

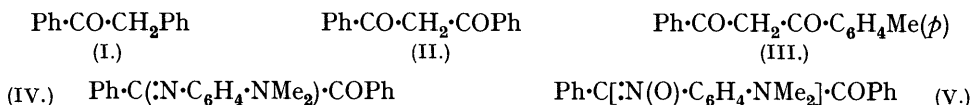
**305. Reactive Methylene Groups and Nitroso-compounds.
Abnormal Action of Acids on 1 : 2 : 3-Triketones.**

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Further examples of the formation of anil oxides by the action of nitrosobenzene and its derivatives on methylene ketones (J., 1937, 627) are reported. The substance hitherto known as benzil-*p*-dimethylaminoanil (IV) is in fact the corresponding *anil oxide* (V).

Benzoin is obtained by the action of syrupy phosphoric acid on diphenyl triketone, but concentrated sulphuric acid or anhydrous aluminium chloride produces benzil. Triketohydrindene hydrate (VII) (ninhydrin) yields bisindandione (VIII) when treated with concentrated sulphuric acid.

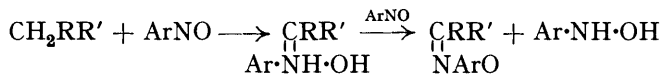
OTHER instances of the formation of anil oxides (nitrones) by the condensation of methylene ketones with aromatic nitroso-compounds (Schönberg and Michaelis, J., 1937, 627) have since been recorded by Bergmann (*ibid.*, p. 1628), Pfeiffer and Milz (*Ber.*, 1938, 71, 272), and Kröhnke (*ibid.*, pp. 2583, 2595). The reaction has now been extended to cases where the methylene group does not form part of a cyclic system : anil oxides have been obtained by the action of nitrosobenzene on the ketones (II) and (III) and of *p*-nitrosodimethyl-aniline on the ketones (I) and (II).



The formation of a nitrone from dibenzoylmethane takes place in the absence of any condensing agent (which must be present in the other cases) ; it cannot yet be decided whether the tendency of dibenzoylmethane to enolise is responsible for this behaviour (compare Abell, J., 1912, 101, 998).

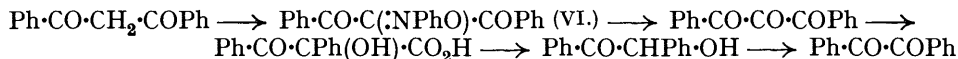
Benzil-p-dimethylaminoanil oxide (V) was obtained under the experimental conditions used by Skraup and Böhm (*Ber.*, 1926, 59, 1015) to prepare the corresponding anil (IV). The supposed anil is in fact the nitrone ; Skraup and Böhm estimated the nitrogen only and were consequently misled. The *anil* (IV) is formed together with the nitrone (V).

In addition to the cases now mentioned, nitrones have been obtained from compounds of the fluorene series, 9-methylacridine, *p*-nitrobenzyl chloride, phenylacetone, and hydrindone derivatives in accordance with the scheme :



Therefore the reaction must be regarded as one of wide application.

The hydrolysis of the *nitrone* (VI) with hot sulphuric acid took a remarkable course : benzil was obtained instead of diphenyl triketone. Diphenyl triketone, treated with sulphuric acid under analogous conditions, also gave benzil ; on the other hand, by the action of syrupy phosphoric acid benzoin was obtained ; finally, benzoin was oxidised to benzil with hot sulphuric acid. It is therefore believed that the nitrone is first hydrolysed to diphenyl triketone, which undergoes a rearrangement somewhat similar to the benzilic acid rearrangement ; carbon dioxide is then split off, and benzoin formed : if sulphuric acid is used, benzoin is oxidised to benzil.

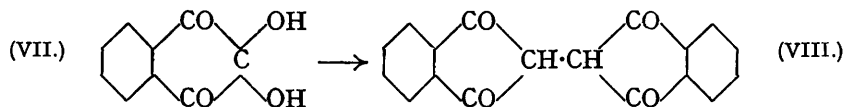


This process furnishes an unexpected method of shortening a carbon chain, namely, the conversion of a diphenylpropane derivative into a diphenylethane derivative.

An analogous process was observed when diphenyl triketone was heated with

aluminium chloride; when the reaction mixture was decomposed with cold dilute acid, benzil was obtained (private communication by A. Schönberg and R. Moubacher).

The action of sulphuric acid on triketohydrindene hydrate (ninhydrin) (VII) did not lead to the removal of a carbonyl group, but by a process not easy to explain the violet-brown bisindandione (VIII) (or its enol form) was obtained :



EXPERIMENTAL.

Action of p-Nitrosodimethylaniline on Deoxybenzoin [with R. MICHAELIS].—A solution of *p*-nitrosodimethylaniline (3 g.; 1 mol.) in warm absolute alcohol (30 c.c.) was heated with freshly crystallised deoxybenzoin (4 g.; 1 mol.) and 6 drops of piperidine on the steam-bath for 3 hours and then left in the ice box for 24 hours. The red solid obtained (3.6 g.) was crystallised from toluene (15 c.c.) and gave *benzil-p-dimethylaminoanil oxide* (V), which, recrystallised from toluene, formed red prisms, m. p. 165—166°, easily soluble in concentrated sulphuric acid, giving a yellow solution, and soluble in benzene, sparingly soluble in petrol (b. p. 60—70°) and in methyl alcohol (Found: C, 77.0; H, 5.9; N, 8.3. $C_{22}H_{20}O_2N_2$ requires C, 76.7; H, 5.8; N, 8.13%). The original toluene mother-liquor, on addition of petrol (b. p. 60—70°), deposited *benzil-p-dimethylaminoanil* (IV); this was repeatedly crystallised from methyl alcohol, forming orange-red needles, m. p. 137—138°, soluble in concentrated sulphuric acid, giving a yellow solution, and in benzene and sparingly soluble in cold methyl alcohol and petrol (Found: C, 80.5; H, 6.0; N, 8.4. $C_{22}H_{20}ON_2$ requires C, 80.6; H, 6.15; N, 8.5%).

Hydrolysis of Benzil-p-dimethylaminoanil Oxide with Sulphuric Acid.—The nitrone (0.2 g.) was heated with 8 c.c. of sulphuric acid (1 vol. of conc. acid and 1 vol. of water) on the steam-bath until the colour of the solution became faint yellow; 6 c.c. of glacial acetic acid were then added and the solution was heated for 30 minutes. After cooling in ice, yellow crystals of benzil (0.1 g.) separated, which did not depress the m. p. of an authentic sample.

The same result was obtained with 0.2 g. of the anil.

Action of Nitrosobenzene on Dibenzoylmethane [with R. MICHAELIS].—Dibenzoylmethane (3.4 g.; 1 mol.) was dissolved in warm absolute alcohol (15 c.c.), nitrosobenzene (3.2 g.; 2 mols.) added, and the solution heated on the steam-bath until the colour turned reddish-brown (20—30 mins.). A strong smell of isonitrile was developed. When the solution was cooled in a freezing mixture, *diphenyl triketone β-anil oxide* (2.2 g.) separated. Recrystallised from absolute alcohol, this formed yellow needles, m. p. 144—145° (decomp.), easily soluble in benzene and in concentrated sulphuric acid, giving a yellow solution, and sparingly soluble in ether and petrol (Found: C, 76.6; H, 4.6; N, 4.3. $C_{21}H_{15}O_3N$ requires C, 76.6; H, 4.6; N, 4.25%).

Action of Sulphuric Acid on Diphenyl Triketone β-Anil Oxide (VI).—The nitrone (0.3 g.) was refluxed for 30 minutes with 9 c.c. of sulphuric acid (1 vol. of conc. acid and 1 vol. of water); 9 c.c. of glacial acetic acid were then added to dissolve the brown oil which had formed and the solution was refluxed again for 30 minutes, cooled, and poured into 50 c.c. of ice-cold water. The solid obtained (0.1 g.) was washed with water and extracted with boiling petrol (b. p. 100—110°); the extract on evaporation left a pasty solid, which was pressed on a porous plate and crystallised from alcohol, giving yellow needles of benzil, m. p. and mixed m. p. 95° (Found: C, 80.0; H, 4.8. Calc.: C, 80.0; H, 4.8%).

Action of p-Nitrosodimethylaniline on Dibenzoylmethane.—A solution of *p*-nitrosodimethylaniline (2.5 g.; 1 mol.) in warm 95% ethyl alcohol (25 c.c.), after being heated with dibenzoylmethane (3.7 g.; 1 mol.) and sodium carbonate (1 g.; 0.6 mol.) at 50—55° for 1½ hours, was cooled and poured into 75 c.c. of ice-cold water. The thick red oil that separated was stirred with 50% methyl alcohol and then with a small amount of 96% methyl alcohol and repeatedly crystallised from the same solvent, forming dark red needles of *diphenyl triketone β-p-dimethylaminoanil oxide*, m. p. 183—185° (decomp.), easily soluble in concentrated sulphuric acid, giving a yellow solution, and in benzene, sparingly soluble in ether and in petrol (Found: C, 73.9; H, 5.6; N, 7.7. $C_{23}H_{20}O_3N_2$ requires C, 74.2; H, 5.4; N, 7.5%).

Action of Nitrosobenzene on p-Methyl-dibenzoylmethane (III).—A solution of *p*-methyl-dibenzoylmethane (Weygand, *Annalen*, 1928, 459, 113) (4.8 g.; 1 mol.) in warm absolute alcohol (20 c.c.) was heated with nitrosobenzene (4.3 g.; 2 mols.) on the steam-bath until the colour changed to orange-red. A smell of isonitrile was developed. The solution was cooled and the

yellow solid (4 g.) that separated was washed with a small amount of cold alcohol and recrystallised from absolute alcohol (40 c.c.), giving yellow silky needles, m. p. 123—130°. By fractional crystallisation two isomeric (probably geometrical) *phenyl p-tolyl triketone β-anil oxides* were separated. The solid was dissolved in hot benzene and the light yellow, silky needles that separated on cooling were recrystallised from benzene; m. p. 141—143° (Found : C, 77.05; H, 5.1; N, 4.2. $C_{22}H_{17}O_3N$ requires C, 76.9; H, 5.0; N, 4.1%). When petrol (b. p. 90—100°) was added to the benzene solution, a yellow substance separated; after repeated crystallisation from petrol this formed canary-yellow needles, m. p. 132—134° (Found : C, 77.1; H, 5.0; N, 4.2%).

Action of Phosphoric Acid on Diphenyl Triketone.—The triketone (0.5 g.) was refluxed for 30 minutes with phosphoric acid (20 c.c., d 1.7), glacial acetic acid (15 c.c.) added to dissolve the brownish oil that separated, and the solution refluxed again for 30 minutes, cooled, and poured into 100 c.c. of ice-cold water. The curdy white solid obtained was washed with water and crystallised from alcohol, giving white prismatic needles of benzoin, m. p. and mixed m. p. 130—133° (Found : C, 78.7; H, 5.7. Calc. : C, 79.2; H, 5.7%).

Action of Sulphuric Acid on Diphenyl Triketone.—The triketone (0.3 g.) was refluxed for 30 minutes with 9 c.c. of sulphuric acid (1 vol. of conc. acid and 1 vol. of water). The subsequent treatment was that described above and the solid obtained after the addition to ice-cold water crystallised from alcohol in yellow needles of benzil, m. p. and mixed m.p. 95° (Found : C, 79.65; H, 4.8. Calc. : C, 80.0; H, 4.8%).

Oxidation of Benzoin to Benzil with Sulphuric Acid.—Benzoin was submitted to the treatment described in the preceding paragraph, and benzil, m. p. and mixed m. p. 95°, obtained.

Action of Anhydrous Aluminium Chloride on Diphenyl Triketone.—The triketone (2 g.) and anhydrous aluminium chloride (4 g.) were mixed quickly and heated in a test-tube (calcium chloride guard tube) in an oil-bath at 100° for 1 hour. After cooling, the product was poured into dilute hydrochloric acid and ice and kept overnight. The yellow solid which separated was washed with dilute hydrochloric acid until free from aluminium, dried in a desiccator, and crystallised from benzene, yielding 1 g. of benzil, m. p. 95° (Found : C, 80.0; H, 4.8%).

Attempts to produce benzil by leaving the reaction mixture at room temperature for 1 hour were unsuccessful.

Action of Sulphuric Acid on Triketohydrindene Hydrate (Ninhydrin) (VII).—The hydrate (2 g.) was boiled with 60 c.c. of sulphuric acid (1 vol. of conc. acid and 1 vol. of water) for 30 minutes, glacial acetic acid (60 c.c.) added to dissolve the dark violet solid that had separated, and the solution boiled for another 30 minutes, cooled, and poured into 200 c.c. of ice-cold water. The dark reddish-brown solid obtained was washed with water until free from acid, dried (yield, 0.9 g.), and crystallised from toluene, giving dark violet-brown needles of bisindandione (VIII), m. p. about 297° (not sharp) (Found : C, 74.5; H, 3.4. Calc. for $C_{18}H_{16}O_4$: C, 74.5; H, 3.5%), identical with the substance obtained by Gabriel and Leupold (*Ber.*, 1898, 31, 1161).