[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# THE ADDITION OF GRIGNARD REAGENTS TO 1,2,3,4-TETRAPHENYLFULVENE

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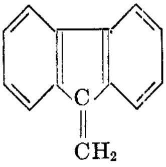
The addition of Grignard reagents to dibenzofulvene (I) and to 2,3-diphenylbenzofulvene (II) (1) suggested that the corresponding tetraphenylfulvene (III) might behave in a similar manner. In the present work it has been possible to verify this prediction. 1,2,3,4-Tetraphenylfulvene reacts additively with *tert*-butylmagnesium chloride and benzylmagnesium chloride to form the adducts IV and V, respectively. As with the fulvenes studied earlier (1–3), the methyl, ethyl, and phenyl reagents failed to add.

The adducts, although they are Grignard reagents, proved to be no more reactive than their analogs previously described in this series. They underwent hydrolysis to yield the corresponding hydrocarbons and could be alkylated by the action of certain alkyl halides. The *tert*-butyl adduct failed to react with *tert*-butyl bromide and phenethyl bromide and did not give an acid with carbon dioxide. However, with benzyl chloride and monochlorodimethyl ether it gave products to which have been assigned structures VI and VII, respectively. Although these structures seem probable on theoretical grounds, it must be recognized that, in view of the allylic nature of the cyclopentadiene anion, two other structures are possible.

Benzylation of the benzyl adduct (V) was actually found to give two isomeric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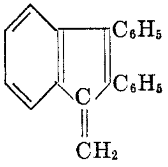
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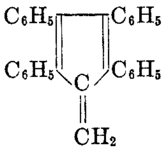
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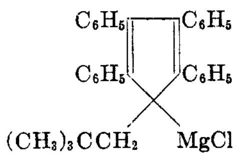
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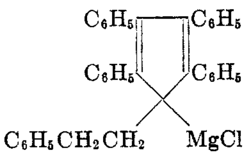
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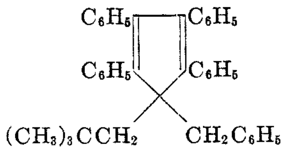
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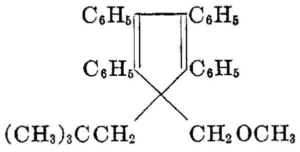
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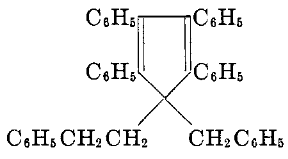
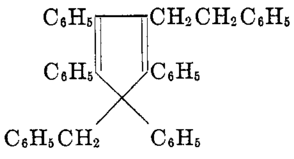
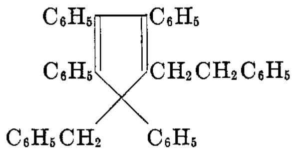


VIII

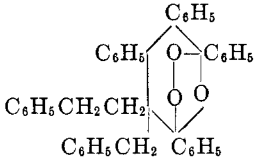


IX

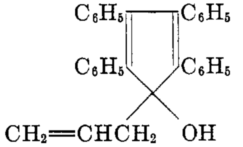


X

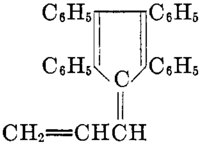
products. The higher-melting, less soluble isomer probably has structure VIII, whereas the other isomer may correspond to one of the less symmetrical structures (IX, X). In an attempt to determine its structure, the higher-melting isomer was subjected to ozonization. The product was a stable trioxide which, in the light of Criegee's work (4), might well be the ozonide XI.



XI



XII



XIII

Attempts to alkylate the benzyl adduct (V) with *tert*-butyl bromide and with monochlorodimethyl ether gave, surprisingly, the higher-melting dibenzyl derivative (VIII). Like similar observations reported earlier (3), this result may be explained by assuming radical interchange between benzylmagnesium chloride, present in excess, and the alkyl halide. The benzyl adduct failed to react with phenethyl bromide and did not give an acid with carbon dioxide.

It seems probable that Grignard reagents might react additively with the vinylogs of the tetraphenylfulvene. An attempt to prepare the butadiene XIII from the allyl carbinol (XII), however, gave a polymeric product; the monomer could not be isolated.

## EXPERIMENTAL[1]

*5-Neopentyl-1,2,3,4-tetraphenylcyclopentadiene.* A Grignard reagent was prepared from 4.7 g. (0.05 mole) of *tert*-butyl chloride, 1.3 g. of magnesium, and 150 ml. of dry ether. After the mixture had been stirred under reflux for 2 hours, the solution was quickly decanted from the excess magnesium into a second flask. While the solution was stirred, 3.8 g. (0.01 mole) of 1,2,3,4-tetraphenylfulvene (5) was added in portions. The red fulvene dissolved immediately imparting a deep red color to the solution. Over a period of 20 minutes the color gradually changed to yellow. Heating was continued overnight under reflux and the reaction mixture was decomposed by pouring into an ice-hydrochloric acid mixture. The yellow ether layer was removed, washed with water, and dried over sodium sulfate. The solvent was evaporated at room temperature, and the pale yellow residue was taken up in hot absolute ethanol. When cooled strongly, the solution deposited a white product which weighed 3.7 g. (85%). This solid was recrystallized from toluene and then from a chloroform-ethanol mixture; m.p. 135.5–136°. The infrared spectrum[2] shows absorption peaks at

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[1] Microanalyses by Miss Emily Davis, Mrs. Katherine Pih, Mrs. Jeanne Fortney, and Mr. Joseph Nemetha.

[2] The infrared spectra were determined and interpreted by Miss Helen Miklas and Mrs. Rosemary Hill.

1366 and 1375 cm.$^{-1}$, attributable to *tert*-butyl and at 1595 and 1698 cm.$^{-1}$, attributable to phenyl.

*Anal.* Calc'd for $C_{34}H_{32}$: C, 92.68; H, 7.32.
Found: C, 92.64; H, 7.47.

*5-(Phenethyl)-1,2,3,4-tetraphenylcyclopentadiene.* To a Grignard reagent, made by the procedure just described, from 6.3 g. (0.05 mole) of benzyl chloride, 1.3 g. of magnesium, and 150 ml. of dry ether, was added 3.8 g. (0.01 mole) of tetraphenylfulvene. The reaction, conducted in the manner indicated for the *tert*-butyl reagent, gave a tarry solid which was taken up in hot ethanol. Water was added until a faint turbidity developed, and the solution was allowed to stand in the refrigerator overnight. The light tan crystalline product melted at 137–138° and weighed 3.8 g. (80%). Subsequent recrystallizations from a chloroform-ethanol mixture gave a cream-colored crystalline product; m.p. 138–139°.

*Anal.* Calc'd for $C_{37}H_{30}$: C, 93.63; H, 6.37.
Found: C, 93.59; H, 6.31.

*Treatment of the tert-butyl adduct* (IV) *with benzyl chloride.* To a Grignard reagent, prepared from 4.7 g. (0.05 mole) of *tert*-butyl chloride, according to the procedure already described, was added 3.8 g. (0.01 mole) of the fulvene, with stirring, and the reaction was allowed to continue for 10 hours. To this solution, 6.3 g. (0.05 mole) of benzyl chloride was added, with stirring, and refluxing and stirring were continued overnight. The product, isolated in the usual way, was a viscous liquid; when this material was subjected to vacuum distillation a small amount of clear liquid distilled at 30–32° (0.3 mm.).

The residue in the distillation pot was taken up in hot absolute ethanol. When the solution was cooled, a light tan product crystallized. Recrystallization from a chloroform-ethanol mixture gave a white product; m.p. 198–199°; yield 2.4 g. (45%). The infrared spectrum shows absorption peaks at 1363 and 1378 cm.$^{-1}$, attributable to *tert*-butyl, and at 1698 and 1595 cm$^{-1}$, to be attributed to phenyl.

*Anal.* Calc'd for $C_{41}H_{38}$: C, 92.78; H, 7.22.
Found: C, 92.48; H, 7.35.

*Treatment of the tert-butyl adduct* (IV) *with monochlorodimethyl ether.* To the *tert*-butyl adduct, prepared as previously described, was added 4.0 g. (0.05 mole) of monochlorodimethyl ether, and the reaction was continued for 10 hours, with stirring, under reflux. The reaction mixture, decomposed in the usual way, gave an oil, which was dissolved in hot high-boiling petroleum ether. The product, a cream colored solid melting at 137–144°, was recrystallized from high-boiling petroleum ether. It separated as white crystals; m.p. 152–152.5°; yield 3.2 g. (66%). The infrared spectrum shows the characteristic absorption for the *tert*-butyl and phenyl groups as well as a peak at 1103 cm.$^{-1}$, which has been ascribed to the presence of the ether linkage.

*Anal.* Calc'd for $C_{36}H_{36}O$: C, 89.21; H, 7.49.
Found: C, 89.01; H, 7.50.

*Treatment of the benzyl adduct* (V) *with benzyl chloride.* To the benzyl adduct, prepared from 6.3 g. (0.05 mole) of benzyl chloride, 1.3 g. of magnesium, and 3.8 g. (0.01 mole) of tetraphenylfulvene in the manner previously described, 6.3 g. (0.05 mole) of benzyl chloride was added with stirring. The reaction was continued overnight with refluxing and stirring. The mixture was then decomposed by pouring into an ice-hydrochloric acid mixture as before. An ether-insoluble material was removed by filtration. This white crystalline product (4.0 g.) was suspended in about 20 ml. of hot ethanol, and chloroform was added until all the solid dissolved. When this solution was cooled, a white crystalline compound appeared which floated on top of the solution; m.p. 231.5–232.5°; yield 2.5 g. (44%). The infrared spectrum shows the characteristic phenyl absorption peaks.

*Anal.* Calc'd for $C_{44}H_{36}$: C, 93.57; H, 6.43.
Found: C, 93.71; H, 6.72.

The ethanol-chloroform filtrate was heated to boiling and about 10 ml. of ethanol was added. The solution was boiled until enough chloroform had evaporated to allow crystallization of the product. When this solution was cooled, 1.5 g. of a white crystalline material, m.p. 163–164°, separated. When the original ether layer was removed, washed, dried, and allowed to evaporate, a solid residue remained. Recrystallization of this residue from a chloroform-ethanol mixture gave a white crystalline product; m.p. 163.5–164.5°. These two products were combined and recrystallized once more from this solvent mixture; m.p. 164.5–165.5°; yield 2.3 g. (41%).

*Anal.* Calc'd for $C_{44}H_{36}$: C, 93.57; H, 6.43.
Found: C, 93.35; H, 6.42.

The infrared spectra of the two compounds produced in this reaction are identical except for a very slight band shift at *ca.* 750 cm.$^{-1}$. This shift has been interpreted as indicating a difference in the position of the groups on the cyclopentadiene ring.

*Treatment of the benzyl adduct* (V) *with tert-butyl bromide.* To the benzyl adduct, prepared as previously described, was added 6.8 g. (0.05 mole) of *tert*-butyl bromide, and the reaction was continued under reflux overnight. The reaction mixture, decomposed in the usual manner, gave an ether-insoluble product; m.p. 230–231°. An additional quantity of this compound was recovered from the ether solution. The product, recrystallized from a chloroform-ethanol mixture, separated as white crystals, m.p. 231.5–232°; yield 3.5 g. (62%). This compound was shown to be identical with the higher melting compound, which was isolated from the treatment of the benzyl adduct with benzyl chloride. The infrared spectra are identical and a mixture melting point showed no depression.

*Anal.* Calc'd for $C_{44}H_{36}$: C, 93.57; H, 6.43.
Found: C, 93.53; H, 6.65.

*Treatment of the dibenzyl compound with ozone.* In 200 ml. of purified chloroform (6) in a gas saturation bottle, 1.5 g. of the dibenzyl compound (m.p. 232°) was dissolved, and the solution was cooled to −50° in an acetone-solid carbon dioxide mixture contained in a Dewar flask. The reaction bottle was connected to the ozone generator (0.018 mole of ozone per hour). The outlet tube of the reaction vessel was connected to a gas trap, which contained an indicator solution of acidified potassium iodide. Ozone was passed through the system for one hour. The low temperature was maintained throughout the reaction period. When the reaction was stopped, the potassium iodide indicator possessed a distinct red color. The chloroform solution was deep blue in color, and it was noted that some of the chloroform solvent had frozen during the reaction period.

When the reaction mixture came to room temperature, the blue color faded. This solution was placed in a flask along with one-half its volume of dilute hydrochloric acid, and the mixture was heated under reflux, with stirring, for 1.5 hours. The chloroform layer was extracted with several portions of 5% sodium hydroxide. Acidification and evaporation of these alkaline extracts yielded a trace of a yellow tarry material, which was not identified.

The chloroform layer was washed and dried over calcium chloride. The residue remaining when the chloroform was evaporated, was taken up in hot ethanol, and water was added until a faint turbidity developed. This solution was allowed to stand in the refrigerator for several days. The light yellow solid was collected on a filter and recrystallized from a low-boiling petroleum ether-ether mixture; m.p. 118–121°. A subsequent recrystallization from ether gave a white crystalline product; m.p. 151–152°; yield 1.0 g. The infrared spectrum shows the characteristic phenyl absorption bands as well as a band at 1140 cm.$^{-1}$, which is similar to that for an aliphatic ether linkage.

*Anal.* Calc'd for $C_{44}H_{36}O_3$: C, 86.24; H, 5.94.
Found: C, 86.32; H, 6.08.

When the reaction was carried out as described, except that the reaction mixture was decomposed with zinc and acetic acid, the results were the same.

*1-Allyl-2,3,4,5-tetraphenylcyclopentadiene-1-ol* (XII). To a Grignard reagent, prepared by the method of Kharasch and Fuchs (7) from 77 g. (1.0 mole) of allyl chloride, was added 38.5 g. (0.1 mole) of tetraphenylcyclopentadienone. The light green reaction mixture was stirred under reflux overnight. Decomposition of the mixture gave an oil which changed to a tan solid. It was dissolved in hot ethanol and treated with Norit. The white crystalline product, resulting from this treatment, changed to a light yellow crystalline compound when dried in an Abderhalden drying pistol for 6 hours at 0.1 mm. and 80°; m.p. 137–138°; yield 37.5 g. (88%). The infrared spectrum shows absorption peaks at 1596 and 1697 cm.$^{-1}$, at 3357 cm.$^{-1}$, and at 919 and 1027 cm.$^{-1}$, attributable, respectively, to phenyl, hydroxyl, and vinyl.

*Anal.* Calc'd for $C_{32}H_{26}O$: C, 90.10; H, 6.15.
Found: C, 89.91; H, 6.25.

Attempts to dehydrate the carbinol gave tarry products. In one experiment, in which hydrogen chloride and glacial acetic acid were employed, a dark red product was collected. It was recrystallized from a methanol-chloroform mixture, giving a dark red solid; m.p. 222–225°; yield 4.2 g. All attempts at further purification failed.

*Anal.* Calc'd for $C_{32}H_{24}$: C, 94.08; H, 5.92.
Found: C, 91.91; H, 6.18.

## SUMMARY

1,2,3,4-Tetraphenylfulvene has been found to react additively with *tert*-butylmagnesium chloride and benzylmagnesium chloride. The adducts, though themselves Grignard reagents, show no tendency to react with the fulvene. Water converts them to the corresponding 5-alkyl-1,2,3,4-tetraphenylcyclopentadienes. Both adducts undergo alkylation, but the structures of the alkylation products have not been established with certainty.

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