117. *The Production of Polycyclic Aromatic Types through the* cyclo*Dehydration of Unsaturated Ketones.*

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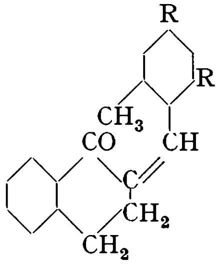
Condensation products of *o*-methyl aromatic aldehydes with various cyclic ketones have been submitted to the action of dehydrating agents. When dehydration was effected, the usual product was a methylfluorene derivative, where this was possible; and it was only when the free ortho-position was blocked that dehydration occurred between the methyl group and the ketonic group. No convenient method for the preparation of 2-methyl-Δ^1-*cyclo*hexenealdehyde, which was required for the study of the dehydration of its condensation products with various ketones, has been found, but the preparation of αβ-unsaturated cyclic aldehydes has been explored. A further extension of the problem has involved a preliminary study of the condensation of crotonaldehyde with certain ketones.

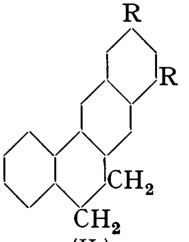
In spite of the poor yields of products obtained by means of it in many cases, the Elbs reaction has been extensively used in recent years in the production of polycyclic aromatic structures. It seemed possible that the cyclodehydration of structures such as (I) might, if it occurred between the methyl and the ketonic group, offer a useful variation of this synthesis. Analogous dehydrations of aliphatic types have been frequently recorded, and at least one such dehydration, that of 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl to yield pyranthrone (Scholl, *Ber.*, 1910, **43**, 346), has been exploited.

Dehydration of (I, R = H) did not yield (II, R = H), but with phosphoric oxide a *hydrocarbon* $C_{18}H_{14}$ was isolated which gave a ketone $C_{18}H_{12}O$ on oxidation with chromic acid. It is presumably 8-*methyl*-3 : 4-*benzfluorene* (III), since 2-*benzylidene*-α-*tetralone* yielded 3 : 4-benzfluorene itself under analogous conditions. These dehydrations are similar to those recorded by Cook, Dansi, Hewett, Mayneord, Iball, and Roe (J., 1935, 1323) in which 2-naphthylmethyl- and 3-phenanthrylmethyl-*cyclo*hexanones yielded fluorene derivatives. Attempts to dehydrate simpler structures such as 2-o-*tolylidene*-cyclo*hexanone* and *o*-tolylideneacetophenone (Weygand and Schachter, *Ber.*, 1935, **68**, 231) met with failure, an experience paralleled by that of Cook *et al.* (*loc. cit.*) with simpler structures of the type studied by them.

Dehydration involving the methyl group was effected in the case of 2-(2′ : 4′ : 6′-*trimethylbenzylidene*)-α-*tetralone* (I, R = Me), which gave a 34% yield of hydrocarbons, $C_{20}H_{18}$, formulated as 5 : 7-*dimethyl*-x : x′-*dihydro*-1 : 2-*benzanthracenes*, of which (II, R = Me) is possibly one. 2-(2′ : 4′ : 6′-*Trimethylbenzylidene*)-α-*hydrindone*, however, yielded no hydrocarbon with phosphoric oxide. This may be due to the fact that it is structurally incapable of enolisation.



(I.)



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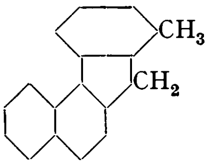
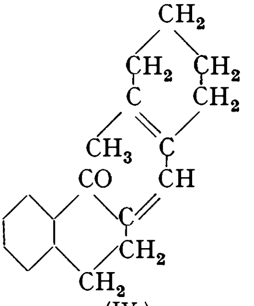


(III.)



(IV.)

In view of these results it was desirable to explore the dehydration of substances such as (IV), in which the methyl group should show increased reactivity; no simple preparation of the necessary 2-methyl-Δ^1-*cyclo*hexenealdehyde, however, has been found. The tetrahydro-*o*-toluonitrile formed by dehydration of the cyanohydrin of 2-methyl*cyclo*hexanone (Linstead and Millidge, J., 1936, 482, 485) is not reduced by the Stephen method. The failure is not due to the steric effect of the methyl group as in *o*-toluonitrile and seems to be common to all cyclic αβ-unsaturated nitriles, since Δ^1-*cyclo*hexenenitrile also was not reduced by this method. Hydrolysis of tetrahydro-*o*-toluonitrile produced under all conditions a homogeneous acid, which was identical neither with the 2-methyl-Δ^1-*cyclo*hexenecarboxylic acid described by Perkin (J., 1905, **87**, 1068) nor with the 6-methyl-Δ^1-*cyclo*hexenecarboxylic acid as described by Mazza and Cremona (*Gazzetta*, 1927, **57**, 318). That it is the latter acid, however, is indicated by its degradation with ozone to yield α-methyladipic acid. It was readily reduced by the method of Sonn and Muller (*Ber.*, 1919, **52**, 1927) to 6-methyl-Δ^1-*cyclo*hexenealdehyde without any shift occurring in the position of the double bond. An attempt to dehydrate its condensation product with acetophenone failed. As other possible procedures for the preparation of the desired aldehyde were all very long, the preparation of (IV) was abandoned.

Attention was then directed to the condensation of crotonaldehyde with ketones, the products of which might yield aromatic structures on dehydration. No condensation could be effected with α-tetralone, the crotonaldehyde undergoing self-condensation. In the case of *cyclo*hexanone a complex mixture of products was formed, which contained crotonylidene*cyclo*hexanone, but it was found impossible to separate it. An aldol-like compound accompanied it, since *cyclo*hexanone was generated on shaking with dilute alkali solution. After hydrogenation of the crude material 2-*n*-butyl*cyclo*hexanol could be separated by fractional distillation. The other product of the hydrogenation was a mixture of C_{10} compounds containing two oxygen atoms in the molecule. Their nature has not been ascertained, but exactly similar products were isolated after condensation of crotonaldehyde with acetone and with *cyclo*pentanone. It seems likely that the ketones react with the crotonaldehyde not only at the carbonyl group, but also at the double bond (cf. Stobbe, *J. pr. Chem.*, 1912, **86**, 209).

EXPERIMENTAL.

α-*Tetralone* (cf. Hartmann and Seiberth, *Helv. Chim. Acta*, 1932, **15**, 1390).—A slow current of air was passed for 3 days through tetralin at 60—80°, a little tin being added as catalyst. The peroxide formed was decomposed by the slow addition, with cooling and shaking, of an excess of concentrated ferrous sulphate solution. The aqueous layer was separated, and the product washed, dried, and distilled. Yield of α-tetralone, 12%.

2-*Benzylidene*-α-*tetralone*.—When a mixture of benzaldehyde (21 g.) and α-tetralone (29 g.) was treated with 4% alcoholic potassium hydroxide (200 c.c.), it became warm and crystals were deposited almost immediately. After 2 hours the solution was neutralised with acetic acid, water added, and the crystals filtered off. The crystals, together with some material derived from an ethereal extraction of the filtrate, gave 2-*benzylidene-α-tetralone* on distillation, b. p. 210—212°/2 mm., which crystallised from alcohol in light yellow rhombohedra (40 g.), m. p. 105° (Found : C, 87·0; H, 6·0. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%).

2-Benzylidene-α-tetralone (25 g.) was dissolved in xylene and refluxed for 15 hours with successive portions of phosphoric oxide. After decantation the xylene was evaporated, and the residue distilled in a vacuum. The distillate (7 g.), on treatment with alcoholic picric acid, slowly formed a picrate, m. p. 130—131°, from which on decomposition with aqueous ammonia a hydrocarbon (0·4 g.), m. p. 124—125°, was obtained. Cook and co-workers (*loc. cit.*) give m. p. 124—125° and 130—131° for 3 : 4-benzfluorene and its picrate respectively.

2-o-*Tolylidene-α-tetralone* (I, R = H).—*o*-Tolualdehyde (12 g.), α-tetralone (14 g.), and 4% alcoholic potassium hydroxide (100 c.c.) were mixed and after 2 hours 2-o-*tolylidene-α-tetralone* (20 g.) was obtained, b. p. 213°/2 mm. It crystallised from aqueous alcohol in light yellow needles, m. p. 68° (Found : C, 86·7; H, 6·6. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%).

8-*Methyl*-3 : 4-*benzfluorene*.—The above product (20 g.) was dissolved in xylene (100 c.c.) and refluxed with phosphoric oxide for 20 hours, the oxide being renewed at intervals. The xylene solution was decanted, the xylene evaporated, and the residue distilled in a vacuum. The distillate (9 g.) was treated with picric acid in absolute alcohol and the picrate formed was filtered off. The material obtained from the mother-liquor after removal of the picric acid was again treated with phosphoric oxide, and in this way a total of 10 g. of picrate was obtained. This *picrate* was recrystallised from ethyl alcohol, separating in red needles, m. p. 127—128° (Found: C, 62·8; H, 3·7. $C_{18}H_{14},C_6H_3O_7N_3$ requires C, 62·8; H, 3·7%). Decomposition of this material with aqueous ammonia yielded the *hydrocarbon* (5 g.), which crystallised from alcohol in colourless plates, m. p. 104—105°, b. p. 203°/2 mm. (Found : C, 93·7; H, 5·8. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%). The same hydrocarbon was obtained by the use of sodamide as condensing agent. It was left (0·5 g.) with sodium dichromate (1 g.) in acetic acid (20 c.c.) for ½ hour, and the mixture then diluted with water. The solid obtained was washed with alkali solution and recrystallised from alcohol, from which it separated in orange needles, m. p. 139·5—140·5°. It is formulated as 8-*methyl*-3 : 4-*benzfluorenone* (III) (Found: C, 88·2; H, 5·2. $C_{18}H_{12}O$ requires C, 88·5; H, 4·9%).

Condensation of o-*Tolualdehyde with* cyclo*Hexanone*.—*o*-Tolualdehyde (9·5 g.) and *cyclo*hexanone (8·5 g.) were suspended in 4% *aqueous* potassium hydroxide solution (100 c.c.) and refluxed for 2·5 hours (cf. Poggi and Guastalla, *Gazzetta*, 1931, **61**, 405; Vorländer and Kunze, *Ber.*, 1926, **59**, 2078). The products, worked up in the usual way, were separated by vacuum distillation. 2-o-*Tolylidene*cyclo*hexanone* (11·3 g.) boiled at 151—154°/4 mm. and crystallised on standing; recrystallised from light petroleum, it formed slightly yellow, elongated plates, m. p. 66—67° (Found : C, 83·8; H, 8·0. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%), very soluble in most organic solvents. The residue in the flask was identified as 2 : 6-*di*-o-*tolylidene*cyclo*hexanone* : it formed the main product when the reaction was carried out in alcoholic medium. It crystallised from alcohol in yellow plates, m. p. 138—139° (Found: C, 87·2; H, 7·3. $C_{22}H_{22}O$ requires C, 87·4; H, 7·3%). Unsuccessful attempts were made to dehydrate the former of these products by prolonged boiling, by the action of sodamide, and by the action of phosphoric oxide.

2-(2′ : 4′ : 6′-*Trimethylbenzylidene*)-α-*tetralone*.—Mesitylaldehyde (18 g.; Hinkel, Ayling, and Beynon, J., 1936, 342) and α-tetralone (18 g.) were left with 4% alcoholic potassium hydroxide (100 c.c.) for 3 hours. The product was isolated by ether extraction, and the residue left after evaporation of the ether was distilled up to 150°/15 mm. to remove unchanged materials and then crystallised from aqueous alcohol, from which it separated in colourless rhombohedra (28·5 g.), m. p. 92—92·5° (Found : C, 86·9; H, 7·2. $C_{20}H_{20}O$ requires C, 86·9; H, 7·2%).

Dehydration of 2-(2′ : 4′ : 6′-*Trimethylbenzylidene*)-α-*tetralone*.—The above substance (10 g.) was refluxed in xylene solution with successive portions of phosphoric oxide for 24 hours. After the usual treatment (see above) the distillate (4·5 g.) was converted into the *picrate* (5 g.), which crystallised from benzene in red needles, m. p. 190—191° (Found: C, 64·3; H, 4·5. $C_{20}H_{18},C_6H_3O_7N_3$ requires C, 64·1; H, 4·3%). Decomposition of the picrate yielded a hydrocarbon, presumably a 5 : 7-*dimethyl*-x : x′-*dihydro*-1 : 2-*benzanthracene* (2·5 g.), which crystallised in colourless rhombohedra, m. p. 146—147°, from glacial acetic acid (Found : C, 92·9; H, 7·0. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%).

Concentration of the mother-liquor from the crystallisation of the above picrate yielded two isomeric picrates. One of these decomposed during recrystallisation, yielding a second hydrocarbon (0·6 g.), also formulated as a 5 : 7-*dimethyl*-x : x′-*dihydro*-1 : 2-*benzanthracene*, which, recrystallised from absolute alcohol, formed colourless rhombohedra, m. p. 114° (Found : C, 92·7; H, 7·2%). The other picrate was stable, separating from absolute alcohol in red needles,

m. p. 165° : there was not sufficient of it available for analysis. On decomposition it yielded a third hydrocarbon (0·1 g.), which crystallised from absolute alcohol in colourless plates, m. p. 115·5—116·5°. It showed marked depression of m. p. with the other two hydrocarbons and is probably a third 5 : 7-*dimethyl*-x : x′-*dihydro*-1 : 2-*benzanthracene* (Found : C, 92·7; H, 7·2%). The total yield of purified hydrocarbons isolated was 3·2 g. or 34%. All showed a faint blue fluorescence in solution.

The hydrocarbon, m. p. 146—147°, was subjected to the action of selenium. Reaction was difficult to control, as the substance sublimed away from the selenium, but a small yield of a substance was obtained, which crystallised from acetic acid and had m. p. 120—121° (Found : H, 6·4. Calc. for $C_{20}H_{16}$: H, 6·3%. An accident to the carbon dioxide absorbing vessel vitiated the carbon value). This substance is formulated as 5 : 7-*dimethyl*-1 : 2-*benzanthracene*.

2-(2′ : 4′ : 6′-*Trimethylbenzylidene*)-α-*hydrindone*.—This was prepared from mesitylaldehyde and α-hydrindone in the usual way. It crystallised from aqueous alcohol in prisms of rectangular outline, m. p. 93·5—94·5°, which turned bright yellow on exposure to light (Found : C, 86·9; H, 7·0. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%). Several attempts were made to effect the elimination of water from this *substance* without success; extensive polymerisation always occurred as in other dehydration experiments, but no hydrocarbon product could be isolated.

6-*Methyl*-Δ^1-cyclo*hexenecarboxylic Acid*.—This was best obtained from the tetrahydro-*o*-toluonitrile of Linstead and Millidge (*loc. cit.*) by hydrolysis with 95% phosphoric acid (cf. Berger and Olivier, *Rec. Trav. chim.*, 1927, **46**, 600). The nitrile (25 g.) was heated for 6—8 hours at 120—130° with 95% phosphoric acid (100 c.c.). After dilution with water, the mixture was extracted with ether, and the acidic fraction separated by shaking with sodium carbonate solution. From the alkaline extracts the above *acid*, m. p. 105·5°, was obtained in 60—70% yield on acidification (Found : C, 68·4; H, 8·3. $C_8H_{12}O_2$ requires C, 68·6; H, 8·6%). It crystallised in colourless needles from water or aqueous alcohol. When a drop of bromine was added to this acid (1·2 g.) in chloroform (10 c.c.), the solution still retained its colour after 3 hours. It could be recovered unchanged after boiling with alkali solution. Repeated attempts to obtain homogeneous degradation products from this acid with potassium permanganate failed. The acid (3 g.) was therefore dissolved in water, the solution made faintly alkaline, and ozonised oxygen passed through it. The ice-cooled solution was then treated with N/10-potassium permanganate till a faint pink coloration was obtained, a stream of carbon dioxide being passed during the addition. The manganese dioxide was dissolved by the addition of sodium bisulphite, and the solution concentrated, acidified, and thoroughly extracted with ether. From the extracts α-methyladipic acid was obtained, its identity being proved by mixed m. p. determination with an authentic specimen. Price (*J. Amer. Chem. Soc.*, 1939, **61**, 1847) has reported failure to obtain α-methyladipic acid on permanganate oxidation of 1-methyl-Δ^2-*cyclo*hexene.

Hydrolysis of the nitrile with sulphuric acid of various strengths gave yields less than that obtained by the above method. Hydrolysis with alcoholic potash proceeded very slowly. The nitrile (5 g.) was added to a solution of potassium hydroxide (7 g.) in the minimum quantity of water, and alcohol added till the mixture was homogeneous. After boiling for 9 days, two products were isolated : an *acid amide* forming colourless plates, m. p. 128°, from alcohol–light petroleum (Found : C, 69·0; H, 9·2. $C_8H_{13}ON$ requires C, 69·1; H, 9·3%), and an acidic substance, m. p. 105·5°, identical with that described above. With shorter reaction periods the yield of acid diminished, and after 24 hours none could be isolated. In the latter case, however, the *amide* isolated had m. p. 146° (Found : C, 68·8; H, 9·3. $C_8H_{13}ON$ requires C, 69·0; H, 9·2%), and was accompanied by a very sparingly soluble material melting above 300° (Found : N, 9·7. $C_8H_{13}ON$ requires N, 10·1%). This *substance* is perhaps a polymerised form of one of the isomeric amides described above. As it was insoluble in camphor and most organic solvents, no molecular weight determination could be made.

6-*Methyl*-Δ^1-cyclo*hexenealdehyde*.—The acid chloride (8 g.), b. p. 92°/12 mm., obtained by the action of thionyl chloride on 6-methyl-Δ^1-*cyclo*hexenecarboxylic acid was dissolved in benzene (25 c.c.), and to the ice-cooled solution a mixture of aniline (15 g.) and chloroform (100 c.c.) was added. By evaporation of the washed and dried reaction mixture, the corresponding *anilide* was obtained (12 g.). It crystallised in needles, m. p. 106·5—107·5°, from light petroleum (Found : C, 78·3; H, 7·6. $C_{14}H_{17}ON$ requires C, 78·1; H, 7·9%). The reaction between this anilide (10 g.) and phosphorus pentachloride (10 g.) in dry toluene (50 c.c.) was completed on the water-bath at 100°, and to the syrup obtained by evaporating the toluene and the phosphorus oxychloride a solution of stannous chloride (25 g.) in ethereal hydrogen chloride (100 c.c.) was added. Crystals separated, and after 2 hours the reaction mixture was distilled with steam. From the ethereal portion of the distillate the above aldehyde (3·5 g.; 60%) was isolated,

b. p. 66—68°/10 mm., $n_D^{17°}$ 1·4898. Its *semicarbazone* was recrystallised from aqueous alcohol and had m. p. 207—209° (Found: C, 60·1; H, 8·5. $C_9H_{15}ON_3$ requires C, 59·7; H, 8·3%). Its 2 : 4-*dinitrophenylhydrazone*, m. p. 179°, was recrystallised from the same solvent (Found: N, 18·3. $C_{14}H_{16}O_4N_4$ requires N, 18·4%). Shaken with an ammoniacal solution of silver nitrate, the above aldehyde gave 6-methyl-Δ^1-*cyclo*hexenecarboxylic acid.

Condensation of Crotonaldehyde with cyclo*Hexanone.*—After trial experiments the following procedure was adopted—with more active condensing agents self-condensation of the crotonaldehyde tended to take place to the exclusion of its condensation with the ketone. Redistilled technical crotonaldehyde (100 c.c.), *cyclo*hexanone (300 c.c.), and alcohol (300 c.c.) were mixed, 1% potassium hydroxide solution (400 c.c.) added, and the flask securely corked and left for 3—4 hours with occasional shaking. The temperature of the reaction mixture was kept below 30° throughout. After neutralisation with acetic acid, the products were isolated by dilution with water and extraction with ether. The residue left on evaporation of the extracts was worked up by vacuum distillation, the main product being a fraction, b. p. 140—155°/14 mm. The resinous residue appeared to undergo considerable decomposition at higher temperatures. Separation of this main product into its components was not possible, owing to the small boiling range and the tendency of part of the material to polymerise on prolonged distillation. The lower-boiling fractions from it, however, were markedly more refractive than the later fractions and yielded a semicarbazone which rapidly turned yellow on exposure to air. This *semicarbazone* sintered at 187° and gave a meniscus at 191°, and is probably the semicarbazone of crotonylidene*cyclo*hexanone, though the analytical figures indicate that in all probability autoxidation had occurred before the material was analysed (Found for material exposed to air: C, 51·7; H, 7·3; N, 15·8. $C_{11}H_{17}ON_3 + H_2O + O_2$ requires C, 51·3; H, 7·4; N, 16·3%). The highest-boiling fractions gave none of this semicarbazone.

The crude product was dissolved in methyl alcohol, a palladium–strontium carbonate catalyst added, and the whole shaken with hydrogen at 1·5—2 atms. The product of the reaction was fractionally distilled, and the following fractions isolated: (a) b. p. 45°/9 mm., identified as *cyclo*hexanol by its oxidation to adipic acid and its lack of ketonic properties; (b) b. p. 90—100°/9 mm. This on redistillation gave 2-*n*-butyl*cyclo*hexanol, b. p. 95°/9 mm., $n_D^{17°}$ 1·4711, which was identified by its oxidation with chromic acid to 2-*n*-butyl*cyclo*hexanone, which has been characterised by Weizmann, Bergmann, and Haskelberg (*Chem. and Ind.*, 1937, **56**, 587). (c) A fraction, b. p. 146—153°/17 mm., which constituted the bulk of the material. This was a mixture, since on further fractionation it yielded fractions of different refractive index (Found: C, 70·1; H, 10·1. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%. $C_{10}H_{20}O_2$ requires C, 69·8; H, 11·6%). Repeated attempts to characterise and identify the constituents of this fraction failed.

Condensation of Crotonaldehyde with cyclo*Pentanone.*—The nature of the product obtained was found to vary considerably with the conditions used. Crotonaldehyde (10 c.c.), *cyclo*pentanone (30 c.c.), alcohol (30 c.c.), and 1% potassium hydroxide solution (20 c.c.) yielded a partially solid product under the conditions described in the case of *cyclo*hexanone. The oily material was washed away by organic solvents on the filter, and a residue of a light yellow to brown resin (5·5 g.) was left, very similar in physical characteristics to the product of the reaction between ethylene dichloride and sodium polysulphide. A portion of this was purified by repeated boiling with organic solvents, in which it was insoluble. The light yellow *product* from its analysis would appear to be derived from the crotonaldehyde by polymerisation [Found: C, 69·1, 68·8; H, 8·3, 8·1. $(C_4H_6O)_n$ requires C, 68·6; H, 8·6%]. With decreasing amounts of alkali, the yield of this resin fell rapidly, and when one quarter of the amount specified above was used no resin could be isolated. The product of the reaction under these conditions was distilled and yielded first *cyclo*pentanone (7·5 g.), and then a fraction (6 g.), b. p. 115—135°/10 mm. A residue of high-boiling material remained. The product, b. p. 115—135°/10 mm., could not be separated into its components, and in trial fractionations, a *semicarbazone*, m. p. 215—216° (decomp.), could be isolated from all fractions of the distillate (Found: C, 62·6; H, 7·5. $C_{10}H_{15}ON_3$ requires C, 62·2; H, 7·8%). This substance, which turned yellow on exposure to air and light, crystallised in needles from aqueous alcohol; its analytical figures correspond with those of the semicarbazone of crotonylidene*cyclo*pentanone.

In an attempt to characterise the other products of the reaction, the material (45 g.) was hydrogenated as described above. From the hydrogenation mixture two distinct fractions were obtained on distillation. A fraction (16 g.), b. p. 89°/10 mm., $n_D^{20°}$ 1·4568, was identified as 2-*n*-butyl*cyclo*pentanone by comparison of its semicarbazone with a synthetic specimen. α-n-*Butyladipic acid*, prepared by hydrolysis of ethyl 3-*n*-butyl*cyclo*pentan-2-one-1-carboxylate, crystallised from benzene–light petroleum, on ice-cooling, in colourless prisms, m. p. 59·5° (Found: C, 59·4; H, 9·0. $C_{10}H_{18}O_4$ requires C, 59·4; H, 8·9%). On distillation from a flask containing a small amount of barium oxide this acid yielded 2-*n*-butyl*cyclo*pentanone (yield, 71%). Its *semicarbazone* separated from aqueous alcohol in needles, m. p. 185—186° (Found: C, 61·1; H, 9·6. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·6%), identical with the semicarbazone mentioned above. A second fraction (18 g.), b. p. 127—135°/10 mm., was obviously a mixture, and presented the same difficulties with regard to its separation into its constituents as the corresponding product from *cyclo*hexanone. Analytical data indicated that it was approximately $C_9H_{16}O_2$.

Condensation of Crotonaldehyde with Acetone.—A mixture of acetone (600 c.c.) and crotonaldehyde (100 c.c.) was neutralised to phenolphthalein, and 1% potassium hydroxide solution (170 c.c.) added with cooling. After 1·5—2 hours the mixture was neutralised with acetic acid, the acetone distilled off, and the residue extracted with ether. Distillation of the product so obtained yielded a fraction (50 g.), b. p. 66—77°/15 mm., and a residue of resin. Fractionation of the distillate effected only its partial separation, though a fraction, b. p. 74—75°/15 mm., $n_D^{16°}$ 1·5210, so obtained was chiefly crotonylideneacetone, since it gave a *semicarbazone*, which separated in white plates, m. p. 164—166°, from aqueous alcohol (Found: C, 57·4; H, 7·7. $C_8H_{13}ON_3$ requires C, 57·5; H, 7·8%). The crystals gradually turned yellow on standing. Attempts to obtain toluene by dehydration of this fraction failed. In an attempt to elucidate the nature of the other products formed, the crude material (50 g.) was hydrogenated, and the product fractionally distilled. Methyl *n*-amyl ketone (20 g.), b. p. 50°/15 mm., was identified as one product of the reduction; the other product was a liquid, b. p. 61—63°/15 mm., $n_D^{18°}$ 1·4253, which gave no reaction with ketonic reagents and analyses for which were inconclusive. It definitely contained two reactive hydrogen atoms, however [Found: C, 62·8, 63·4; H, 10·7, 10·9 (different samples); reactive H (Zerewitinow), 1·47. Calc. for $C_7H_{14}O_2$ (2 reactive H's): C, 64·6; H, 10·8; reactive H, 1·54%. Calc. for $C_7H_{16}O_2$: C, 63·6; H, 12·1; reactive H, 1·51%).

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