

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## PHENYL-PARA-TOLYLACETOPHENONE

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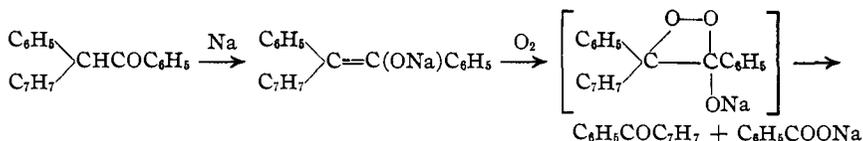
By the action of phenyl-*p*-tolylacetyl chloride on benzene in the presence of aluminum chloride, McKenzie and Widdows<sup>2</sup> obtained in poor yield a compound melting at 160° which they believed to be phenyl-*p*-tolylacetophenone. Recently McKenzie, Mills and Myles<sup>3</sup> by the dehydration of  $\alpha,\beta$ -diphenyl- $\alpha$ -*p*-tolylethylene glycol obtained the isomeric *p*-diphenylacetotoluene which melted at 97–99.5°.

Needing some phenyl-*p*-tolylacetophenone, the writer essayed its preparation by the method of McKenzie and Widdows. All attempts, however, to duplicate the results of these authors were unsuccessful; the only product which could be isolated was diphenylmethane. This was quite surprising in view of the fact that diphenylacetyl chloride and toluene under the usual conditions of the Friedel–Crafts reaction were found to give an excellent yield of *p*-diphenylacetotoluene.

Phenyl-*p*-tolylacetophenone was finally obtained in nearly quantitative yield from toluene, desyl chloride, and aluminum chloride, but it melted at 98° and not at 160° as reported by McKenzie and Widdows. That the product actually had the structure assigned to it was shown by its reactions.

Cleavage by boiling with alcoholic potash gave benzoic acid and phenyl-*p*-tolylmethane.

Sodium in boiling toluene reacted slowly to give a sodium salt which was cleaved by oxygen, probably through an intermediate peroxide, into phenyl-*p*-tolyl ketone and sodium benzoate.<sup>4</sup>



With phenylmagnesium bromide there was obtained a carbinol isomeric with the one obtained from *p*-tolylmagnesium bromide and diphenylacetophenone. Both of these carbinols gave triphenyl-*p*-tolylethylene on dehydration.

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<sup>2</sup> McKenzie and Widdows, *J. Chem. Soc.*, 107, 708 (1915).

<sup>3</sup> McKenzie, Mills and Myles, *Ber.*, 63, 904 (1930).

<sup>4</sup> For analogous reactions see Kohler, *Am. Chem. J.*, 36, 531 (1906); Staudinger, *Helv. Chim. Acta*, 5, 663 (1922).



Phenyl-*p*-tolylacetophenone.—To a solution of 25 g. of desyl chloride<sup>8</sup> in 150 ml. of toluene was added with cooling 16 g. of anhydrous aluminum chloride in small portions. The mixture, which evolved hydrogen chloride slowly in the cold, was refluxed for thirty minutes, cooled and decomposed with iced hydrochloric acid. Steam distillation of the toluene layer left a yellow residue which became solid on cooling. Crystallization from alcohol gave 24 g. melting at 94–95° which was still slightly colored. Recrystallization from benzene–ligroin gave a pure white product melting at 97–98°. The substance distilled undecomposed at 270–275° (29 mm.).

*Anal.* Calcd. for C<sub>21</sub>H<sub>18</sub>O: C, 88.0; H, 6.30. Found: C, 87.8; H, 6.33.

Diphenylacetophenone.—Twenty-five grams of desyl chloride, 125 ml. of benzene, and 16 g. of aluminum chloride refluxed for fifteen minutes gave diphenylacetophenone, which after one crystallization from acetic acid melted at 135–136° and weighed 23 g.

Cleavage of Phenyl-*p*-tolylacetophenone with Alkali.—Ten grams of phenyl-*p*-tolylacetophenone was refluxed for five hours with a solution of 5 g. of potassium hydroxide in 60 ml. of alcohol. Most of the alcohol was then distilled, and the residue was steam distilled. From the distillate was obtained 3.8 g. of phenyl-*p*-tolylmethane boiling at 275–280°; from the non-volatile part there was obtained 2.5 g. of benzoic acid, identified by melting point and neutral equivalent. There was recovered 3.8 g. of unchanged ketone.

Cleavage of the Sodium Salt with Oxygen.—A solution of 10 g. of phenyl-*p*-tolylacetophenone in 75 ml. of dry toluene was refluxed with 0.8 g. of sodium. A pale yellow flocculent substance appeared as the metal reacted, and after six hours no more sodium was present. Dry air was then aspirated through the cooled suspension for two hours. Washing with water removed sodium benzoate, from which there was obtained 2.75 g. (65%) of benzoic acid. The non-aqueous layer, after the toluene was steam distilled, gave 3.5 g. of phenyl *p*-tolyl ketone boiling at 190–210° (35 mm.) and melting at 52° (mixed melting point). This cleavage product was further identified by the formation of diphenyl-*p*-tolylcarbinol melting at 69–70° from it and phenylmagnesium bromide.

$\alpha,\alpha,\beta$ -Triphenyl- $\beta$ -*p*-tolylethanol.—Six grams of phenyl-*p*-tolylacetophenone was added to the Grignard reagent from 7.9 g. of phenyl bromide. After refluxing for thirty minutes, the solution was decomposed with iced ammonium chloride. The residue after removal of the ether was boiled out with alcohol, and the undissolved part was crystallized from ligroin (80–110°) and then from methanol, giving 1.2 g. which melted at 169–170°.

*Anal.* Calcd. for C<sub>27</sub>H<sub>24</sub>O: C, 88.9; H, 6.58. Found: C, 88.7; H, 6.27.

$\alpha,\beta,\beta$ -Triphenyl- $\alpha$ -*p*-tolylethanol.—The reaction product from 5.5 g. of diphenylacetophenone and the Grignard reagent from 9 g. of *p*-tolyl bromide was worked up in the usual way, giving 1.2 g. which melted at 185–187°. (McKenzie, Mills and Myles<sup>9</sup> give 180–181° for the compound prepared from *p*-diphenylacetotoluene and phenylmagnesium bromide.)

*Anal.* Calcd. for C<sub>27</sub>H<sub>24</sub>O: C, 88.9; H, 6.58. Found: C, 88.8; H, 6.40.

$\alpha,\alpha,\beta$ -Triphenyl- $\beta$ -*p*-tolylethylene.—Eight-tenths of a gram of  $\alpha,\alpha,\beta$ -triphenyl- $\beta$ -*p*-tolylethanol was refluxed for one hour with 10 ml. of acetyl chloride. The product was crystallized from acetic acid, giving 0.55 g. of the hydrocarbon, which melted at 150–151°.

*Anal.* Calcd. for C<sub>27</sub>H<sub>22</sub>: C, 93.6; H, 6.35. Found: C, 93.4; H, 5.90.

The dehydration of  $\alpha,\beta,\beta$ -triphenyl- $\alpha$ -*p*-tolylethanol was carried out in the same way. A mixed melting point showed the identity of the products.

<sup>8</sup> Prepared according to Schroeter and Caspar, *Ber.*, **42**, 2348 (1909).

### Summary

Phenyl-*p*-tolylacetophenone could not be prepared from phenyl-*p*-tolyl-acetyl chloride and benzene, but it was obtained from desyl chloride and toluene. It reacted normally with phenylmagnesium bromide, and it gave a sodium salt which oxygen cleaved into phenyl *p*-tolyl ketone and sodium benzoate.

The work of McKenzie, Mills and Myles on the dehydration of  $\alpha,\beta$ -diphenyl- $\alpha$ -*p*-tolylethylene glycol has been repeated and confirmed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

## THE HYDROGEN CHLORIDE ADDITION PRODUCTS OF TYROSINE N-PHENYLACETIC ACID AND OF THE CORRESPONDING METHYL AND ETHYL ESTERS

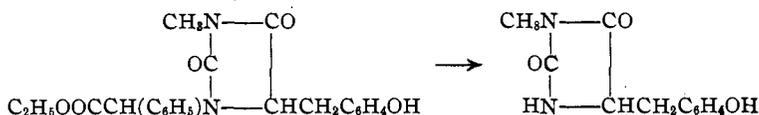
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The following account of certain transformations of the N-phenylacetic acid derivative of tyrosine,  $\text{NH}(\text{CHC}_6\text{H}_5\text{COOH})\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{OH})\text{COOH}$ , represents a continuation of work previously reported.<sup>2</sup> The imino dibasic acid was prepared by the same general method that has already been described,<sup>3</sup> but due to the fact that larger quantities of material were used in the reactions, a few additional facts in regard to this preparation need to be noted.

It was found, for example, during the process of digesting 50 g. of ethyl N-3-methyl-5-anisalhydantoin-N-1-phenylacetate<sup>4</sup> with hydrogen iodide and then hydrolyzing the product with barium hydroxide, that a slight amount of decomposition had taken place in the sense



The decomposition product, N-3-methyl-5-*p*-hydroxybenzylhydantoin, was found mixed with the imino dibasic acid in the filtrate from the barium sulfate. Both substances separated in crystalline condition on concentrating the solution and were readily separated due to the fact that the hydantoin is very soluble in hot water while the imino acid is relatively insoluble. After several recrystallizations from water the hydantoin was

<sup>1</sup> This work was offered in partial fulfillment of the requirements for the degree of Master of Arts at Mount Holyoke College.

<sup>2</sup> Hahn and Dyer, *THIS JOURNAL*, **52**, 2494 (1930).

<sup>3</sup> Hahn and Dyer, *ibid.*, p. 2503.

<sup>4</sup> Hahn and Dyer, *ibid.*, p. 2497.