aa-DIMENTHYL-β-PHENYLINDENE.

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The dehydrogenating action of aluminium chloride was made the subject of a series of studies by Scholl and his collaborators (Annalen, 1912, 394, 111; 1913, 398, 82; Ber., 1922, 55B, 109, 118, 324 and later papers). Apart from this work, other instances of a similar effect have been recorded, but not exhaustively studied. In the number of examples quoted by Scholl, the union of aromatic nuclei by the elimination of aromatic hydrogen is involved, and it is pointed out in the first paper of the series that this is analogous to the change brought about in many pyrogenic reactions. The present communication describes the production of a similar effect by aluminium bromide, with the added interest that ring-formation by the simultaneous elimination of aromatic and aliphatic hydrogen is observed.

When aluminium bromide is allowed to act upon a solution of trimethylethylene dibromide in benzene, a solid hydrocarbon of the composition C₁₇H₁₆ is formed in considerable quantities. A study of the break-down by various means of this hydrocarbon leads to the conclusion that it is aa-dimethyl-β-phenyl-indene (1). On exhaustive oxidation by sulphuric acid in the presence of mercuric sulphate, phthalic acid is obtained, while less drastic oxidation by chromic acid in glacial acetic acid leads to the formation of a very stable acid of the composition C₁₇H₁₆O₃.
This acid is apparently a γ- or δ-keto-acid, since, when it is heated with acetic anhydride, an acetyl derivative, \( \text{C}_{17}\text{H}_{15}\text{O}_2\cdot\text{OOC}\cdot\text{CH}_3 \), is obtained. The formation of this derivative is quite in accord with the structure (II) indicated for the acid.

In most acids of the type, whether of a purely aliphatic nature or, as in this case, containing an aromatic nucleus, the alternatives of unsaturated lactone formation and acetylation are available:

In the case of the acid under consideration, however, the gem-dimethyl grouping would prevent the elimination of water, so that, in consequence, acetylation and not dehydration is brought about by heating with acetic anhydride, with the formation of the acetyl derivative (III). Further confirmation of the structure (II) assigned to the acid is afforded (a) by its behaviour on heating with baryta, when cumene is produced, and can be identified by its conversion into the \( p \)-sulphonamide (m.p. 106-107° C.); and (b) by its oxidation with alkaline permanganate to phthalic acid.
With aqueous nitric acid the hydrocarbon readily undergoes nitration, yielding a mono-nitroderivative which is insoluble in alkalies, and which on oxidation yields the same acid (II) as is obtained from the hydrocarbon itself. The nitro-compound must, therefore, be assigned the structure (IV).

The formation of the hydrocarbon can be explained by the following scheme:

**Experimental.**

Preparation of \( \alpha \alpha \)-dimethyl-\( \beta \)-phenyl-indene.

Trimethylethylene dibromide (113 grams) was dissolved in dry benzene (375 cc.) and aluminium bromide (189 grams) added in small portions. Since aluminium bromide possesses a low melting point, it was used in the liquid condition, a few cubic centimetres at a time being poured into the reaction-mixture. After all the bromide had been added, the mixture was heated on a boiling water-bath for half an hour. It was then poured into ice-water, the benzene layer being separated off and washed successively with sodium carbonate solution and water. After drying,
most of the benzene was evaporated off. Since, during this process, some hydrobromic acid appeared to be formed, it was found advisable, to prevent conversion of the dimethylphenylindene into tarry products, to add a little calcium carbonate to the solution before evaporating. The concentrated benzene solution was filtered, the remaining benzene removed, and the residual liquid distilled at 35-40 mm. pressure. The fraction boiling between 150° and 230° C. was collected, and again distilled at 36-38 mm. The portion of the distillate collected between 190° and 205° C. solidified after some days’ standing, and was re-crystallised from alcohol, 6.5 grams of white crystalline hydrocarbon melting at 48° C. being obtained. From the mother-liquors and from the other fractions a further 4.3 grams of crystalline hydrocarbon melting at 45-46° C. were recovered. Further recrystallisation raised the melting point to 51° C. Found: C 92.5, H 7.5 per cent.; calculated for C_{17}H_{16}O_3, C 92.7, H 7.3 per cent.

Oxidation of the hydrocarbon by sulphuric acid in the presence of mercuric sulphate.

The hydrocarbon (1 gram) was heated in a retort with concentrated sulphuric acid (10 cc.) and mercuric sulphate (0.5 gram). When the contents of the retort were no longer liquid, the crystalline sublimate in the neck of the retort was dissolved out with caustic soda solution and united with the acid distillate. After being rendered acid, the combined solutions were extracted with ether. By this means 0.05 gram of crystalline phthalic acid was obtained, its identity being established by its melting point, conversion into the anhydride, and by the fluorescein reaction.

Oxidation of the hydrocarbon by chromic acid in glacial acetic acid.

To a warm solution of the hydrocarbon (4.0 grams) in glacial acetic acid (100 cc.), a boiling solution of chromic acid (8.5 grams) in glacial acetic acid (300 cc.) was
added. After being boiled for 5 minutes, the combined solution was poured into cold water. The mixture was then extracted repeatedly with benzene, the total volume of the united extracts being about 500 cc. After being washed with water, the benzene solution was shaken with dilute caustic soda solution, which was then separated and made acid with hydrochloric acid. The precipitated acid was purified by re-dissolving in alkali and again precipitating with acid. By this means 3.4 grams of acid melting at 196-7° C. were obtained. After reerystallisation from benzene and ligroin it melted at 198° C. Found: C 75.8, 76.1, H 6.1, 6.4 per cent.; calculated for C_{17}H_{15}O_{2}, C 76.1, H 6.0 per cent. Equivalent by titration with standard alkali, found, 274; calculated, 268.

**Action of acetic anhydride on the acid.**

The acid (1.0 gram) was dissolved in acetic anhydride (25 cc.) and the solution boiled for half an hour. After pouring the mixture into water, a solid separated which was washed with dilute caustic soda and with water. The crude material (1.1 grams) melted at 133-4° C., and was reerystallised from ligroin, the melting point of the purified material being 137° C. Found: C 73.5, H 5.9 per cent.; calculated for C_{19}H_{18}O_{4}, C 73.5, H 5.8 per cent.

**Distillation of the acid with baryta.**

The acid (2.0 grams) was intimately mixed with crystalline barium hydrate (12.0 grams) and heated until no more distillate passed over. The distillate, which had separated into two layers, was extracted with ether. After removal of the solvent, the residual oil was distilled, the portion up to 155° C. being collected. This was shown to consist principally of cumene, by sulphonation, separation of the characteristic barium salt of the p-sulphonic acid, and conversion of this successively into the sodium salt, the sulphonic chloride, and finally into the sulphonamide,
which was identified by its melting point (106.7°C, not depressing the melting point of an authentic sample of p-cumenesulphonamide).

Oxidation of the acid with alkaline permanganate.
The acid (0.1 gram) was dissolved in sodium carbonate solution (5 cc. of 10%), potassium permanganate solution (20 cc. of 2%) added, and the solution allowed to stand for twenty-four hours at room temperature. After de-colorisation with sulphur dioxide, the solution was evaporated to 10 cc., filtered, and concentrated hydrochloric acid added. The resulting precipitate was filtered off and readily identified as phthalic acid as before.

Nitration of the hydrocarbon.
The hydrocarbon (2.0 grams) was mixed with nitric acid of specific gravity 1.2 (100 cc.). At room temperature the hydrocarbon soon passed into an oil, and, on boiling the mixture for 30 minutes, this oil solidified completely to a yellow crystalline mass. The crude product, after washing, and drying on a porous tile, weighed 1.65 grams, was bright yellow in colour and melted at 139-140°C. Reerystallisation from aqueous alcohol raised the melting point to 142°C. Found (micro): N, 5.6 per cent.; calculated for C$_{17}$H$_{15}$NO$_2$, N, 5.3 per cent.

The nitro compound was insoluble in caustic soda solution, and, on oxidation with chromic acid in an exactly similar way to the parent hydrocarbon, it yielded the same acid, viz., C$_{17}$H$_{15}$NO$_2$, N, 5.3% (m.p. 198°C).

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