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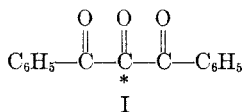
**Diphenyltriketone-Benzoin Rearrangement in an Acidic Medium**

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The formation of benzoin and benzil from diphenyltriketone and diphenyltetraketone is described and the reaction mechanism discussed.

The diphenyltriketone-benzoin rearrangement in an alkaline medium was discovered by de Neufville and Pechmann<sup>1</sup> who did not give the yield. Roberts *et al.*<sup>2</sup> who worked with C<sup>14</sup>-labelled triketone I (using a 15% carbonate-free sodium hydroxide solution) reported a 5% yield.

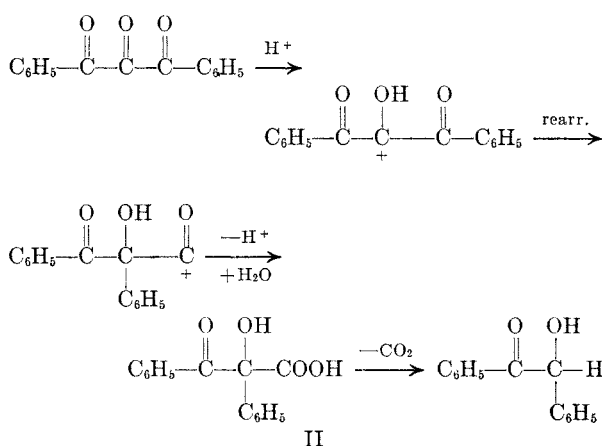


The diphenyltriketone-benzoin rearrangement in alkaline medium could have been expected and is to be considered as a type of benzilic acid rearrangement: the sodium salt of  $\alpha$ -benzoylmandelic acid being an intermediate which, on acidification, is converted to benzoin with elimination of carbon dioxide.

The diphenyltriketone-benzoin rearrangement effected by the action of mineral acids<sup>3</sup> was discovered much later,<sup>4</sup> but has been described only very fragmentarily. This paper describes the best experimental conditions for the rearrangement, discusses the reaction mechanism and reports also on the formation of benzil from diphenyltriketone and diphenyltetraketone by the action of mineral acids.

*Diphenyltriketone-benzoin rearrangement effected by dilute phosphoric and dilute sulfuric acids.* By a careful study of the experimental conditions yields up to 55% have been obtained. The question whether the central carbonyl group is eliminated in the process can only be decided by working<sup>5</sup> with labelled triketone (*cf.* I). In case the terminal CO

group is eliminated the following scheme (*inter alia*) may be considered:



The elimination of CO<sub>2</sub> has been proved in experiment II by absorption in lime water.

*Formation of benzil by the action of mineral acids on diphenyltriketone or diphenyltetraketone.* Besides benzoin, benzil is formed by the action of mineral acids on diphenyltriketone, *e.g.* when working with relatively strong sulfuric acids. As under these conditions benzoin is oxidized to benzil, it is most probable that at least a portion of the benzil so obtained from the triketone is formed *via* benzoin. The oxidation is not due to the action of air as benzil is also formed when the experiment is carried out in an atmosphere of carbon dioxide. Benzil was also obtained from diphenyltriketone when phosphoric acid was used and it seems possible that the formation of benzil does not proceed, in part, *via* the oxidation of benzoin. The formation of benzil may be explained by the loss of water and carbon monoxide from II.

When diphenyltriketone was treated with a mixture of acetic, sulfuric, and nitric acids benzil, but not benzoin, was isolated: benzoin is first formed but is oxidized to benzil by the action of nitric acid. Under the same conditions benzil was obtained from diphenyltetraketone. It is believed that the tetraketone is first transformed into IIIa or IIIb (compare with the formation of benzoin from the triketone), II is then oxidized by the action of nitric acid to diphenyltriketone which is finally changed into benzil as described above.

(1) R. de Neufville and H. v. Pechmann, *Ber.*, **23**, 3375 (1890).

(2) J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 618 (1951).

(3) J. D. Roberts *et al.* (*cf.* footnote 2) stated that the triketone is not changed by prolonged refluxing with glacial acetic acid.

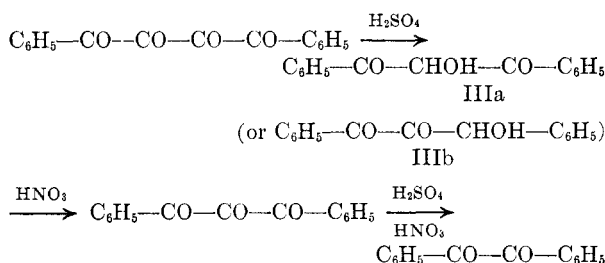
(4) A. Schönberg and R. C. Azzam, *J. Chem. Soc.*, 1428 (1939). J. D. Roberts *et al.* stated that they could not duplicate the decarboxylations of diphenyltriketone induced by sulfuric and phosphoric acids which had been reported by Schönberg and Azzam. For the decarboxylation with sulfuric acid *cf.* J. Wegmann and H. Dahn, *Helv. Chim. Acta*, **29**, 1248 (1946).

(5) This department is not equipped for investigations of this type.

TABLE I

Exp. No. <sup>a</sup>	Substance Used and Amount	Mineral Acid Used and Amount	Time of Boil, Min.		Wt. of Crude Product	Pure Subst. Isolated
			With mineral acid	After addn. of AcOH <sup>b</sup>		
Ia	2 g. Diphenyltriketone	20 ml. H <sub>2</sub> SO <sub>4</sub> (B)	30	30	1.11 g.	Benzil
II	1 g. Diphenyltriketone	10 ml. H <sub>3</sub> PO <sub>4</sub> (D)	30	75	0.54 g.	Benzoin
III	1 g. Diphenyltriketone	10 ml. H <sub>3</sub> PO <sub>4</sub> (C)	30	75	0.55 g.	Benzoin Benzil
IVa	2 g. Benzoin	15 ml. H <sub>2</sub> SO <sub>4</sub> (B)	30	60	1.52 g.	Benzil
Va	2 g. Benzoin	15 ml. H <sub>3</sub> PO <sub>4</sub> (C)	30	60	1.93 g.	Benzoin
VIa	1 g. Benzil	10 ml. H <sub>3</sub> PO <sub>4</sub> (D)	30	75	0.94 g.	Benzil

<sup>a</sup> The whole operation was carried out in an atmosphere of carbon dioxide. <sup>b</sup> The volume of acetic acid added was the same as that of the mineral acid used.



## EXPERIMENTAL

The mineral acids used in these experiments were pure analytical reagents from Carlo Erba (Milan).

Sulfuric acid (sp. gr. 1.84) was diluted either (A) with 1.7 volume of distilled water or (B) with an equal volume of water. Phosphoric acid (sp. gr. 1.71) was either (C) used as such or (D) diluted with an equal volume of water.

The pure benzoin and benzil obtained in the various experiments always had the correct melting points which were not depressed by mixing with authentic samples of the substances.

*Action of sulfuric acid on diphenyltriketone.* Pure diphenyltriketone (1.00g.) was gently boiled under reflux with 10 ml. of sulfuric acid (diluted as in A) for 30 min. Ten milliliters of glacial acetic acid were then added and boiling continued for 30 min. more. The faintly yellow solution was cooled, poured into 150 ml. of cold water, and allowed to stand overnight. The solid which separated was filtered off, washed successively with water, sodium bicarbonate solution, and water, and dried in an exsiccator. The crude product (0.49 g.) was crystallized twice from 10 ml. of ethyl alcohol and pure benzoin (0.32 g.) was obtained.

The other experiments were carried out in a similar way and are summarized in Table I.

*Procedure used for the isolation of the pure products in the above experiments:*

(I) The pasty brownish crude product was extracted with three portions of petroleum ether (b.p. ca. 50°) and the combined extracts (45 ml.) were evaporated to dryness leaving an orange oil which solidified on cooling and scratching. By crystallizing from 5 ml. of ethyl alcohol pure benzil (0.26 g.) was obtained. The residue from extraction failed to give any crystalline substance.

(II) The crude product was crystallized twice from small volumes of ethyl alcohol and pure benzoin (0.12 g.) was obtained. This experiment was carried out in a slight current of air washed from carbon dioxide and the gases coming out of the flask were passed in lime water and made it turbid.

(III) The crude product was dissolved in 10 ml. of ethyl alcohol and after concentration by slow evaporation (avoiding direct sunlight) a crystalline mass was deposited con-

sisting of clusters of colorless needles and long yellow prismatic needles which were separated mechanically and found to be respectively benzoin (0.11 g.) and benzil (0.15 g.). That benzil was a genuine product of the reaction was proved by allowing an alcoholic solution of benzoin to stand under the same conditions for several days whereby no benzil was detected.

(IV) The crude product was not separated by filtration but by extraction with ether. After evaporation of the solvent the yellow oil which was left was extracted with petrol as in (I). The petrol was then evaporated and the product crystallized from 5 ml. of ethyl alcohol. Pure benzil (0.24 g.) was obtained. The residue from the petrol extraction failed to give any crystalline substance.

(V) When the acid mixture was poured into water a yellow sticky substance collected at the bottom of the beaker but soon a voluminous crystalline solid filled the liquid and was separated by filtration and found to be benzoin (0.23 g.) after being crystallized twice from ethyl alcohol. The noncrystalline fraction (1.7 g.) was dissolved in 15 ml. of ethyl alcohol, 5 ml. of conc. hydrochloric acid added and the solution boiled for 15 min. It was then poured into water, extracted with ether, the extract washed, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The residue was repeatedly crystallized from ethyl alcohol to give a mass of ill-defined crystals from which no pure product could be obtained.

(VI) The product (0.94 g.) proved to be unchanged benzil.

*Action of sulfuric and nitric acids on diphenyltriketone.* Pure diphenyltriketone (1.00 g.) was boiled for 30 min. with a mixture of 10 ml. of sulfuric acid (A) and 10 ml. of glacial acetic acid. One ml. of nitric acid (sp. gr. 1.4) was then added and the mixture boiled for 1 hr. more, cooled, and poured into 100 ml. of ice-cold water. The yellowish solid (0.3 g.) was crystallized from 5 ml. of ethyl alcohol and found to be benzil.

*Action of sulfuric and nitric acids on diphenyltetra-ketone.* Diphenyltetra-ketone monohydrate (m.p. 83–85°; 1.00 g.) was boiled for 1 hr. with a mixture of 10 ml. of sulfuric acid (A) and 3 ml. of nitric acid (sp. gr. 1.4). Ten milliliters of glacial acetic acid were then added and boiling continued for 2 more hr. The crude yellowish product (0.22 g.), separated as in the previous experiment, was extracted twice with hot petroleum ether, the extract (20 ml.) concentrated to a small volume and cooled. Yellow needles (0.11 g.) separated and upon crystallization from 3 ml. of ethyl alcohol pure benzil was obtained.

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CAIRO, EGYPT