[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Action of Phosphorus Pentachloride on β-Phenylbenzalacetophenone

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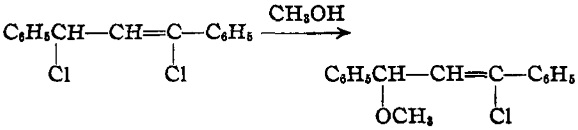
When phosphorus pentachloride acts on acetone or other ketones of the type R_2CO, a ketochloride is formed

$$R_2CO + PCl_5 \longrightarrow R_2CCl_2 + POCl_3$$

Straus and others[1] tried this reagent on α,β-unsaturated ketones and found the resulting compounds to be very different from the ketochlorides of the saturated ketones. Straus[2] found, for example, that one of the halogen atoms is much more easily replaced than the other, and obtained the monochloromethoxyl derivatives of many of his unsaturated compounds by boiling their methyl alcohol solutions. He proved the structure of the unsaturated products by ozonization. Typical reactions may be represented as

$$C_6H_5CH{=}CH{-}CO{-}CH{=}CHC_6H_5 \xrightarrow{PCl_5} C_6H_5CHCl{-}CH{=}CCl{-}CH{=}CHC_6H_5$$

$$C_6H_5CH{=}CH{-}CO{-}C_6H_5 \xrightarrow{PCl_5} C_6H_5CHCl{-}CH{=}CCl{-}C_6H_5$$

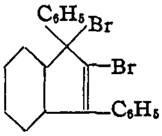


$$\underset{\textstyle Cl}{C_6H_5CH}{-}CH{=}\underset{\textstyle Cl}{C}{-}C_6H_5 \xrightarrow{CH_3OH} \underset{\textstyle OCH_3}{C_6H_5CH}{-}CH{=}\underset{\textstyle Cl}{C}{-}C_6H_5$$

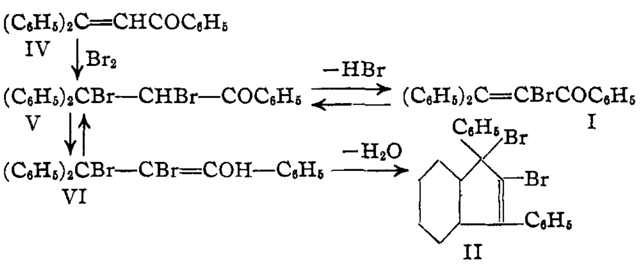
Although several α,β-unsaturated ketones react in this manner, it could not be assumed that β-phenylbenzalacetophenone would give a similar product, since the presence of a second phenyl group on the β-carbon atom may prevent a chlorine atom from attaching itself there. The surprising difference in the action of the β-phenyl derivative as compared to the benzalacetophenone itself is well illustrated by the work of Barre and Kohler,[3] who brominated β-phenylbenzalacetophenone and isolated both α-bromo-β-diphenylpropiophenone and 1,2-dibromo-1,3-diphenylindene. In the light of the above facts it appeared that the action of phosphorus pentachloride on the phenylated ketone would be of interest and this has been tried experimentally.

The β-phenylbenzalacetophenone was treated with phosphorus pentachloride in a manner very similar to that employed by Straus, and the product was handled at reduced temperature to avoid the hydrolysis of any chloro derivatives that might be formed. The product obtained was not a ketochloride; an ethoxy group was easily introduced by boiling in ethyl alcohol, yet the compounds did not correspond to the products isolated by Straus.

The product of the reaction is 1,2-dichloro-1,3-diphenylindene which reacts rapidly with ethyl alcohol to give 1-ethoxy-2-chloro-1,3-diphenylindene. Barre and Kohler have already shown that the halogen in the 1-position is unusually active since it is on a carbon joined to two benzene rings and a double bond.



The above results show that the phosphorus pentachloride is a chlorinating agent acting in a manner similar to the bromine used by Barre and Kohler. In their experiments, however, the conditions of the bromination and the method of handling the product could be used to control the nature of the substance isolated. They offer the following supposition concerning the nature of the reaction. "First the unsaturated ketone (IV) would be expected to react with a molecule of bromine to form a dibromide (V). This dibromide (V) which contains a bromine atom linked to a carbon atom which also holds the two phenyl groups is very unstable and loses hydrogen bromide very easily. The loss of hydrogen bromide from the dibromide is reversible as is shown by the fact that the dibromoindene (II) is also ob-



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* This work was done at the suggestion and under the direction of Professor E. P. Kohler (who died in 1938), and was accepted in partial fulfilment of the requirement for the degree of Ph.D. at Harvard University.

(1) Straus, *Ber.*, **39**, 2977 (1906); **40**, 2689 (1907); **42**, 1804 (1909).

(2) Straus, *Ann.*, **393**, 235–337 (1912).

(3) Barre and Kohler, THIS JOURNAL, **50**, 2038 (1928).

tained from α-bromo-β-phenylbenzalacetophenone by the action of hydrogen bromide. Since hydrogen bromide is also a dehydrating agent, the formation of the indene derivative (II) from the enolic form (VI) of the dibromide (V) is easily explained under the conditions of the reaction."

Inasmuch as phosphorus pentachloride is an active dehydrating agent and at the same time produces hydrogen chloride, it would be expected that the loss of hydrogen chloride to form the monochloro ketone corresponding to their compound (I) would be prevented, and that the dehydrating action would favor the formation of an indene corresponding to (II). It, therefore, seems likely that the suppositions of Barre and Kohler are equally applicable to the action of phosphorus pentachloride on β-phenylbenzalacetophenone.

Experimental

Treatment of β-Phenylbenzalacetophenone with Phosphorus Pentachloride.—In attempts to isolate products corresponding to those found by Straus, several variations in the procedure were employed. Each time a reddish oil was produced from which no crystals were obtained.

Five grams of the ketone was dissolved in 50 cc. of dry benzene, 5.5–6 g. of phosphorus pentachloride added, the mixture allowed to reflux on the steam-bath for one hour, cooled and poured over cracked ice. The ice was removed as soon as the benzene had melted and the liquids were separated. The benzene layer was washed several times with cold water, dried over sodium sulfate or calcium chloride, and concentrated at room temperature to a thick reddish oil which must have contained 1,2-dichloro-1,3-diphenylindene.

A product having the same appearance and properties was obtained when 5 g. of ketone dissolved in benzene was treated with 4.5 g. of phosphorus pentachloride and the mixture, after standing at room temperature for four days, was poured over cracked ice, washed with water, washed with sodium bicarbonate solution, dried over calcium chloride, and concentrated.

Better yields of secondary products are obtained when the ketone is treated with 2.2 mols of phosphorus pentachloride, the flask being fitted with a reflux condenser carrying a tube for the removal of hydrogen chloride fumes. The mixture is boiled for one to two hours, after which it may be concentrated by evaporation, since most of the hydrogen chloride has already escaped.

Ozonization of 1,2-Dichloro-1,3-diphenylindene.—Since products similar to those found by Straus were possible, it was considered wise to ozonize the red oil (uncrystallized product) to see what evidence could be obtained. The concentrated residue from the phosphorus pentachloride treatment was taken up in carbon tetrachloride. The solution was ozonized for four hours using a slow stream of 6–8% ozone, and the ozonide decomposed by shaking with cold sodium bisulfite solution for several hours. The carbon tetrachloride was evaporated and the resulting mixture was extracted with ether. After evaporating the ether, the residue was steam distilled, the distillate extracted with ether, and the ether solution evaporated, leaving a product which proved to be benzophenone, doubtless coming from unchanged ketone.

The residue from the steam distillation was taken up in ether, dried over calcium chloride, and allowed to crystallize. After recrystallization from methyl alcohol, this melted at 145–146.5°. A mixed melting point with an authentic sample proved this substance to be *o*-dibenzoylbenzene.

Preparation of 1-Ethoxy-2-chloro-1,3-diphenylindene.—The concentrated benzene solution from the phosphorus pentachloride treatment is dissolved in ethyl alcohol and evaporated by boiling to one-third the original volume or less and enough ethyl alcohol added to bring the solution to the original volume, which may again be evaporated by boiling. This method of heating serves not only to cause a reaction with the ethyl alcohol but also to remove the benzene, in which the indene has a high solubility. A nicely crystalline product separates, which may be recrystallized from ethyl alcohol, m. p. 135.5–136°.

Anal. Calcd. for $C_{23}H_{19}OCl$: C, 79.6; H, 5.5; Cl, 10.2; OC_2H_5, 13.0. Found: C, 80.1, 79.3, 79.6; H, 5.4 (4.3), 5.7; Cl, 10.2, 10.0; OC_2H_5, 12.1, 12.7.

Ozonization of the 1-Ethoxy-2-chloro-1,3-diphenylindene.—One gram of the 1-ethoxy-2-chloro-1,3-diphenylindene dissolved in carbon tetrachloride was ozonized for four and a half hours. The ozonide was decomposed by shaking with a cold dilute (1%) solution of hydrogen peroxide and the carbon tetrachloride removed by evaporation. The apparatus was washed with alcohol and the washings were added to the main solution. The mixture was allowed to stand on the steam-bath for about eight hours, serving to remove the alcohol and ensuring the liberation of carbon dioxide from any α-ketocarboxylic acid, to give the ketone sought. The mixture was cooled, extracted with ether, the ether solution dried over calcium chloride and on standing overnight the *o*-dibenzoylbenzene had crystallized out. The product was recrystallized from methyl alcohol and a mixed melting point proved its identity.

Summary

1,2-Dichloro-1,3-diphenylindene has been prepared by the action of phosphorus pentachloride on β-phenylbenzalacetophenone, its identity shown by ozonization, and an ethoxy derivative prepared and ozonized.

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