

Summary

A convenient method is described for the preparation of tetraethylgermane which gives excellent yields.

The preparation of the triethylgermanium halides and of di-triethylgermanium oxide is described and some of their more common properties are recorded.

The reaction of the triethylgermanium halides with ammonia and with solutions of the alkali metals in ammonia and ethylamine have been studied. The preparation of di-triethylgermanyylimine is described.

The preparation of hexaethyldigermane is described. The reaction of this digermane with the alkali metals in ammonia and ethylamine has been studied. The preparation of triethylgermane is described as are also some of its reactions.

A method is described for the preparation of potassium triethylgermanide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE FRIEDRICH WILHELM UNIVERSITY IN BERLIN]

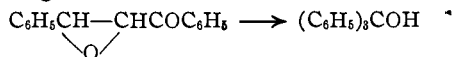
THE REACTION BETWEEN KETOXIDO COMPOUNDS AND GRIGNARD REAGENTS

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In a recent communication¹ Kohler and co-workers describe experiments on the reaction of ketoxido compounds with Grignard reagents. Benzalacetophenone oxide, for instance, is transformed into triphenylcarbinol by phenylmagnesium bromide



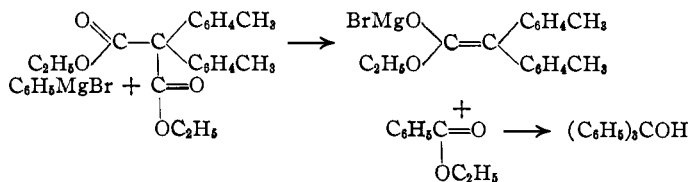
and Kohler assumes on the basis of many experiments that in the first step of the reaction the benzoyl group is split off as benzophenone, which is then transformed into the carbinol.

The same reaction has been studied in our laboratory during the past year, some of Kohler's experiments have been carried out also by us and we wish to report some evidence confirming his results.

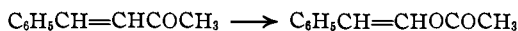
Although in most cases Grignard reagents react with ketoxido compounds in the same way as with benzalacetophenone oxide, benzal-*p*-phenylacetophenone oxide (I) is not converted into a triarylcarbinol by phenylmagnesium bromide; instead, two different products are isolated. One of these is the pinacol of phenyl biphenyl ketone (II). Its formation can hardly be understood unless we assume, as does Kohler, that in the pri-

¹ Kohler, Richtmyer and Hester, *THIS JOURNAL*, 53, 205 (1931).

In our laboratory we have observed in many cases the scission of relatively highly phenylated compounds by means of Grignard reagents. For example,⁴ ethyl di-*p*-tolylmalonate and an excess of phenylmagnesium bromide produce triphenylcarbinol and ethyl di-*p*-tolylacetate. Doubtless, in the first step, ethyl benzoate and the enolate of ethyl di-*p*-tolylacetate are formed. The latter cannot react with the Grignard compound, so the former is converted into triphenylcarbinol



In this connection it is of interest that Boeseken and Kremer⁵ recently have observed that benzalacetone, in a closely analogous manner, is transformed by means of peracetic acid into styryl acetate



Experimental Part

Cinnamoyl chloride was prepared by boiling 120 g. of cinnamic acid with 250 g. of thionyl chloride for two hours. The excess of thionyl chloride was evaporated on the steam-bath and the residue was distilled *in vacuo*, b. p. 130° (14 mm.). The yield was 120 g.

Benzal-*p*-methoxyacetophenone was prepared according to the procedure of Stockhausen and Gattermann,⁶ by condensing 44 g. of anisole and 67 g. of cinnamoyl chloride in 100 cc. of carbon disulfide by means of 50 g. of finely powdered aluminum chloride. The reaction is a vigorous one and was completed by four hours of boiling on the water-bath. The mass was decomposed by means of ice and fuming hydrochloric acid, the solution dried and distilled. The ketone boils at 265° (21 mm.) and crystallizes rapidly, m. p. 107°. The yield is very good.

Benzal-*p*-methoxyacetophenone Oxide (VI).—A solution of 12 g. of the unsaturated ketone in 150 cc. of hot methanol was rapidly cooled and the crystalline powder formed was shaken with 10 cc. of a 20% solution of potassium hydroxide and 15 cc. of a 15% solution of hydrogen peroxide. After half an hour the mixture was poured into water and the precipitate recrystallized from methanol as colorless crystals, m. p. 75°.

Anal. Calcd. for C₁₆H₁₄O₃: C, 75.6; H, 5.5. Found: C, 75.3; H, 5.5.

1,2,3-Triphenyl-3-*p*-anisyl-1,3-dihydroxypropane (VII).—Five grams of the oxide VI was added to a Grignard solution prepared from 10.5 cc. of bromobenzene and 2 g. of magnesium turnings. After decomposing with ice and dilute sulfuric acid and evaporating the ether, the glycol was recrystallized from benzene or ethyl acetate as needles of m. p. 131–132°. The yield was 3 g.

Anal. Calcd. for C₂₈H₂₆O₃: C, 82.0; H, 6.3; OCH₃, 7.5; mol. wt., 410. Found: C, 82.2; H, 6.5; OCH₃, 7.2; mol. wt., 390, 397.

⁴ Cf. H. Mirau, Thesis, Berlin, 1927.

⁵ Boeseken and Kremer, *Rec. trav. chim.*, 50, 827 (1931).

⁶ Stockhausen and Gattermann, *Ber.*, 25, 3336 (1892).

Benzal-*p*-phenylacetophenone.—To a solution of 60 g. of diphenyl and 60 g. of cinnamoyl chloride in 300 cc. of carbon disulfide, 50 g. of aluminum chloride was added in small portions during fifteen minutes. The reaction product was boiled for two hours, decomposed with ice and fuming hydrochloric acid and worked up in the usual manner. The ketone crystallized from propanol in small prisms, m. p. 165°. The yield was 70 g.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.7; H, 5.6. Found: C, 88.5; H, 6.0.

Benzal-*p*-phenylacetophenone Oxide. (I).—To a well-stirred solution of 20 g. of benzal-*p*-phenylacetophenone in 100 cc. of 1,4-dioxane 20 cc. of a 25% solution of potassium hydroxide and 25 cc. of a 15% solution of hydrogen peroxide were added. After half an hour the mixture was poured into water, filtered and dried. The lower melting isomer is soluble in boiling alcohol and crystallizes on cooling; yield, 15 g.; m. p. 126°.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3. Found: C, 84.5; H, 5.4.

The other isomer, which is insoluble in alcohol, was recrystallized from glacial acetic acid. The yield was 1.5 g. of m. p. 162°.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3; mol. wt., 300. Found: C, 84.4; H, 5.4; mol. wt., 293.

Both the isomers oxidize potassium iodide in acetic acid solution, a reaction typical of ketoxido compounds.⁷

Benzal-*p*-phenylacetophenone Oxide (I) and Phenylmagnesium Bromide.—Ten grams of oxide I was added to a Grignard solution prepared from 20 cc. of bromobenzene and 5 g. of magnesium. The reaction product was worked up in the usual manner and gave a thick oil from which, on digestion with glacial acetic acid, crystals were deposited. It crystallized from xylene in prisms of m. p. 181° which were identified as a pinacol (II) of phenyl biphenyl ketone by analysis and by its color reaction on addition of sodium ethoxide.

Anal. Calcd. for $C_{33}H_{26}O_2$: C, 88.0; H, 5.8. Found: C, 87.9; H, 5.9.

From the mother liquors, on standing, an oil was obtained which crystallized gradually. The crystals gave a violet color reaction with concentrated sulfuric acid. The substance was recrystallized from xylene, m. p. 159°. The compound is 1,1,3-triphenyl-3-biphenyl-1,3-dihydroxypropane (V).

Anal. Calcd. for $C_{33}H_{26}O_2$: C, 86.8; H, 6.1; mol. wt., 456. Found: C, 87.1; H, 6.2; mol. wt., 456.

Summary

According to Kohler and his co-workers, ketoxido compounds such as benzalacetophenone oxide are cleaved by means of aromatic Grignard reagents. In the first step the aroyl group is converted into a diaryl ketone.

From benzal-*p*-phenylacetophenone oxide and phenylmagnesium bromide two products are formed, a pinacol of phenyl biphenyl ketone, this being formed in the first reaction, and the "normal reaction product," 1,1,3-triphenyl-3-biphenyl-1,3-dihydroxypropane.

From benzal-*p*-methoxyacetophenone oxide and phenylmagnesium bromide 1,1,3-triphenyl-3-*p*-anisyl-1,3-dihydroxypropane is obtained as the sole product.

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⁷ Cf. Bergmann and Hervey, *Ber.*, **62**, 896 (1929).