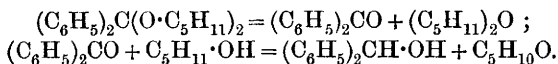


LXXIX.—*The Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzylidene Chloride. Part II.*

By JOHN EDWIN MACKENZIE and ALFRED FRANCIS JOSEPH.

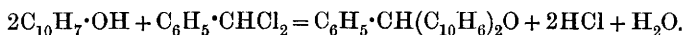
IN a previous paper on this subject, one of us described the preparation of dipropoxy- and diisobutyloxy-diphenylmethanes and dihydroxy-tetraphenylmethane as well as the products obtained by the action of certain sodium alkyloxides on benzylidene chloride. The research has been extended to the naphthols, and some experiments with aliphatic alcohols have been repeated.

By the action of sodium *iso*amyloxide on benzophenone chloride, a minute quantity of crystals melting at 66—67° had been obtained, the constitution of which could not then be explained, but on repeating the experiment larger amounts have been separated, and the crystals have been proved to be benzhydrol. The formation of benzhydrol may be explained by supposing that di*iso*amylxydiphenylmethane is first decomposed into benzophenone and *iso*amyl ether, the former being then reduced by the *iso*amyl alcohol present :



This substance is also formed in the preparation of di*isobutyl*oxy- and di*isopropyl*oxy-diphenylmethanes. It is curious that this reaction should take place only in the case of secondary alcohols.

Satisfactory products have not yet been obtained as a result of the action of α -naphthol on benzylidene chloride, but from β -naphthol a substance has been isolated which is identical with that produced by Claisen (*Annalen*, 1887, 237, 261) on condensing β -naphthol with benzaldehyde in the presence of hydrochloric acid under increased pressure, or of acetic and sulphuric acids under the atmospheric pressure. The reaction may be supposed to take place according to the equation :



A study of the interactions of the naphthols and benzophenone chloride is being carried on by Mr. Albert Shrimpton.

EXPERIMENTAL.

Benzhydrol.

In attempting to prepare di*iso*amylxydiphenylmethane, 4.6 grams of sodium dissolved in 80.5 grams of amyl alcohol (b. p. 131—131.5°) were heated at 150° for 14 hours with 23.7 grams of benzophenone chloride, and as the product was still alkaline, 2.3 grams of benzophenone chloride were then added and the heating continued for another 10 hours. Ether was added to the cold product in order to precipitate the sodium chloride, and, after evaporating the ether, the excess of amyl alcohol was distilled off under reduced pressure. The residue, when placed in a mixture of ice and salt, became semi-solid and remained so at the ordinary temperature, but melted at a slightly higher temperature. An analysis of this product indicated that it is a mixture of amyl alcohol with di*iso*amylxydiphenylmethane.

As the product still contained sodium chloride (0.0153 gram being found in the platinum boat after the combustion of 0.71 gram), it was

extracted with dry ether, the solution filtered and evaporated, and the residue cooled in a freezing mixture. In this way, crystals were separated which melted at 65—66°, the melting point not altering when the substance was mixed with benzhydrol prepared by other methods. On combustion, the following figures were obtained :

0.3376 gave 1.0473 CO₂ and 0.2082 H₂O. C = 84.60 ; H = 6.85.

C₁₃H₁₂O requires C = 84.78 ; H = 6.52 per cent.

The following cryoscopic determinations were made by Mr. G. W. Clough :

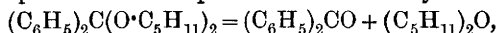
0.0402 in 16.448 benzene gave $\Delta t = 0.079^\circ$. M. W. = 154.7.

0.0968 „ 16.448 „ „ $\Delta t = 0.185^\circ$. M. W. = 159.0.

C₁₈H₁₂O requires M. W. = 184.0.

To prove the absence of optical activity, polarimetric readings were taken of a 5 per cent. solution in benzene, but no rotation was observed in a polarimeter reading to 0.01°.

As a further proof that the substance was benzhydrol, some crystals were kept over sulphuric acid in a vacuum desiccator for twelve days, at the end of which time the loss in weight only amounted to 1 per cent. Had the substance been the diisoamyl compound, it should have become decomposed into benzophenone and diisoamyl ether,



in accordance with the behaviour of its homologues.

In the former description of the preparation of diisobutyloxydiphenylmethane (Trans., 1901, 79, 1207), it will be noticed that a very small amount of crystalline substance melting at 62—64° and generally agreeing in properties with benzhydrol was obtained. The analytical numbers (C = 84.53 ; H = 6.86 per cent.) showed it to have a composition agreeing closely with that of benzhydrol.

Dibenzoxydiphenylmethane.

To the description of this substance formerly given (Trans., 1896, 69, 992) may be added the fact that, like its homologues, it may be decomposed into benzophenone and dibenzyl ether. On heating in a dry test-tube at 220° for half an hour, a colourless liquid condensed on the upper part of the tube, and the residual oil solidified on cooling. The solid distilled between 250° and 300° under atmospheric pressure, and the colourless crystals which separated in the distillate, after drying on a porous plate, melted at 48—49° and showed the characteristic properties of benzophenone.

The Anhydride of Phenyl-di-β-hydroxynaphthylmethane.

Benzylidene chloride (14·7 grams) was mixed with a large excess of β-naphthol (52 grams) in a round-bottomed flask and heated at 100°, at which temperature a copious evolution of hydrogen chloride took place. As the reaction subsided, the temperature was raised to 120° and kept there for eight hours, at the end of which time no further evolution of gas took place. The loss in weight amounted to 7·3 grams, the theoretical loss calculated for 2HCl being 6·6 and that for 2HCl + H₂O being 8·3. In another experiment, the actual loss was 8·3 grams, the calculated numbers being 7·3 and 9 respectively. The violet residue was powdered and extracted with carbon disulphide, in which it readily dissolved. From the solution, a colourless, crystalline powder was precipitated by the addition of a large volume of alcohol, the yield amounting to 73 per cent. of the calculated amount. This powder was found to be sparingly soluble in cold alcohol, ether, or acetic acid, easily so in chloroform or carbon disulphide, and moderately so in hot acetic acid. By recrystallisation from the last-named solvent, colourless, glistening leaflets were obtained, melting at 190—191° (Claisen gives 189—190°). A specimen which had been kept in a vacuum desiccator over soda-lime was employed in the following analysis:

0·1632 gave 0·5397 CO₂ and 0·07887 H₂O. C = 90·19; H = 5·37.

C₂₇H₁₈O requires C = 90·50; H = 5·03 per cent.

Attempts to determine the molecular weight by the cryoscopic method were unsuccessful owing to the slight solubility of the substance. The following results were obtained by the ebullioscopic method, using chloroform as solvent:

0·2034 in 21·24 chloroform gave Δ*t* 0·108°. M. W. = 325.

C₂₇H₁₈O requires M. W. = 358.

This substance does not yield β-naphthol on fusion with caustic potash.

Other modifications of the method of preparation have been tried, but with less favourable results. On gradually adding a xylene solution of benzylidene chloride to a boiling solution of β-naphthol in the same solvent, a steady evolution of hydrogen chloride takes place, but the product is decolorised with great difficulty.

In the hope of obtaining phenyl-di-β-hydroxynaphthylmethane, C₂₇H₂₀O₂, itself, experiments were made with sodium naphthoxide and benzylidene chloride, but only the anhydride, C₂₇H₁₈O, could be isolated. An alcoholic solution of 15·7 grams of β-naphthol was added to

794 MACKENZIE AND JOSEPH: BENZOPHENONE CHLORIDE

a solution of 2.5 grams of sodium in the same solvent, and the alcohol removed by heating first in a water-bath and then in an air-bath, a current of dry air being passed over the residue, which was then mixed with 8.7 grams of benzylidene chloride and the mixture heated at 130° for 15 hours. No hydrogen chloride was evolved, and the solid mixture was extracted with carbon disulphide, leaving a residue of sodium chloride which weighed 6.5 grams, the calculated amount being 6.3 grams. The solution, when concentrated and treated with alcohol, gave a sandy, crystalline precipitate. When crystallised from glacial acetic acid, the crystals melted at 191° and agreed in all their properties with the foregoing anhydride.

Qualitative experiments with acetylated naphthols and benzylidene chloride yielded negative results.

Nitration of the Anhydride.

Although the experimental conditions were varied, pure compounds could not be isolated, the analytical numbers indicating that di-, tri-, penta-, and hexa-nitro-compounds had been formed.

A mixture of 20 grams of fuming nitric acid (sp. gr. 1.5) and 100 grams of glacial acetic acid was added to 5 grams of the anhydride suspended in 50 grams of glacial acetic acid, the whole being well cooled. A yellow powder and a deep orange solution resulted, the former being collected, then washed with boiling glacial acetic acid and dried in a vacuum desiccator over solid caustic soda. This substance melted with decomposition at 252—253° and was analysed with the following result, which indicated a dinitro-derivative:

0.4074 gave 23.3 c.c. moist nitrogen at 20° and 766 mm. $N = 6.59$.

$C_{27}H_{16}O(NO_2)_2$ requires $N = 6.25$ per cent.

In another experiment, 1.8 grams of the anhydride mixed with 20 c.c. of nitric acid (sp. gr. 1.4) were heated in a water-bath for 3 hours, a red solution being produced, from which a yellow powder separated on cooling. The filtrate from this powder was poured into a large volume of water, and the yellow precipitate thus obtained was heated with glacial acetic acid, in which it only partially dissolved. The portion insoluble in acetic acid charred at about 250° and gave the numbers recorded in analysis I.

The solution in acetic acid on dilution with water yielded a precipitate, the analysis (II) of which showed it to consist mainly of the trinitro-compound.

I. 0.16069 gave 9.6 c.c. moist nitrogen at 16.2° and 762 mm.
 $N = 7.0$.

II. 0.13122 gave 10.3 c.c. moist nitrogen at 13° and 744 mm.
N = 9.03.

$C_{27}H_{16}O(NO_2)_2$ requires N = 6.25 per cent.

$C_{27}H_{15}O(NO_2)_3$ „ N = 8.52 „

In a third experiment, the anhydride (3.5 grams) was added to 40 c.c. of nitric acid (sp. gr. 1.5) cooled in ice; it dissolved with effervescence, and after half an hour the mixture was poured on to crushed ice. The yellow precipitate (I) thus obtained was dissolved in glacial acetic acid, and on cooling a yellowish-red powder separated which charred at about 200°. Fractional precipitation of the acetic acid solution by the addition of water gave several precipitates, the last of which was analysed (II).

I. 0.1118 gave 11.7 c.c. moist nitrogen at 14.2° and 752 mm.
N = 12.17.

II. 0.1633 gave 18.75 c.c. moist nitrogen at 15.5° and 760 mm.
N = 13.5.

$C_{27}H_{18}O(NO_2)_5$ requires N = 12.0 per cent.

$C_{27}H_{12}O(NO_2)_6$ „ N = 13.38 „

Action of Sulphuric Acid on the Anhydride.

According to Trzcinski (*Ber.*, 1883, 16, 2839, and 1884, 17, 500), an acid, which he calls "melinoïn-trisulphonic acid," is obtained by the action of concentrated sulphuric acid on benzaldehyde and β -naphthol. In our experiments, the only product obtained was a β -naphthol-disulphonic acid, which was isolated in the form of its barium salt.

Five grams of the powdered anhydride were mixed with 20 c.c. of fuming sulphuric acid and left for a week, after which the mixture was poured on to ice; the product, which dissolved completely, was neutralised with barium carbonate, and on concentrating the clear solution, crystals were obtained, which, when recrystallised from hot water, yielded colourless needles (1.8 grams). Analysis of these crystals (I) showed them to be a barium β -naphtholdisulphonate containing six molecules of water of crystallisation. By evaporating the mother liquors, 3.6 grams of a red, glassy substance (II) were obtained having approximately the same composition:

I. 0.6408 at 105° lost 0.1216. $H_2O = 18.98$.

II. 0.7526 „ 105° „ 0.1404. $H_2O = 18.68$.

I. 0.4225 salt dried at 105° gave 0.212 $BaSO_4$. Ba = 29.27.

II. 0.5347 salt not dried at 105° gave 0.235 $BaSO_4$. Ba = 25.86.

I. 0.452 salt dried at 105° gave 0.4532 CO_2 and 0.0902 H_2O .

C = 27.34; H = 2.2.

$C_{10}H_6O_7S_2Ba \cdot 6H_2O$ requires $H_2O = 19.72$; Ba = 25.05 per cent.

$C_{10}H_6O_7S_2Ba$ requires C = 27.4. H = 1.38; Ba = 31.26 „

These results show that the anhydride has undergone decomposition.

When warmed in the water-bath for some hours with concentrated sulphuric acid (sp. gr. 1.84), the anhydride gives a red solution, which, when poured on to ice, slowly deposits an orange-red powder, leaving a bright red liquid. The colour is removed from both powder and liquid by the addition of caustic alkalis, and is restored by acids.

BIRKBECK COLLEGE,
LONDON, E.C.
