[Contribution from the San Jose Research Laboratory of the International Business Machines Corp., San Jose 14, Calif.]

The Formation of 1,4-Bisdiphenylene-2,3-diphenylbutadiene, an Abnormal Grignard Reaction[1]

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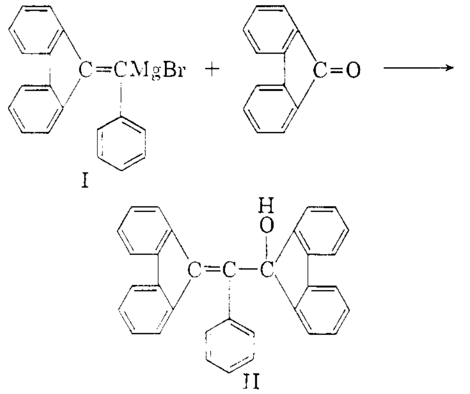
The Grignard reaction between α-phenyl-β-diphenylenevinylmagnesium bromide (I) and 9-fluorenone has been reported by Koelsch[2] to give in good yield, α,γ-bisdiphenylene-β-phenylallyl alcohol (II). In many of our attempts to synthesize this compound, as an intermediate in the preparation of the stable free radical, α,γ-bisdiphenylene-β-phenylallyl, we have found as the major product, a high-melting hydrocarbon, $C_{40}H_{26}$. None of the expected tertiary alcohol was recovered. This hydrocarbon, previously unreported, is now believed to be 1,4-bisdiphenylene-2,3-diphenylbutadiene (VI), arising from the coupling of the radical derived from the dissociation of α-phenyl-β-diphenylenevinylmagnesium bromide (I).

In the reported synthesis of α,γ-bisdiphenylene-β-phenylallyl alcohol (II), the Grignard reagent, I, prepared in the usual manner from α-phenyl-β-diphenylenevinyl bromide and magnesium, is treated with a solution of 9-fluorenone in dry toluene to form the alkoxide which is subsequently decomposed by aqueous ammonium chloride yielding the tertiary alcohol II, yellow crystals, m.p. 192–193°.



I

II

In our early attempts to repeat this work, our reactions appeared to follow the course described in the literature, but our final product melted at 302.5–303.5°. The infrared spectrum of this compound did not have a hydroxyl absorption band, and elemental analysis showed it to be a hydrocarbon.

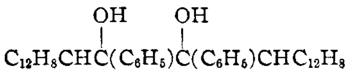
The preparation of the Grignard reagent was therefore repeated and carbon dioxide was added to the reaction mixture. The final product was a carboxylic acid (III), m.p. 180–182° as reported by Koelsch.[3] No hydrocarbon was found in this reaction.

This result indicated that the proper Grignard reagent had been formed and that the reaction was going awry during, or subsequent to, the addition of the ketone. The effect of ketones other than 9-fluorenone was therefore tested. When, however, benzophenone or 2-bromo-9-fluorenone was used in the reaction, the same high-melting hydrocarbon was formed. This showed that although the ketone appeared to be involved in the process in some way, the hydrocarbon was derived solely from the Grignard reagent.

The proposed structure has been confirmed by an independent synthesis. A solution of 9-benzoylfluorene (IV) in ether and benzene was treated with magnesium and iodine by the method of Gomberg and Bachmann[4] to yield the pinacol V which is then dehydrated with concentrated sulfuric acid at room temperature giving 1,4-bisdiphenylene-2,3-diphenylbutadiene (VI).

$$C_{12}H_8CHC(C_6H_5){=}O \xrightarrow[I_2]{Mg}$$

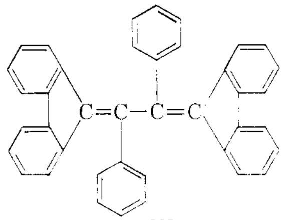
IV



$$C_{12}H_8CH\overset{OH}{C}(C_6H_5)\overset{OH}{C}(C_6H_5)CHC_{12}H_8$$

V

$$\Big\downarrow \begin{matrix} H_2SO_4 \\ -H_2O \end{matrix}$$



VI

The identity of this product with the yellow hydrocarbon from the Grignard reaction was established by the fact that there was no depression of the melting point when the products were mixed and by comparison of their infrared spectra.

A hydrocarbon, purported to be 1,4-bisdiphenylene-2,3-diphenylbutadiene (VI), has been reported by Krasner and Heger[5] to have been isolated in 0.4% yield from the reaction between benzil and fluorene in alcoholic potassium hydroxide.

The melting point of this material was given as 369.3°. Comparison of the infrared spectra shows that this product is not identical with the hydrocarbon isolated from the Grignard reaction.

Krasner and Heger have reduced the above product with hydriodic acid and red phosphorus in a sealed tube and obtained a white hydrocarbon, melting at 228°, which they identify as 1,4-bisdiphenylene-2,3-diphenylbutane (VII). The only other evidence cited for the structure of the first compound is the formation of benzoic acid and fluorene upon oxidation with chromic acid. Sev-

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(1) Reported at the 135th A. C. S. Meeting, Atlantic City, N. J., September, 1959.

(2) C. F. Koelsch, This Journal, **54**, 4744 (1932).

(3) C. F. Koelsch, private communication.

(4) M. Gomberg and W. E. Bachmann, This Journal, **49**, 236 (1927).

(5) L. Krasner and J. Heger, *Chem. Zvesti*, **8**, 333 (1954).

eral other authors[6-8] have reported the preparation of the latter compound and give the melting point as 320–321° (cubes) or 345° (needles). Fuson and co-workers have isolated both forms. The identity of the 369° hydrocarbon therefore remains in doubt.

It might be assumed that the radical reaction forming the hydrocarbon is catalyzed by metallic impurities such as cobalt or cobalt salts. However, we feel that this assumption has been disproved by the fact that the hydrocarbon is not formed until the ketone is added.

This would indicate that metallic impurities were not the source of difficulty. In addition, no hydrocarbon is formed in the carbonation reaction.

Study of the reaction conditions showed that traces of acetic acid, probably occluded during recrystallization of the α-phenyl-β-diphenylenevinyl bromide, invariably led to formation of the high-melting hydrocarbon. Elimination of the acid by washing with sodium bicarbonate solution and recrystallizing from benzene resulted in the normal Grignard product. Since the primary product of the reaction of the Grignard reagent (I) with acetic acid is 9-benzalfluorene, it was thought that this latter compound might be the actual catalyst in the abnormal reaction. Experiments showed that the addition of as little as 0.1 mole per cent. of either acetic acid or 9-benzalfluorene to an otherwise normal reaction caused the formation of the yellow hydrocarbon in preference to the desired tertiary alcohol.

The following mechanism, consistent with our experimental results is proposed for the formation of 1,4-bisdiphenylene-2,3-diphenylbutadiene (VI).

$$\mathrm{C_{12}H_8C{=}C(C_6H_5)MgBr} + \mathrm{C_{12}H_8C{=}CH(C_6H_5)} \rightleftharpoons$$

$$\text{I} \quad \mathrm{C_{12}H_8C{=}C(C_6H_5)\cdot} + \underset{\text{IX}}{\mathrm{C_{12}H_8\dot{C}CH(C_6H_5)MgBr}} \qquad (1)$$

$$\Big\downarrow \text{dimerization}$$

$$\text{VI}$$

$$\text{IX} + \mathrm{C_{12}H_8C{=}O} \rightleftharpoons$$

$$\mathrm{C_{12}H_8C(OMgBr)\cdot} + \mathrm{C_{12}H_8C{=}CHC_6H_5}$$

$$\Big\downarrow \text{dimerization}$$

$$\underset{\text{VIII}}{\mathrm{C_{12}H_8C(OH)C(OH)C_{12}H_8}} \qquad (2)$$

In the first equation, the single electron transfer of MgBr from α-phenyl-β-diphenylenevinylmagnesium bromide (I) to 9-benzalfluorene generates the α-phenyl-β-diphenylenevinyl radical which couples to give the hydrocarbon.

The transfer of MgBr to the ketone as in the second equation regenerates the 9-benzalfluorene. The resulting alkoxy radical couples and finally yields the glycol, 1,2-bisdiphenylene-1,2-ethanediol (VIII).

9-Benzoylfluorene (IV), which may also be found among the reaction products, is probably formed by oxidation of the Grignard reagent by atmospheric oxygen.

Experimental

α,γ-Bisdiphenylene-β-phenylallyl alcohol (II) was prepared according to the method of Koelsch,[2] except that the α-phenyl-β-diphenylenevinyl bromide was washed with sodium bicarbonate solution and recrystallized from benzene before use.

α-Phenyl-β-diphenyleneacrylic Acid (III).—A stream of dry carbon dioxide was bubbled through the Grignard reagent I from 4.3 g. (0.013 mole) of α-phenyl-β-diphenylenevinyl bromide until all the Grignard reagent was consumed. The reaction mixture was poured into an excess of ice-cold dilute hydrochloric acid and stirred for 10 minutes. The mixture was made alkaline with sodium carbonate solution and extracted with ethyl ether. The aqueous solution was re-acidified and extracted with three-50-ml. portions of ethyl ether. The ether solution was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness at room temperature. The residue (1.8 g.) was recrystallized from carbon tetrachloride; m.p. 181–182° (cor.).

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.56; H, 4.66; neut. equiv., 298. Found: C, 84.18; H, 4.63; neut. equiv., 307.

1,4-Bisdiphenylene-2,3-diphenylbutadiene (VI). **a.** *Via* **Grignard Reaction.**—1. To the Grignard reagent I from 7.0 g. (0.021 mole) of α-phenyl-β-diphenylenevinyl bromide in 100 ml. of ethyl ether was added a saturated solution of 3.7 g. (0.0205 mole) of 9-fluorenone (Eastman Kodak Co., white label) in dry toluene containing 4 mg. of glacial acetic acid. The mixture was refluxed, with stirring, for 1 hour and then allowed to stand at room temperature overnight. The solid product was filtered off, washed with ether and then decomposed with ice-cold ammonium chloride solution. The mixture was warmed to remove the excess ether and filtered. The bright yellow residue was washed with ethanol and then recrystallized from carbon tetrachloride to yield 4.1 g. of bright yellow crystals, m.p. 302.5–303.5° (cor.)

Anal. Calcd. for $C_{40}H_{26}$: C, 94.82; H, 5.18. Found: C, 94.64; H, 5.38.

Treatment of the ether solution with iced ammonium chloride solution yielded 2.8 g. of 1,2-bisdiphenylene-1,2-ethanediol (VIII), m.p. 191–192° (cor.).

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.18; H, 4.97. Found: C, 86.33; H, 5.20.

2. The reaction was repeated as above, except for the addition of 20 mg. of 9-benzoylfluorene ($C_{20}H_{14}$) with the 9-fluorenone solution in place of the acetic acid. The product in this case was the same hydrocarbon as that previously obtained.

b. *Via* **1,4-Bisdiphenylene-2,3-diphenylbutan-2,3-diol (V).**—The method of Gomberg and Bachmann[4] was followed. From 15.5 g. (0.06 mole) of 9-benzalfluorene, 3.5 g. of the pinacol V was obtained after crystallization from a mixture of ethanol and chloroform; light yellow crystals, m.p. 190–191°. It was used for the next step without further purification.

Dehydration of V was accomplished by dissolving 120 mg. in 5 ml. of concentrated sulfuric acid at room temperature to give a deep blood-red solution. After 10 minutes, the reaction was quenched by pouring the solution onto cracked ice. The precipitated solid was separated by centrifugation and washed in the centrifuge tube with water and with methanol. After recrystallization from carbon tetrachloride, 20 mg. of a yellow solid was obtained, m.p. 302–303°. The melting point was not depressed on admixture with the yellow hydrocarbon VI from the Grignard reaction. The infrared spectra of the two samples were identical.

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(6) W. Schlenk and E. Bergmann, *et al.*, *Ann.*, **463**, 1 (1928).

(7) R. C. Fuson, H. A. DeWald and R. Gaertner, *J. Org. Chem.*, **16**, 21 (1951).

(8) E. Lavie and E. D. Bergmann, *J. Org. Chem.*, **18**, 367 (1953).