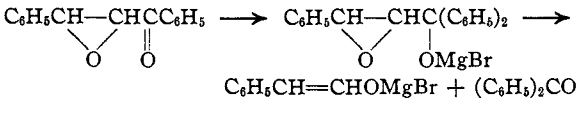
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Reduction by Magnesium + Magnesium Halide. XIII. The Reaction between Epoxy Ketones and Grignard Reagents

BY W. E. BACHMANN AND F. Y. WISELOGLE

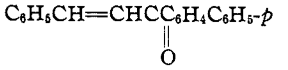
Kohler, Richtmyer and Hester[1] found that α,β-epoxy-β-phenylpropiophenone (benzalacetophenone oxide) reacted with one equivalent of phenylmagnesium bromide and gave an addition product from which benzophenone was split off at room temperature; with excess of Grignard reagent triphenylcarbinol was formed.



$$\underset{\diagdown\!\diagup\ \ \ \ \ \ \ \mathrm{O}\qquad\ \ \mathrm{O}}{\mathrm{C_6H_5CH{-}CHCC_6H_5}} \longrightarrow \underset{\diagdown\!\diagup\ \ \ \ \ \ \ \mathrm{O}\qquad\ \ \mathrm{OMgBr}}{\mathrm{C_6H_5CH{-}CHC(C_6H_5)_2}} \longrightarrow \mathrm{C_6H_5CH{=}CHOMgBr + (C_6H_5)_2CO}$$

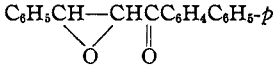
It occurred to us that the presence of benzophenone could be further verified by treating the reaction mixture with the binary system magnesium + magnesium bromide,[2] a reagent capable of reducing aromatic ketones to pinacols. Actually we obtained a 50% yield of benzopinacol by this procedure.

Bergmann and Wolff[3] reported that α,β-epoxy-β,p-diphenylpropiophenone (II) did not yield the expected 4-phenyltriphenylcarbinol (III) with excess of phenylmagnesium bromide; instead two different products were obtained.



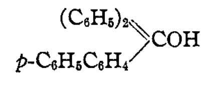
$$\underset{\mathrm{O}}{\mathrm{C_6H_5CH{=}CH\overset{\|}{C}C_6H_4C_6H_5}\text{-}p}$$

I

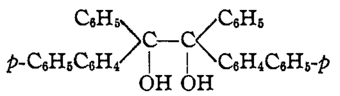


$$\underset{\diagdown\!\diagup\ \ \mathrm{O}\quad\ \mathrm{O}}{\mathrm{C_6H_5CH{-}CHCC_6H_4C_6H_5}\text{-}p}$$

II



III



IV

One of these was 4,4′-diphenylbenzopinacol (IV) produced presumably from 4-phenylbenzophenone through reduction by magnesium which was allowed to remain in the Grignard reagent. They were unable to decide whether their pinacol (m. p. 181°) was the same as that obtained by Gomberg and Bachmann[2] (m. p. 198°) or its diastereoisomer. Inasmuch as we have never experienced any difficulty in characterizing 4,4′-diphenylbenzopinacol, we set out to repeat their experiments in order to determine the nature of their pinacol.

Although we followed exactly the directions of Bergmann and Wolff for making 4′-phenylchalcone (I), we did not obtain the product described by them. From the condensation between cinnamoyl chloride and biphenyl by means of aluminum chloride we obtained 4′-phenylchalcone of m. p. 156° and not the product of m. p. 165° obtained by them from the same reagents. Our compound was identical with 4′-phenylchalcone prepared by condensation of p-acetylbiphenyl and benzaldehyde by means of alkali.[4] Likewise, oxidation of the unsaturated ketone by alkaline hydrogen peroxide gave α,β-epoxy-β-p-diphenylpropiophenone (II) which differed from the two oxides reported by Bergmann and Wolff.

We found that our α,β-epoxy-β-p-diphenylpropiophenone (II) reacted with one equivalent of phenylmagnesium bromide and gave a product from which a 60% yield of 4-phenylbenzophenone was isolated; with excess of the Grignard reagent a 51% yield of 4-phenyltriphenylcarbinol (III) was obtained. By adding magnesium and magnesium bromide to a mixture of α,β-epoxy-β-p-diphenylpropiophenone and phenylmagnesium bromide we obtained a 45% yield of 4,4′-diphenyl benzopinacol (IV) of m. p. 198° which was found to be identical with the pinacol of Gomberg and Bachmann obtained by reduction of 4-phenylbenzophenone with the binary system.[2]

Experimental

4′-Phenylchalcone (I).—We followed in every detail the directions of Bergmann and Wolff from the preparation of cinnamoyl chloride to the recrystallization of the unsaturated ketone from propanol. We obtained 4′-phenylchalcone of m. p. 155–156° in 78% yield; a number of runs were made and in no case did we find any of the product of m. p. 165° which Bergmann and Wolff reported was formed to the extent of 68% in this reaction. We prepared 4′-phenylchalcone, identical with our product, in 92% yield by the method of Dilthey.[4]

α,β-Epoxy-β-p-diphenylpropiophenone (II).—We found the procedure of Bergmann and Wolff to be inadequate for complete oxidation of our 4′-phenylchalcone; the product consisted of a mixture of chalcone and epoxy ketone which was difficult to separate completely, a behavior exhibited by synthetic mixtures of chalcone and epoxy ketone. Complete oxidation was effected by treating a cold solution of 2 g. of 4′-phenylchalcone in 40 cc. of dioxane with 2 cc. of 40% potassium hydroxide and 10 cc. of 30% hydrogen peroxide; after four hours the

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[1] THIS JOURNAL, **53**, 205 (1931).

[2] Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

[3] Bergmann and Wolff, *ibid.*, **54**, 1644 (1932).

[4] Dilthey, *J. prakt. Chem.*, **101**, 196 (1920).

mixture was poured into water. The epoxy ketone crystallized in colorless plates from acetone; wt. 2.03 g. (97%); m. p. 136–137°. From their ketone Bergmann and Wolff obtained two oxides melting at 126 and 162°.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3. Found: C, 83.9; H, 5.4.

α,β-Epoxy-β-*p*-diphenylpropiophenone + Excess of Phenylmagnesium Bromide.—Five grams of solid oxide was added in portions to the filtered Grignard reagent from 12 g. of bromobenzene in 20 cc. of ether and 30 cc. of benzene. After twenty hours at room temperature the solution was hydrolyzed with dilute acid and concentrated to a small volume; addition of alcohol induced crystallization of 4-phenyltriphenylcarbinol (m. p. 135–136°), wt. 2.8 g.; the remainder was a thick gum which did not crystallize. No 4,4'-diphenylbenzopinacol was formed in the reaction.

Reduction by Mg + $MgBr_2$.—Five grams of solid oxide was added gradually to an ether (15 cc.) and benzene (20 cc.) solution of phenylmagnesium bromide containing 0.54 g. of magnesium at −10°; to the clear yellow solution was added 1 g. of magnesium powder and a filtered solution of magnesium bromide prepared from 4 g. of mercuric bromide[2] in 20 cc. of ether and 10 cc. of benzene. After being shaken for two days in a stoppered flask the solution was filtered from the excess of magnesium and hydrolyzed with dilute acid; a considerable amount of 4,4'-diphenylbenzopinacol precipitated from the ether–benzene solution. A further quantity was obtained by evaporation of the solution at room temperature, followed by digestion of the residue with alcohol and acetone. Recrystallization from a mixture of chloroform and alcohol gave fine colorless needles of 4,4'-diphenylbenzopinacol; wt., 2.0 g.; m. p. 198°. The identity of the pinacol was established by a mixed melting point determination with authentic 4,4'-diphenylbenzopinacol and by rearrangement of a sample by hot acetic acid and iodine to the pinacolone, benzoylphenyl-di-*p*-biphenylmethane.

In another similar experiment with one equivalent of Grignard reagent in which no reducing mixture was present 2.6 g. of 4-phenylbenzophenone was obtained on hydrolysis; none of the corresponding pinacol was found.

α,β-Epoxy-β-phenylpropiophenone (benzalacetophenone oxide) was treated with one equivalent of phenylmagnesium bromide and then with Mg + $MgBr_2$; from 6.7 g. of the epoxy ketone we obtained 2.7 g. of benzopinacol.

α,β-Epoxy-β-anisyl-*p*-phenylpropiophenone.—This oxide was treated with the Grignard reagent, followed by the binary mixture, but no diphenylbenzopinacol was obtained. Since the oxide is new, its preparation is described. We prepared 4-methoxy-4'-phenylchalcone in 82% yield by the method of Dilthey; our product melted at 146° after recrystallization from benzene, while Dilthey reported a value of 140°. Five grams of the ketone was dissolved in 200 cc. of acetone; 75 cc. of 95% alcohol was added and the solution was cooled. Then 10 cc. of 30% hydrogen peroxide and 2 cc. of 50% potassium hydroxide were added and the mixture was kept in a refrigerator at 5° for twenty hours. The mixture was then poured into a liter of water and the alkali neutralized with dilute hydrochloric acid. The epoxy ketone was filtered off and dried; yield 4.98 g. (94%); m. p. 156–160°. The product is practically pure as obtained in this manner. Recrystallization from benzene gave colorless hexagonal plates; wt. 3.68 g. (70%); the compound softens and then melts at 158–161° with decomposition. The recrystallization should be carried out rapidly as the compound decomposes with prolonged heating. It is soluble to the extent of about 1 g. in 10 cc. of hot chloroform, 1 g. in 50 cc. of hot acetone and 1 g. in 35 cc. of boiling benzene.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 80.0; H, 5.5. Found: C, 80.0; H, 5.6.

Summary

Benzopinacol is formed by the action of Mg + $MgBr_2$ on a mixture of α,β-epoxy-β-phenylpropiophenone and phenylmagnesium bromide.

α,β - Epoxy - β - *p* - diphenylpropiophenone with phenylmagnesium bromide gives a product from which 4-phenylbenzophenone is split off; with excess of Grignard reagent 4-phenyltriphenylcarbinol is formed; with Mg + $MgBr_2$ 4,4'-diphenylbenzopinacol is produced.

Ann Arbor, Michigan Received February 23, 1934