266°, is regarded by them as the impure anhydride. The 3:6-dinitro-acid was characterised by reaction with *o*-phenylenediamine to give a benziminazole derivative, m. p. 301°.

Hodgson and Ward (*J.*, 1945, 590) by the method of Anselm and Zuckmayer obtained an 85% yield of the crude 3:6-dinitro-anhydride, which was practically insoluble in water but formed needles, m. p. 214°, from toluene or xylene. Solution of the dinitro-anhydride (10 g.) in boiling nitric acid furnished tetranitronaphthalene (0.2 g.), m. p. >295° (decomp.), soluble in 10% sodium carbonate solution and reprecipitated as a colourless solid, m. p. >310° (decomp.). Francesconi and Bargellini's compound, m. p. 266°, is taken by these authors to be impure tetranitronaphthalene.

It will be seen that the various descriptions of the nitration of naphthalic anhydride do not accord and, further, it is difficult to reconcile the exclusive nitration of naphthalic anhydride in the 3:6-positions with the nitration of 4-nitronaphthalic anhydride, under very similar conditions, to the 4:5-dinitro-derivative only. The experiments were repeated in the hope of resolving these anomalies.

*Experimental.*—4:5-Dinitronaphthalic anhydride was prepared by methods (a), (b) [dinitro-acenaphthenequinone has m. p. 317° (lit., >300°)], and (c). Rule and Thompson's method gave the yield stated (37%); slight modification results in improvement. A mixture of nitric acid (*d* 1.5; 2 c.c.) and sulphuric acid (3 c.c.) was added to 4-nitronaphthalic anhydride (3 g.) in sulphuric acid (18 c.c.). The resultant solution was placed on a boiling water-bath for  $\frac{1}{4}$  hour, cooled, and poured on ice. The precipitate (2.85 g.) was crystallised from boiling nitric acid giving 1.9 g. (54%), m. p. 321°. The nitric acid mother-liquor on dilution with water remained clear.

*Nitration of Naphthalic Anhydride.*—Hodgson and Ward's method gave the stated yield of crude product. Solution of the crude product (22 g.) in hot concentrated nitric acid gave on cooling 4:5-dinitronaphthalic anhydride (1.6 g.), m. p. 322°, alone or mixed with an authentic specimen and unchanged by recrystallisation from acetic anhydride. Identity was further confirmed by interaction with *o*-phenylenediamine. The nitric acid filtrate, when poured into water, gave 3:6-dinitronaphthalic anhydride (18 g.), m. p. 216° after crystallisation from xylene or acetic anhydride. The anhydride can be recrystallised from nitric acid (about 4 c.c. for 1 g.) and then separates in stout prisms. The pure anhydride can be heated with concentrated nitric acid for a considerable time without change. Solution of the anhydride in aqueous sodium carbonate followed by reprecipitation with hydrochloric acid furnishes 3:6-dinitronaphthalic acid, which crystallises from boiling water in silvery scales, m. p. 212°. It is insoluble in boiling xylene but dissolves in boiling acetic anhydride with some decomposition leading to evolution of oxides of nitrogen.

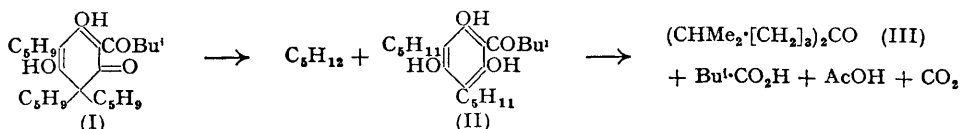
It appears probable, therefore, that Francesconi and Bargellini's compound, m. p. 266°, Rule and Thompson's 3:6-dinitronaphthalic anhydride, and Hodgson and Ward's tetranitronaphthalene were all 4:5-dinitronaphthalic anhydride in varying degrees of purity. Further, Rule and Thompson in preparing the benziminazole, m. p. 301°, must have used the "acid" and not the "anhydride, m. p. 330°" or they would have perceived that the latter was actually the 4:5-dinitro-compound.

Since naphthalic anhydride on nitration gives some 4:5-dinitro-derivative and since 4-nitronaphthalic anhydride gives a yield of only 54% of the 4:5-dinitro-derivative (leaving it possible that the loss is in part occasioned by the production of the 4:6-dinitro-derivative), the nitration results can be regarded as reconciled.

### 362. Structure of the Hydrogenation Product of Lupulone.

By M. VERZELE.

LUPULONE (I), one of the bitter constituents of hops, is cleaved on hydrogenation to 2-methylbutane and a product believed to be (II) (Wöllmer, *Ber.*, 1925, **58**, 672) which on degradation by concentrated alkali affords an oily ketone believed to be 2 : 10-dimethylundecan-6-one (III), as well as isovaleric and acetic acids and carbon dioxide (cf. Verzele and Govaert, *Bull. Soc. chim. Belg.*, 1949, **58**, 432, for a similar reaction with lupulone).



The structure of (III), and hence of (II) and (I), has been confirmed by synthesis from 5-methylhexanoic acid by passage over thoria.

*Experimental.*—The hydrogenation product (5.25 g.; obtained from 6.25 g. of lupulone by Wöllmer's method, *loc. cit.*) gave, by alkali fission (see Verzele *et al.*, *loc. cit.*), isovaleric acid (1.25 g., 75%), b. p. 174—175° (amide, m. p. 128° alone or mixed with authentic material), and 2 : 10-dimethylundecan-6-one (2.25 g., 75%), b. p. 135—137°/20 mm., m. p. —30°. The semicarbazone of the ketone, prepared in the usual way, had m. p. 83° (Found : N, 16.4, 16.3.  $\text{C}_{14}\text{H}_{28}\text{ON}_3$  requires N, 16.7%).

Passage of 5-methylhexanoic acid (13 g.) over thoria at 420° gave sweet-smelling 2 : 10-dimethylundecan-6-one (8 g., 73%), b. p. 127°/13 mm., the semicarbazone of which had m. p. 82° alone or mixed with the material mentioned above.

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### 363. Preparation of 3-Aryl-7-hydroxy-4-methylcoumarins.

By WALTER FREUND.

MEERWEIN, BUCHNER, and VAN EMSTER (*J. pr. Chem.*, 1939, **152**, 237; B.P. 480 617) have arylated coumarin and 7-hydroxycoumarin (umbelliferone) at position 3 by treating these compounds with diazo-solutions in aqueous acetone, the reaction mixture being buffered with sodium acetate and chloroacetate respectively. 4-Methylumbelliferone gives very poor yields, but l'Ecuyer and Olivier (*Canad. J. Res.*, 1950, **28**, B, 648) obtained the corresponding stilbenes in good yield from  $\beta$ -methylcinnamic acid and diazo-compounds under Meerwein's conditions. 7-Hydroxy-3-*p*-methoxyphenyl-4-methylcoumarin has been prepared by another method by Mentzer, Gley, Molho, and Billet (*Bull. Soc. chim.*, 1946, 271); it is weakly oestrogenic (Gley and Mentzer, *Compt. rend. Soc. Biol.*, 1945, 139, 1055).

*Experimental.*—(M. p.s are uncorrected.)

A filtered diazo-solution prepared from *p*-chloroaniline (6.4 g.), sodium nitrite (3.65 g.), and 25% hydrochloric acid (22 g.) was added to a mixture of 4-methylumbelliferone (8.8 g.) in acetone (800 c.c.), and sodium chloroacetate (25 g.) in a small amount of water, the pH being then approx. 5. No gas evolution was noticeable (temp. 20°). On gentle warming and addition of copper chloride (3 g.) in a small amount of water, gas evolution set in. Finally, the solution was heated to 35° with continual shaking. The mixture was steam-distilled to remove the acetone. The remaining solid was extracted several times with boiling water, and the residue digested with a little cold alcohol and dried on a porous tile. On recrystallisation from glacial acetic acid, a small amount of 3-*p*-chlorophenyl-7-hydroxy-4-methylcoumarin separated in plates, m. p. 233—234° (Found : C, 67.0, 67.1; H, 4.0, 4.0; Cl, 12.4.  $\text{C}_{16}\text{H}_{11}\text{O}_3\text{Cl}$  requires C, 67.0; H, 3.8; Cl, 12.4%).

3-*p*-Bromophenyl-7-hydroxy-4-methylcoumarin, prepared similarly, separated from glacial acetic acid in plates, m. p. 256—259° (Found: C, 58·3, 58·1; H, 3·5, 3·4; Br, 24·3.  $C_{16}H_{11}O_3Br$  requires C, 58·0; H, 3·3; Br, 24·2%).

7-Hydroxy-3-*p*-methoxyphenyl-4-methylcoumarin was also prepared similarly, except that 850 c.c. of acetone were used. The yield was very poor. The m. p. was 230—231° (Mentzer *et al.*, *loc. cit.*, give m. p. 232°) (Found: C, 72·4, 72·4; H, 5·0, 5·1; MeO, 11·1. Calc. for  $C_{17}H_{14}O_4$ : C, 72·3; H, 5·0; MeO, 11·0%).

I thank Dr. K. F. Tettweiler, formerly of the University of Melbourne, for the microanalyses. This work was supported in part by a grant from the National Council for Health and Medical Research, Canberra.

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### 364. Adsorption from Binary Solutions of Completely Miscible Liquids. Part II.\* Thermodynamic Requirement for Complete Preferential Adsorption.

By G. A. H. ELTON.

THE various types of isotherms obtained experimentally for adsorption from a binary solution of two completely miscible liquids A and B were discussed in Part I,\* where it was shown that, from measurements of concentration change brought about by adsorption, the mole-fraction of each component in the adsorbed surface layer could be calculated by using the expressions

$$x_B^s = \frac{A(x_B + \Delta x_B) - a_A(n_A + n_B)\Delta x_B}{A + (n_A + n_B)(a_B - a_A)\Delta x_B} \quad (1)$$

$$x_A^s = 1 - x_B^s \quad (2)$$

where  $x_A^s$ ,  $x_B^s$  are the surface mole-fractions of A and B respectively,  $x_B$  the equilibrium bulk mole-fraction of B,  $\Delta x_B$  the change in bulk mole-fraction produced by adsorption,  $a_A$ ,  $a_B$  the effective areas per mole in the surface layer,  $n_A$ ,  $n_B$  the number of moles of each component in the whole system, and  $A$  the surface area of the adsorbent. If the surface mole-fraction of one component is found to exceed its bulk mole-fraction over the whole range between zero and unity, we may say that it is "completely preferred" by the adsorbent. Failing this, the graph of  $x_B^s$  against  $x_B$  will cut the line  $x_B^s = x_B$  at some point intermediate between zero and unity: *i.e.*, the "net adsorption" of B changes sign at this point.

It is of interest to examine the thermodynamic requirements for the existence of each of these cases. For equilibrium between the adsorbed layer and solution in a given solid-solution system, we have the following general relations between the activities  $a_A$ ,  $a_B$ , in the solution, and  $a_A^s$ ,  $a_B^s$  in the adsorbed layer:

$$a_A^s/a_A = \exp \{[(\mu_A)_0 - (\mu_A^s)_0]/RT\} \quad (3)$$

$$a_B^s/a_B = \exp \{[(\mu_B)_0 - (\mu_B^s)_0]/RT\} \quad (4)$$

where  $(\mu_A)_0$ ,  $(\mu_B)_0$  are the chemical potentials of A and B in arbitrarily defined standard states in the solution, and  $(\mu_A^s)_0$ ,  $(\mu_B^s)_0$  are the corresponding chemical potentials in suitable standard states in the surface layer. Convenient standard states which we will take are (i) for  $(\mu_A)_0$  and  $(\mu_B)_0$ , infinite dilution for the appropriate component in the bulk solution, and (ii) for  $(\mu_A^s)_0$  and  $(\mu_B^s)_0$ , infinite dilution for the appropriate component in the surface layer. The quantities  $[(\mu_A)_0 - (\mu_A^s)_0]$  and  $[(\mu_B)_0 - (\mu_B^s)_0]$  may be conveniently termed the "adsorption potentials" of A and B. By analogy with the work of Fu, Hansen, and Bartell (*J. Physical Chem.*, 1948, **52**, 374) we may write, in the limit as  $x_A$  tends to zero,  $(x_A^s/x_A)_0 = (a_A^s/a_A)_0$ , and as  $x_B$  tends to zero,  $(x_B^s/x_B)_0 = (a_B^s/a_B)_0$ . For complete preferential adsorption of one component, the adsorption potentials must, in order to

\* Part I, *J.*, 1951, 2958.

produce a graph of  $x_B^s$  against  $x_B$  of the appropriate shape, be opposite in sign, whilst in all other cases they will be of similar sign. Inserting these requirements in equations (3) and (4), we reach the conclusion that if both components have positive adsorption potentials, no preferential adsorption can occur. Since, from kinetic considerations, negative values of the adsorption potential are not very likely, it is to be expected that cases of complete preferential adsorption will be rarely found. This seems in practice to be the case (see, e.g., Bartell and Sloan, *J. Amer. Chem. Soc.*, 1929, **51**, 1643).

From the example of the calculation of a surface mole-fraction isotherm by use of equation (1), given in Part I (*loc. cit.*), we may obtain approximate values of the adsorption potentials of the two components on charcoal from the limiting slopes of the surface mole-fraction isotherms. The values obtained are 1.0 kcal. for methanol, and 1.1 kcal. for carbon tetrachloride.

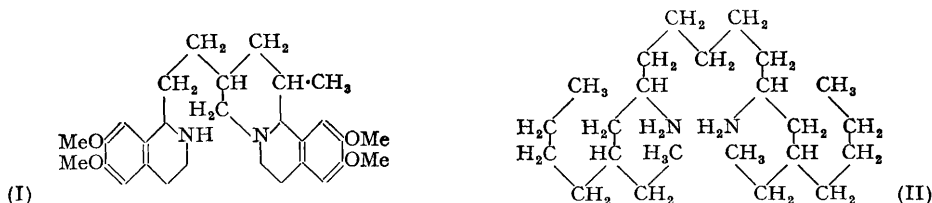
BATTERSEA POLYTECHNIC, S.W.11.

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### 365. Structure and Amoebicidal Activity. Part III.\* Aliphatic Diamines.

By D. MURIEL HALL, SARDAR MAHBOOB, and E. E. TURNER.

SINCE there is little prospect of our being able to continue the synthetic work described in Parts I and II of this series (*J.*, 1950, 1842; 1952, 149) we should like to draw attention to the curious fact that 7 : 13-diamino-5 : 15-diethylnonadecane (II) which we synthesised under the stimulus of Pymán's formula (I) for emetine (*J.*, 1927, 1069) [subsequently shown to be incorrect (Robinson, *Nature*, 1948, **162**, 524; Pailer and Porschinski, *Monatsh.*, 1949, **80**, 94; Battersby, Openshaw, and Wood, *Experientia*, 1949, **5**, 114; Battersby and Openshaw, *J.*, 1949, 3207)], in a particular configuration bears a pictorial resemblance to (I). As stated in Part II, this base (II) has as high an amoebicidal activity *in vitro* as emetine itself.



A further remarkable result is that within the series  $\text{NH}_2 \cdot \text{CHR} \cdot [\text{CH}_2]_n \cdot \text{CHR} \cdot \text{NH}_2 \cdot 2\text{HCl}$ , R being 2-ethylhexyl, the amoebicidal activity is 1 in 100,000 for  $n = 3$ , is zero for  $n = 4$ , but reappears augmented for  $n = 5$ . (The first two compounds are described in Part I and the third in Part II.)

We now describe the synthesis of 5 : 9-diamino-7 : 7-dimethyltridecane dihydrochloride, the preparation of which was complicated by the presence of a *neopentyl* structure and by the fact that the final dihydrochloride was more than usually deliquescent. This hydrochloride has an activity *in vitro* of 1 in 1000 against *Entamoeba histolytica*.

*Experimental.*—Microanalyses by Drs. Weiler and Strauss.

7 : 7-Dimethyltridecane-5 : 5 : 9 : 9-tetracarboxylic acid. Condensation of 1 : 3-dibromo-2 : 2-dimethylpropane with an alcoholic solution of sodium ethoxide and ethyl *n*-butylmalonate during 136 hours gave ethyl 7 : 7-dimethyltridecane-5 : 5 : 9 : 9-tetracarboxylate (13%), b. p.  $164^\circ/4$  mm. The acid derived from this crude ester crystallised, with partial decarboxylation, from benzene-light petroleum (b. p.  $60$ — $80^\circ$ ) and had m. p.  $155$ — $157^\circ$  (Found : C, 60.8; H, 9.5.  $\text{C}_{19}\text{H}_{32}\text{O}_8$  requires C, 58.7; H, 8.3%).

5 : 9-Diamino-7 : 7-dimethyltridecane. 7 : 7-Dimethyltridecane-5 : 9-dicarboxylic acid (5.8 g.), obtained as a thick liquid by heating the tetracarboxylic acid at  $210^\circ$ , was dissolved in benzene

\* Part II, *J.*, 1952, 149.



(50 c.c.), and concentrated sulphuric acid (30 c.c.) was added. Sodium azide (2.6 g.) was added and the temperature kept at 40–45° until reaction was complete. The mixture was cooled, diluted with ice, and made alkaline with 30% sodium hydroxide at <30°. The base was extracted with benzene-ether. Part of it was converted into the *dihydrochloride* by passing in hydrogen chloride and removing the solvent in a vacuum. It was exceedingly deliquescent and decomposed >100° (Found: C, 58.2; H, 11.7; N, 8.55; Cl, 21.3.  $C_{15}H_{36}N_2Cl_2$  requires C, 57.1; H, 11.5; N, 8.85; Cl, 22.5%).

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### 366. *A Synthesis of 3 : 4 : 6-Trimethyl Glucose.*

By G. D. GREVILLE and D. H. NORTHCOTE.

3 : 4 : 6-TRIMETHYL GLUCOSE has been obtained during structural investigation of certain polysaccharides (Granichstädten and Percival, *J.*, 1943, 54; Putman, Potter, Hodgson, and Hassid, *J. Amer. Chem. Soc.*, 1950, **72**, 5024), and its  $\beta$ -methylglucoside has been prepared from 4 : 6-dimethyl 2 : 3-anhydro- $\beta$ -methylalloside (Peat and Wiggins, *J.*, 1938, 1810). Haworth, Hirst, and Panizzon (*J.*, 1934, 154) synthesised the sugar in an amorphous state by a route through 2-tosyl  $\beta$ -methylglucoside. Sundberg, McCloskey, Rees, and Coleman (*J. Amer. Chem. Soc.*, 1945, **67**, 1080) obtained it in crystalline form from 2-benzyl 3-methyl  $\beta$ -methylglucoside. In this laboratory we had easy access to 2-benzoyl 3-methyl  $\beta$ -methylglucoside (Bell and Greville, *J.*, 1950, 1902), and Dr. D. J. Bell suggested that, provided the benzoyl radical did not migrate, a simple synthesis of the sugar should be possible from this substance. We therefore methylated it to obtain 2-benzoyl 3 : 4 : 6-trimethyl  $\beta$ -methylglucoside which, when heated under reflux with aqueous ethanolic sodium hydroxide, was converted easily and in good yield into crystalline 3 : 4 : 6-trimethyl  $\beta$ -methylglucoside. The latter was then hydrolysed to the crystalline sugar.

*Experimental.*—M. p.s (uncorr.) and rotations (measured in 2-dm. tubes) were determined on specimens dried *in vacuo* over phosphoric oxide at room temperature. Elementary analyses were by Drs. Weiler and Strauss, Oxford. Solvents were removed under reduced pressure, and solvents distilled in glass were used for recrystallisations.

*2-Benzoyl 3 : 4 : 6-trimethyl  $\beta$ -methylglucoside.* 2-Benzoyl 3-methyl  $\beta$ -methylglucoside (Dewar and Fort, *J.*, 1944, 496; prepared according to Bell and Greville, *loc. cit.*) (1.42 g.) was methylated three times with Purdie's reagents, *ca.* 20 mols. of methyl iodide being used each time. The product (1.46 g.) crystallised on seeding, and recrystallisation from light petroleum (b. p. 60–80°) gave 2-benzoyl 3 : 4 : 6-trimethyl  $\beta$ -methylglucoside as needles, m. p. 78–80° (1.29 g., 83%). After further recrystallisation from ether-light petroleum (b. p. 40–60°) the substance had m. p. 79.5–80° (not raised by another recrystallisation) and  $[\alpha]_D^{20} + 34.4^\circ$  in chloroform (*c.* 1.9) (Found: C, 60.1; H, 7.0; OMe, 36.5;  $C_6H_5 \cdot CO$ , 31.1.  $C_{17}H_{24}O_7$  requires C, 60.0; H, 7.05; OMe, 36.5;  $C_6H_5 \cdot CO$ , 30.9%).

*3 : 4 : 6-Trimethyl  $\beta$ -methylglucoside.* To the benzoyl compound (1.35 g.) dissolved in 27 ml. of ethanol, 27 ml. of 0.3N-sodium hydroxide were added. After 30 minutes' boiling under reflux, water was added, and the solution concentrated to remove ethanol and extracted five times with an equal volume of chloroform. The combined extracts were dried ( $Na_2SO_4$ ) and evaporated. Recrystallisation of the residue (0.92 g.) from light petroleum (b. p. 60–80°) containing a little chloroform gave the glucoside (0.79 g., 84%), m. p. 51.5–52.5° (not raised by further recrystallisation from ether-light petroleum, b. p. 40–60°),  $[\alpha]_D^{20} - 17.5^\circ$  in chloroform (*c.* 2.0) (Found: OMe, 52.8. Calc. for  $C_{10}H_{20}O_6$ : OMe, 52.5%). After another recrystallisation the substance again had  $[\alpha]_D - 17.5^\circ$ . Previous values are:  $[\alpha]_D^{20} - 20^\circ$  (Haworth *et al.*, *loc. cit.*),  $[\alpha]_D^{19} - 20.9^\circ$  (Peat and Wiggins, *loc. cit.*),  $[\alpha]_D^{25} - 16.4^\circ$  (Sundberg *et al.*, *loc. cit.*).

*3 : 4 : 6-Trimethyl glucose.* The glucoside (1.04 g.) was hydrolysed according to Sundberg *et al.* (*loc. cit.*). A solution of the product in boiling diisopropyl ether, after being cooled and seeded with a specimen of the  $\beta$ -anomer, kindly given by Dr. G. H. Coleman of the State

University of Iowa, deposited crystals in 75% yield. Unlike Sundberg *et al.* (*loc. cit.*), we were unable to separate the material into  $\alpha$ - and  $\beta$ -forms, but a small specimen was obtained with m. p. 94–97°. On admixture with Dr. Coleman's specimen (m. p. 97–98°) the m. p. was 96–98°. The remainder of our material was recrystallised from dry peroxide-free diisopropyl ether to give two crops. The first (0.43 g.) had  $[\alpha]_D^{19} +67.7^\circ$  (9 minutes),  $+77.9^\circ$  (540 minutes, equilibrium value) in water (*c.* 1.7) (Found: OMe, 42.0. Calc. for  $C_9H_8O_6$ : OMe, 41.9%). The second crop (0.18 g.) had  $[\alpha]_D^{20} +46.5^\circ$  (17 minutes),  $+78.2^\circ$  (1140 minutes, equilibrium value) in water (*c.* 1.8). Comparison of the mutarotation curve with that of Sundberg *et al.* (*loc. cit.*) showed that this crop contained a high proportion of the  $\beta$ -anomer. Sundberg *et al.* give  $[\alpha]_D^{20} +77.4^\circ$  and  $78.0^\circ$  at equilibrium. Our material gave a single compact spot on a paper chromatogram (*n*-butanol–water), and 1 mole reduced 1.00 mole of metaperiodate (Greville and Northcote, *J.*, 1952, 1945).

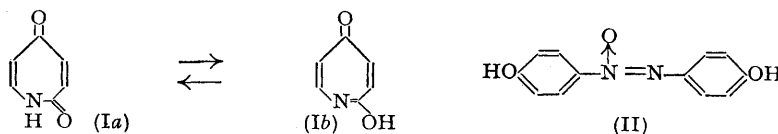
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### 367. The Alleged Beckmann Rearrangement of Quinone Monoxime.

By R. A. RAPHAEL and EMANUEL VOGEL.

DURING studies on the rearrangement of oximes, Beckmann and Liesche (*Ber.*, 1923, 56, 12) investigated that of quinone monoxime (*p*-nitrosophenol). As use of the usual acid conditions (hydrogen chloride, phosphorus pentachloride in ether) was unsuccessful the rearrangement was carried out by means of benzenesulphonyl chloride–pyridine. This treatment gave a homogeneous product to which the above workers assigned the expected seven-membered structure (Ia) on the basis of elementary analysis and molecular-weight determination. This substance in its tautomeric imidol form (Ib) may be regarded as an aza- $\gamma$ -tropolone, and indeed some of the properties recorded by Beckmann and Liesche (*e.g.*, lack of carbonyl reactivity and solubility in alkali) gave support to this conception. It was clearly desirable therefore to re-examine this compound in the light of recently acquired knowledge of the tropolone system.



Quinone monoxime reacted violently with benzenesulphonyl chloride in pyridine, giving a tar from which the relatively pure product was readily isolated by extraction with ether. The melting points of the compound and its benzoyl derivative, its lack of carbonyl reactivity, and its solubility in alkali were found to be as described by the previous workers, but elementary analysis showed it to possess the empirical formula  $C_{12}H_{10}O_3N_2$  rather than  $C_6H_5O_2N$  as required by (I). It was, in fact, *pp'*-dihydroxyazoxybenzene (II), identical with an authentic specimen prepared in an unequivocal manner by peracetic acid oxidation of *pp'*-dihydroxyazobenzene (Bigiavi and Carrara, *Gazzetta*, 1923, 53, 287). This formulation accounts for all the properties observed by the above authors and in particular for a positive Liebermann nitroso-reaction which is difficult to explain on the basis of (I).

The mechanism of formation of the azoxy-compound from *p*-nitrosophenol remains obscure. It is well known that an aromatic nitroso-compound can yield the corresponding azoxy-compound in a mild reducing medium, part being reduced to the phenylhydroxylamine which then condenses with unchanged nitroso-compound (Sidgwick, Taylor, and Baker, "Organic Chemistry of Nitrogen," 1942, p. 427; cf. Fischer and Wacker, *Ber.*, 1888, 21, 2616). It seems difficult, however, to discern any easily oxidisable component of the present medium which would enable it to function in this manner; that pyridine should fulfil this role by conversion into its *N*-oxide is highly unlikely.

Although Beckmann and Liesche were thus in error concerning the rearrangement of quinone monoxime, there seems little doubt that from anthraquinone monoxime, they did

in fact obtain the dibenz-analogue of (I), for hydrolysis of this product readily gave *o*-aminobenzophenone-*o*'-carboxylic acid. This analogue exhibited no tropolone-like properties; it behaved as a typical keto-amide, giving carbonyl derivatives and showing no solubility in alkali.

*Experimental.*—*Attempted rearrangement of quinone monoxime.* To a solution of the oxime (9 g.) in dry pyridine (70 c.c.) benzenesulphonyl chloride (10 g.) was added slowly. The solution became warm and darkened and, on being kept overnight, deposited yellow needles of quinone monoxime benzenesulphonate. The reaction mixture was then cautiously heated on a water-bath under a reflux condenser until the inception of the violent reaction (*ca.* 20 min.). After the abatement of the reaction the cooled, dark-red solution was poured into sulphuric acid (25% ; 200 c.c.), and the resulting tarry suspension well extracted with ether; the yellow ethereal extract was washed well with water and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent gave crude *pp'*-dihydroxyazoxybenzene (II) (4.7 g.), crystallising from acetic acid in long yellowish-brown plates, m. p. 224° (decomp.) alone or mixed with an authentic sample, m. p. 224° (decomp.) (Bigiavi and Carrara, *loc. cit.*). From aqueous solvents the compound crystallised as a hydrate which readily lost water above 110° (Found : C, 62.2; H, 4.65; N, 12.25. Calc. for  $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_2$  : C, 62.55; H, 4.35; N, 12.15%). The diacetate, prepared in quantitative yield by pyridine-acetic anhydride, crystallised from acetic acid in pale yellow needles, m. p. 163–164° alone or mixed with an authentic sample (Found : C 61.2; H, 4.85; N, 8.6. Calc. for  $\text{C}_{16}\text{H}_{14}\text{O}_5\text{N}_2$  : C, 61.15; H, 4.45; N, 8.9%). The similarly prepared dibenzoate, crystallising in pale yellow plates, m. p. 190–191°, from benzene, likewise gave no depression in m. p. on being mixed with the dibenzoate of (II) (Bigiavi and Guarducci, *Gazzetta*, 1927, 57, 153) (Found : C, 70.95; H, 3.85; N, 6.9. Calc. for  $\text{C}_{26}\text{H}_{18}\text{O}_5\text{N}_2$  : C, 71.25; H, 4.1; N, 6.4%). The latter compound showed strong anisotropy at the m. p., the melt remaining turbid even at 240°; this effect is a well-known property of many azoxy-compounds.

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### 368. *An Improved Synthesis of 4-Bromo-4'-hydroxydiphenyl.*

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DURING synthetic work 4-bromo-4'-hydroxydiphenyl was needed in quantity. Bromination of the esters of 4-hydroxydiphenyl, which according to Hazlet (*J. Amer. Chem. Soc.*, 1937, **59**, 1087; 1939, **61**, 1447) gives 4'-bromo-derivatives, led to such poor yields that the less direct method, based on the bromination of 4-nitrodiphenyl and its subsequent reduction and diazotisation, was adopted. These later steps have been much improved and can be operated on a large scale to give high yields of pure products.

*Experimental.*—M. p.s are corrected. Diphenyl was nitrated by the method of Bell, Kenyon, and Robinson (*J.*, 1926, 1242), except that the temperature was maintained at  $86^\circ \pm 2^\circ$ . In this way the yield of 4-nitrodiphenyl which crystallised from the nitration liquors was the same as that obtained previously after fractional distillation of the product. 4-Bromo-4'-nitrodiphenyl was prepared by the method of Le Fèvre and Turner (*J.*, 1926, 2045), but the yield was only 50%.

*4-Amino-4'-bromodiphenyl.* A mixture of 4-bromo-4'-nitrodiphenyl (81 g.), iron pin-dust (58 g.), ethyl alcohol (500 c.c.; 90%), and concentrated hydrochloric acid (29 c.c.) was stirred under reflux on a boiling-water bath for approx. 12 hours. The theoretical amount of sodium carbonate (22 g.) was added and stirring was continued for 30 minutes, whereafter a slight excess of dilute aqueous ammonia was added. After the resulting mixture had been cooled quickly, ether was added and the whole filtered (to ensure the complete removal of the amine the precipitated ferric oxide was washed with more ether). After removal of the ether from the filtrate, the warm alcoholic solution was poured into an equal volume of cold water to



precipitate the amine. This was obtained as a grey powder, m. p. 145.5° (69 g., 94%) and was virtually pure: its m. p. was unchanged by crystallisation from alcohol.

*4-Bromo-4'-hydroxydiphenyl.* A solution of the amine suitable for rapid diazotisation was prepared by dissolving 4-amino-4'-bromodiphenyl (60 g., 1 mol.) in glacial acetic (360 c.c.) at 90° and, while this was vigorously agitated, adding quickly 360 c.c. of a 40% (w/w) solution of sulphuric acid at 80°. Stirring was continued while the mixture was cooled to 0°. A solution of sodium nitrite (41.6 g.) in water (100 c.c.) was then added at 0° ± 1° and the mixture stirred at 0—5° until a clear solution was obtained (15—20 minutes). Urea was next added in small portions until the solution was free from nitrite (20—25 minutes). The ice-cold diazonium solution was run immediately into a vigorously stirred and boiling solution of sulphuric acid (135 c.c.; 40% w/w) in 30 minutes. The solution was added slowly at first, until suspended particles were visible in the reaction mixture, after which the rate of addition was increased. When the solution had been refluxed for 15 minutes it was cooled and diluted with an equal volume of water. The solid deposited was collected and digested with hot N-sodium hydroxide (300 c.c.). After removal of insoluble material by filtration, the orange-coloured filtrate was acidified, to give colourless 4-bromo-4'-hydroxydiphenyl, m. p. 166—167° (51 g., 85%). This material was almost pure, for crystallisation from alcohol left the m. p. at 167°.

By these procedures 43 g. (17.2%) of 4-bromo-4'-hydroxydiphenyl were obtained from 154 g. of diphenyl. These figures compare favourably with the overall yield (14.4 g., 5.8%) obtained by previous workers. Although this synthesis involves a number of steps it is reliable.

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