

5. A structure for convicine is proposed. It is represented as a hexoside of 4-iminodialuric acid.

6. This research is being continued.

NEW HAVEN, CONNECTICUT

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

TRIPHENYLVINYLMAGNESIUM BROMIDE

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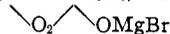
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During the course of an investigation on the unusual reactivity of the halogen in benzoyldiphenylmethyl bromide, a need was felt for a method by which substituted derivatives of the parent diphenylacetophenone could be prepared. It was thought that the enol forms of such ketones might be obtained by a reaction analogous to that sometimes used for the preparation of phenols, namely, by the oxidation of a properly chosen Grignard reagent. Such a Grignard reagent would have the —MgX group attached to an unsaturated carbon atom and would be of the type $\text{RR}'\text{C}=\text{C}(\text{MgX})\text{C}_6\text{H}_5$, where R and R' are aromatic radicals.

A compound of this type has not been prepared previously. The most closely related Grignard reagents are styrylmagnesium bromide² and β,β -diphenylvinylmagnesium bromide.³ Whether or not the more highly substituted triphenylvinylmagnesium bromide could be obtained was a question which had to be settled by experiment. In the present paper it is shown that triphenylvinyl bromide forms a Grignard reagent, and some reactions of this compound are described.

A number of so-called negative results were obtained in the study of this Grignard reagent. With *dry air* or *oxygen*, a yellow ether-insoluble substance was formed, but decomposition of this with dilute acids gave a tarry oil from which no diphenylacetophenone could be obtained; on steam distillation of this tar no trace of benzophenone, which would be formed from a possible peroxide, $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$, was obtained.



Thionyl chloride reacted vigorously to give an unworkable oil, while *benzyl chloride* was recovered nearly quantitatively after six hours' refluxing in ether; *triphenylchloromethane* was rapidly and completely converted into triphenylmethyl, isolated as the peroxide; the other product was a yellow ether-soluble glassy substance from which no crystalline material could be obtained. *Acetone* was apparently condensed by the reagent with the formation of mesityl oxide and triphenylethylene. *Benzophenone* gave a deep red solution, but carbonation followed by hydrolysis showed that the whole of the Grignard reagent was still present, and the ketone was recovered unchanged.

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² Rupe and Proske, *Ber.*, **43**, 1231 (1910).

³ Lipp, *ibid.*, **56**, 571 (1923); Ziegler, *ibid.*, **55**, 2257 (1922); Ziegler and co-workers, *Ann.*, **443**, 161 (1925); and previous papers.

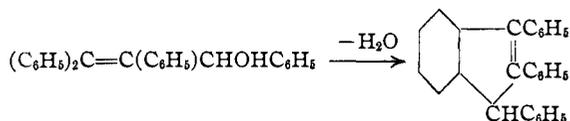
More significant and interesting results were obtained when the Grignard reagent was treated with certain other substances.

With *iodine*, triphenylvinyl iodide was obtained. Contrary to expectations, no iodide dichloride could be obtained from this compound. When a carbon tetrachloride solution of it was treated with chlorine, iodine was liberated immediately even at -5° .

Treatment of the Grignard reagent with *water* gave the hydrocarbon from which it is derived, triphenylethylene.

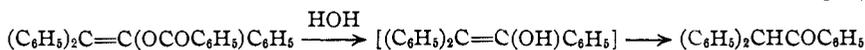
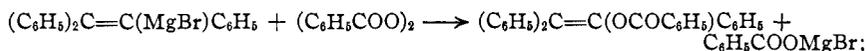
Formaldehyde gave β, γ, γ -triphenylallyl alcohol. This alcohol was etherified by allowing it to stand in methyl or ethyl alcoholic solution in the presence of sulfuric acid. The ethers obtained were also prepared from β, γ, γ -triphenylallyl bromide by boiling with the corresponding alcohol.⁴

Benzaldehyde gave $\alpha, \beta, \gamma, \gamma$ -tetraphenylallyl alcohol, which, however, could not be obtained crystalline or pure enough for analysis. By treating this alcohol with sulfuric acid in acetic acid, the known 1,2,3-triphenylindene⁵ was formed.



Benzoyl chloride gave the long known triphenylacrylophenone $\text{C}_6\text{H}_5\text{-COC}(\text{C}_6\text{H}_5)=\text{C}(\text{C}_6\text{H}_5)_2$.

Benzoyl peroxide reacted vigorously to give the enol benzoate of diphenylacetophenone,⁶ which was hydrolyzed to diphenylacetophenone by warming with alkali.



In this indirect way the original object of this research was attained, but the reactions involved are impractical from a preparative standpoint.

Carbon dioxide gave triphenylacrylic acid, and *carbon disulfide* gave the sulfur analog, triphenylvinylcarbithionic acid, a beautifully crystalline red substance.

Experimental

Triphenylvinyl Bromide.—To a solution of 40 g. of triphenylethylene⁷ in 250 ml. of glacial acetic acid was added with cooling 25 g. of bromine at such a rate that the temperature remained below 40° . The solution was distilled for a short time to drive off the hydrogen bromide, water was added almost to turbidity, and the solution was

⁴ Cf. Meisenheimer, *Ann.*, **456**, 147 (1927).

⁵ Kohler, *Am. Chem. J.*, **40**, 230 (1908).

⁶ Cf. Gilman and Adams, *THIS JOURNAL*, **47**, 2816 (1925).

⁷ Hell and Wiegandt, *Ber.*, **37**, 1431 (1904).

cooled. The product was pure after one washing with dilute acetic acid and melted at 114–115.5°; yield, 95–98%.

Triphenylvinylmagnesium Bromide.—Ten grams of triphenylvinyl bromide, 0.8 g. of magnesium, and a small crystal of iodine were covered with 200 ml. of dry ether, 0.05 ml. of ethyl bromide was added, and the mixture was refluxed. The reaction usually started within ten minutes; in even the most obstinate cases, reaction could be started by the addition of a small piece of magnesium separately etched with ethyl bromide. Nearly all of the magnesium was dissolved in less than two hours after the reaction had started. A U-shaped mercury seal closing the top of the condenser satisfactorily prevented the diffusion of air.

In most cases one-half the quantity of ether specified above was used. Then the reagent separated as a crystalline solid toward the end of the reaction, but its yield and its reactivity appeared to be unaffected.

Reaction with Iodine.—To the Grignard reagent from 10 g. of triphenylvinyl bromide was added solid iodine until the color was permanent. After hydrolysis with dilute sulfuric acid and removal of the ether, the product was crystallized from alcohol and finally from ligroin. There was obtained 6 g. of triphenylvinyl iodide which melted at 125–126°.

Anal. Calcd. for $C_{20}H_{15}I$: C, 62.8; H, 3.92. Found: C, 63.0; H, 3.94.

Reaction with Water.—Hydrolysis of the Grignard reagent from 10 g. of triphenylvinyl bromide gave 5 g. of triphenylethylene which boiled at 240–250° (33 mm.) and melted at 66–68°. This took up the calculated quantity of bromine to give triphenylvinyl bromide melting at 114–115°.

Reaction with Formaldehyde.—An excess of formaldehyde was led over the Grignard reagent from 5 g. of triphenylvinyl bromide. After the exothermic reaction was over, the product was decomposed with dilute ammonium chloride solution. Evaporation of the ether left a sirup which crystallized on rubbing with petroleum ether. Recrystallization from 50% ethanol gave 2.05 g. of β,γ,γ -triphenylallyl alcohol which melted at 126–128°, and was easily soluble in the common solvents. It gave a yellow solution in cold concd. sulfuric acid which became green on warming.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.29. Found: C, 88.0; H, 5.96.

α -Methoxy- β,γ,γ -triphenyl- β -propene.—A solution of 0.5 g. of β,γ,γ -triphenylallyl alcohol in 15 ml. of methanol containing 2 drops of concd. sulfuric acid was refluxed for fifteen minutes. The product crystallized out on cooling, and was recrystallized from methanol. It melted at 131–132.5°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.66. Found: C, 87.9; H, 6.35.

A mixed melting point showed the identity of the product with the one obtained when β,γ,γ -triphenylallyl bromide was boiled with methanol.

α -Ethoxy- β,γ,γ -triphenyl- β -propene.—The ethyl ether was prepared in the same way from β,γ,γ -triphenylallyl alcohol and ethanol. It melted at 125–128° alone or mixed with a sample of the same compound prepared according to the method of Meisenheimer.⁴ Mixtures of the methyl and ethyl ethers or of either of these with the parent alcohol melted at 100–115°.

Reaction with Benzaldehyde.—To the Grignard reagent from 5 g. of triphenylvinyl bromide was added 1.6 g. of freshly distilled benzaldehyde. The crystalline magnesium compound which separated on standing was filtered off and decomposed with dilute sulfuric acid. An oil was obtained which could not be induced to crystallize. A portion (2.7 g.) was boiled for two minutes with 20 ml. of acetic acid containing 3 drops of concd. sulfuric acid. The 1,2,3-triphenylindene which crystallized out on cooling

weighed 2.3 g. and melted at 128–131°. Two recrystallizations from alcohol raised the melting point to 132–134°.

Anal. Calcd. for $C_{27}H_{20}$: C, 94.2; H, 5.82. Found: C, 94.1; H, 5.90.

A solution of 0.9 g. of the crude tetraphenylallyl alcohol in 15 ml. of methanol containing 2 drops of concd. sulfuric acid was allowed to stand at room temperature for six hours in an attempt to form a methyl ether, but again triphenylindene crystallized out.

Reaction with Benzoyl Chloride.—To the Grignard reagent from 10 g. of triphenylvinyl bromide was added 4 ml. of benzoyl chloride, and the mixture was refluxed for two hours. Hydrolysis with dilute sulfuric acid and removal of the ether left an oil which solidified on rubbing with alcohol. Recrystallization from ligroin gave 5 g. of triphenylbenzoylethylene which melted at 147–149° and whose melting point was not depressed by admixture with the same compound prepared by the method of Kohler.⁸

Reaction with Benzoyl Peroxide.—To the Grignard reagent from 5 g. of triphenylvinyl bromide was added slowly and with cooling 3.5 g. of finely powdered benzoyl peroxide. After forty-eight hours the mixture was decomposed with dilute sulfuric acid. Most of the triphenylvinyl benzoate crystallized from the ether layer. A total of 1.05 g. of the compound was obtained which after one recrystallization from alcohol melted at 151–153°. On boiling this for three minutes with a little 5% alcoholic potash there was obtained diphenylacetophenone which melted at 134–136° alone or mixed with an authentic sample.

Reaction with Carbon Dioxide.—Carbonation of the Grignard reagent from 10 g. of triphenylvinyl bromide was carried out in the usual way. After acid hydrolysis of the magnesium compound, the product was extracted from the ether layer with sodium carbonate solution, and was precipitated from this with hydrochloric acid. Crystallization from acetic acid gave 8.0 g. of triphenylacrylic acid which melted at 217–218° and gave the red diphenylindone melting at 151–152° on heating with zinc chloride.

Reaction with Carbon Disulfide.—To the Grignard reagent from 10 g. of triphenylvinyl bromide was added 2 ml. of carbon disulfide. The mixture slowly became orange in color and deposited a lemon-yellow crystalline substance. After forty-eight hours the ether was decanted, and the deposit was washed with a little dry ether. It was then dissolved in water. The addition of hydrochloric acid to the red solution obtained precipitated an oil which rapidly solidified. Crystallization from hot glacial acetic acid gave 4.7 g. of triphenylvinylcarbithionic acid which separated in the form of deep red plates that melted at 135°.

Anal. Calcd. for $C_{21}H_{16}S_2$: S, 19.3. Found: S, 19.4.

Summary

Triphenylvinyl bromide with magnesium forms a Grignard reagent. Although this compound does not react or reacts abnormally with some few substances, it gives normal products with iodine, water, formaldehyde, benzaldehyde, benzoyl chloride, benzoyl peroxide, carbon dioxide and carbon disulfide.

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⁸ Kohler, *Am. Chem. J.*, **38**, 559 (1907).