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

THE ADDITION OF GRIGNARD REAGENTS TO BENZOFULVENES

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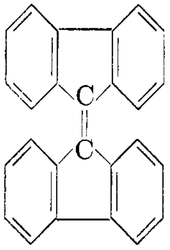
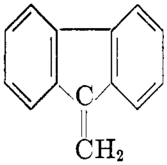
The explanation advanced (1) for the addition of Grignard reagents to the bifulvene, dibiphenyleneëthylene (I), carried the suggestion that this type of reactivity might be exhibited by fulvenes in general. Against this view is the observation that dibenzofulvene (II) did not react with either phenylmagnesium bromide or methylmagnesium iodide (2). These reagents, however, had failed also to combine with the bifulvene (I). More significant perhaps is the report that benzalfluorene (III) failed to condense with *tert*-butylmagnesium chloride (3).



I



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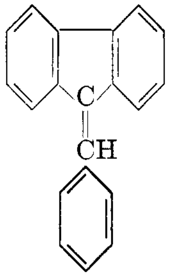
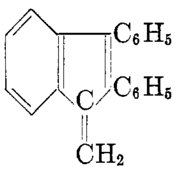
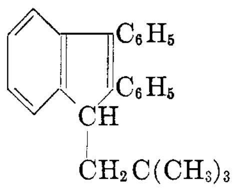


III

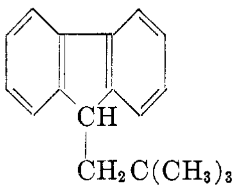
Further study has revealed that *tert*-butylmagnesium chloride reacts additively not only with dibenzofulvene (II) but also with 2,3-diphenylbenzofulvene (IV). The product obtained from the diphenylfulvene (IV) has been shown to be 1-neopentyl-2,3-diphenylindene (V), and by analogy that from dibenzofulvene (II) has been identified as 9-neopentylfluorene (VI).



IV



V



VI

Attachment of the alkyl radical to the methylene group is demanded by the theory that the cyclopentadiene nucleus absorbs an electron pair from the semicyclic bond, forcing the nucleophilic attack of the Grignard reagent to occur at the methylene group. Moreover, this manner of addition has been observed in the condensation of phenyllithium with benzalindene and benzalfluorene (III) (4).

Dibenzofulvene was prepared by the excellent method of Wieland and Krause

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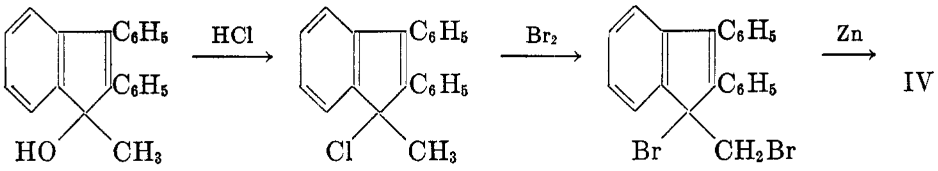
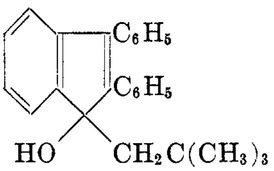
(2). The diphenylfulvene (IV) was synthesized from 2,3-diphenylindone by the following scheme.

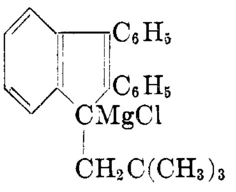


The independent synthesis of 1-neopentyl-2,3-diphenylindene (V) was achieved by condensing neopentylmagnesium chloride with 2,3-diphenylindone and reducing the resulting carbinol (VII) with hydriodic acid. This product has the same melting point and the same infrared absorption spectrum[2] as that of the compound obtained from the fulvene. Further, a mixture melting point of the two samples showed no depression.

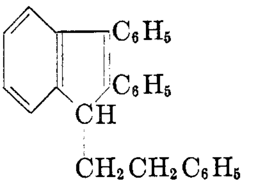
The condensation of Grignard reagents with olefins is especially interesting because the products are Grignard reagents and might be expected to react with the unsaturated compounds to yield dimeric or polymeric Grignard reagents. The product (VIII) from 2,3-diphenylbenzofulvene (IV) and *tert*-butylmagnesium chloride, like those in the bifulvene series, showed no tendency to react with the fulvene. In fact, it could not be induced to undergo alkylation with *tert*-butyl chloride or benzyl chloride or to yield an acid with carbon dioxide.



VII



VIII



IX

Efforts to condense the diphenylfulvene (IV) with ethylmagnesium bromide and benzylmagnesium chloride failed to give isolable crystalline products. However, the benzyl reagent, in the presence of magnesium, acted on the fulvene to give two compounds, the structures of which have not yet been determined. One of these (m.p. 219–220°) had the composition[3] of the monobenzyl derivative, but its melting point is much higher than that which would be expected for 1-phenethyl-2,3-diphenylindene (IX). The other substance (m.p. 246–247°) has the composition calculated for the reduced dimer of the fulvene. This product was also obtained when an ethylmagnesium bromide-magnesium mixture was allowed to react with the diphenylfulvene.

Two hydrocarbons were isolated from the reaction between dibenzofulvene (II) and benzylmagnesium chloride. Although the structure of these compounds has not been proven, one of them (m.p. 209–210°) had an infrared absorption spectrum with the characteristic monosubstituted phenyl bands at 697 and

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[2] Infrared absorption data and interpretation by Miss Elizabeth Petersen.

[3] Microanalyses by Miss Emily Davis and Mrs. Jean Fortney.

756 cm.$^{-1}$. This observation indicated that addition of the benzylmagnesium chloride to the fulvene (II) had occurred. The carbon-hydrogen analysis of the adduct was favorable for $C_{21}H_{18}$ and thus it is possible that this product is 9-phenethylfluorene.

EXPERIMENTAL

SYNTHESIS OF 2,3-DIPHENYLBENZOFULVENE

1-Methyl-2,3-diphenyl-1-indenol. This compound was prepared in a manner similar to that described for 1-methyl-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol by Dilthey and Huchtemann (5). Solid 2,3-diphenylindone (6) (11.2 g.) was added slowly to a cold solution of 0.06 mole of methylmagnesium bromide in 300 ml. of ether. This mixture was stirred under reflux for four hours and then decomposed in the usual manner. The ether layer was washed with water and dried. The dry solution was concentrated to about 15 ml. and 50 ml. of high-boiling petroleum ether was added. When the solution was cooled 10.5 g. (88%) of light yellow crystals was obtained; m.p. 145.5–147°. Recrystallization of the crude alcohol from a mixture of ether and high-boiling petroleum ether gave white, cube-shaped crystals; m.p. 147–148°.

Anal. Calc'd for $C_{22}H_{18}O$: C, 88.56; H, 6.08.

Found: C, 88.44; H, 6.08.

1-Chloro-1-methyl-2,3-diphenylindene. This compound was prepared by a method similar to that used by Wieland and Krause for 9-chloro-9-methylfluorene (2). 1-Methyl-2,3-diphenyl-1-indenol (20.9 g.) was covered with 100 ml. of dry ether, and the mixture was cooled to about 10°. A stream of dry hydrogee chloride was then passed through the ether for two hours, at the end of which time all the alcohol had dissolved. After being allowed to stand two hours the yellow solution was poured on cracked ice. The ether layer was washed thoroughly with cold 2% sodium hydroxide solution, then with water. After the solution had been dried the ether was removed under reduced pressure at room temperature. The crude chloro compound, obtained in a yield of 20 g. (90%), was subjected to bromination without further purification. An analytical sample was prepared by recrystallization of a small amount of the crude material from ether. The pure chloro compound did not have a sharp melting point; it began to evolve gas at 87° and melted completely at 99°.

Anal. Calc'd for $C_{22}H_{17}Cl$: C, 83.39; H, 5.41.

Found: C, 83.14; H, 5.08.

1-Bromo-1-bromomethyl-2,3-diphenylindene. The procedure used was essentially that of Wieland and Krause (2). A suspension of 15.8 g. of 1-chloro-1-methyl-2,3-diphenylindene in 450 ml. of glacial acetic acid was stirred until all the chloro compound dissolved (about 2½ hours). To the resulting clear orange solution was added, with stirring, a mixture of 9.9 g. of bromine in 50 ml. of glacial acetic acid over a period of 30 minutes. Stirring was continued two more hours during which time the dibromide precipitated. Filtration of the reaction mixture yielded 16.5 g. of the light orange, crystalline dibromide; m.p. 129–131°. Concentration of the filtrate gave another 4 g. of product. The crude product was recrystallized from high-boiling petroleum ether; m.p. 129.5–131°; yield 17.5 g. (80%).

Anal. Calc'd for $C_{22}H_{16}Br_2$: C, 60.02; H, 3.66.

Found: C, 60.19; H, 3.85.

2,3-Diphenylbenzofulvene (IV). The procedure was similar to that employed by Wieland and Krause (2) for dibenzofulvene. The entire reaction was carried out in a dark room. 1-Bromo-1-bromomethyl-2,3-diphenylbenzofulvene (2.2 g.) was covered with 30 ml. of methanol and about 0.8 g. of powdered zinc was added. Then the reaction mixture was blanketed with nitrogen and 2 ml. of acetic acid was added dropwise with agitation. The solution evolved considerable heat during the addition of the acetic acid. After the initial reaction had subsided, 0.8 g. more of zinc and another 2 ml. of acetic were added. The suspension was allowed to stand one-half hour; then 50 ml. of ether was added and the solution was filtered. The filtrate was washed with water, 10% sodium hydroxide solution, and again with water. The yellow ether solution was dried and the solvent evaporated under reduced pressure at room temperature. The yield of crude fulvene was 1.3 g. (93%). The yellow fulvene turned red-orange on standing. Attempts to purify the compound by distillation failed because of extensive polymerization and decomposition of the fulvene when it was heated. Analysis of the freshly prepared fulvene indicated it to be fairly pure, and this material was used directly in the reactions with the Grignard reagents.

Anal. Calc'd for $C_{22}H_{16}$: C, 94.25; H, 5.75.
Found: C, 92.67; H, 5.83.

REACTIONS OF 2,3-DIPHENYLBENZOFULVENE WITH GRIGNARD REAGENTS

1-Neopentyl-2,3-diphenylindene (V). *tert*-Butylmagnesium chloride was prepared by stirring a mixture of 4.6 g. of *tert*-butyl chloride and 2.4 g. of magnesium in 100 ml. of dry ether under reflux for two hours. The Grignard solution was quickly decanted into a flask containing 2,3-diphenylbenzofulvene, prepared from 2.2 g. of the dibromide as previously described, in 100 ml. of ether. The resulting mixture was stirred under reflux for 11 hours in an atmosphere of nitrogen. During this time the yellow color of the solution faded and a white precipitate appeared. The complex was decomposed by an ice-hydrochloric acid mixture, and the ether layer was then washed with water and dried. The dry solution was concentrated to 10 ml. and allowed to stand overnight. A total of 0.6 g. of fine, white needles was collected; m.p. 120–122°. Treatment of the filtrate with 5 ml. of acetic acid and evaporation of the ether allowed isolation of 0.2 g. more of product; m.p. 95–110°; yield 52%. By two recrystallizations from a small volume of acetic acid, pure 1-neopentyl-2,3-diphenylindene was obtained in the form of small white needles; m.p. 124–125°.

Anal. Calc'd for $C_{26}H_{26}$: C, 92.25; H, 7.74.
Found: C, 92.31; H, 7.55.

The infrared absorption spectrum had bands (1366 and 1392 cm^{-1}) characteristic of the *tert*-butyl group.

When the addition product formed by the fulvene and *tert*-butylmagnesium chloride was treated with *tert*-butyl chloride, no reaction was noted; 1-neopentyl-2,3-diphenylfulvene was isolated from the mixture. A similar result was obtained when carbon dioxide was passed through the solution of the addition product.

Reaction of benzylmagnesium chloride with 2,3-diphenylbenzofulvene in the presence of magnesium metal. A solution of 2,3-diphenylbenzofulvene, prepared from 2.2 g. of the dibromide as previously described, in 30 ml. of dry ether was added to a Grignard solution obtained from 6.3 g. of benzyl chloride and 1.5 g. of magnesium in the usual manner. This suspension was stirred under reflux in an atmosphere of nitrogen for eight hours. The reaction mixture was decomposed and the ether layer was washed with water and dried. The solution was concentrated to 40 ml.; the white needles which separated melted at 245–250°. This product (0.1 g.) was practically insoluble in hot acetic acid, but could be recrystallized from a benzene-acetic acid solution to give a compound which melted at 246–247°. Its high melting point and carbon-hydrogen analysis suggest that this material is possibly a reduced dimer of 2,3-diphenylbenzofulvene.

Anal. Calc'd for $C_{44}H_{34}$: C, 93.91; H, 6.09.
Found: C, 93.80; H, 6.28.

Concentration of the ether solution from which the high-melting fraction was obtained gave 0.07 g. of white needles melting at 218–224°. This fraction was treated with a small volume of hot acetic acid, and the solution was filtered. From the filtrate there was obtained 0.05 g. of fine, white needles; m.p. 217–218°. Recrystallization from 8 ml. of acetic acid gave a product which melted at 218–219°. Analysis suggested that this fraction might be the monobenzyl derivative (IX).

Anal. Calc'd for $C_{29}H_{24}$: C, 93.51; H, 6.49.
Found: C, 93.19; H, 6.18.

Reaction of ethylmagnesium bromide with 2,3-diphenylbenzofulvene in the presence of mag-

nesium metal. Ethylmagnesium bromide did not appear to react additively with the fulvene; only a yellow oil was isolated from the reaction mixture. The following procedure was then tried. A solution of 2,3-diphenylbenzofulvene, prepared from 2.2 g. of the dibromide in the manner previously described, in 20 ml. of ether was added to a Grignard solution obtained from 5.45 g. of ethyl bromide and 2.4 g. of magnesium. The resulting mixture was stirred under an atmosphere of nitrogen for 12 hours and decomposed in the usual manner. The precipitate (0.54 g.) which separated at the ether-water interface melted at 220–247°. This product partially dissolved in 30 ml. of hot acetic acid. The insoluble fraction, 0.3 g. melting at 240–245°, was recrystallized from a benzene-acetic acid solution to give a compound melting at 245.5–247.5°. A mixture melting point with the high-melting fraction obtained from the reaction of the benzylmagnesium chloride-magnesium mixture and 2,3-diphenylbenzofulvene showed no depression.

Anal. Calc'd for $C_{44}H_{24}$: C, 93.91; H, 6.09.
Found: C, 94.10; H, 6.22.

The acetic acid-soluble material was not resolved into a pure compound.

From the ether solution from which the ether-insoluble fraction precipitated, 0.14 g. of white crystals was obtained; m.p. 189–230°.

INDEPENDENT SYNTHESIS OF 1-NEOPENTYL-2,3-DIPHENYLINDENE

Neopentyl chloride. This procedure is essentially that of Whitmore and Fleming (7). From 12.3 g. of neopentane and 7.1 g. of chlorine a colorless liquid was obtained, which was distilled at atmospheric pressure. The first fraction boiled at 79–83° and amounted to 7.04 g.; n_D^{20} 1.4042–1.4050. Six grams of a higher-boiling fraction was collected at 96–98°; n_D^{20} 1.4462. The lower-boiling fraction was redistilled to give 6.74 g. (37%) of pure neopentyl chloride; b.p. 81–83°; n_D^{20} 1.4040.

1-Neopentyl-2,3-diphenylindenol. A mixture of 3.2 g. of neopentyl chloride and 1.5 g. of finely divided magnesium in 50 ml. of dry ether was stirred for ten hours under reflux in a nitrogen atmosphere. The Grignard solution was decanted into a chilled solution of 5.6 g. of 2,3-diphenylindone in 100 ml. of dry ether. The resulting suspension was stirred under reflux for one hour. During this period a white complex separated, but the ether solution remained red. The reaction mixture was decomposed, and the red ether layer was washed with water and dried. The ether was evaporated and 50 ml. of high-boiling petroleum ether was added to the residue. When the solution was cooled 2.25 g. of crystalline material separated; part of the crystals were red and the rest were yellow. A rough separation of the two compounds was achieved by adding a small volume of ether to the mixture of crystals and decanting the solution of the more soluble yellow product. The red residue was unchanged 2,3-diphenylindone. The ether was evaporated from the decanted solution and 15 ml. of high-boiling petroleum ether was added. A total of 1.6 g. of product was obtained from this solution; m.p. 132–134°. Several recrystallizations of this material from high-boiling petroleum ether were required to give white crystals of 1-neopentyl-2,3-diphenylindenol; m.p. 134–135°.

Anal. Calc'd for $C_{26}H_{26}O$: C, 88.09; H, 7.39.
Found: C, 87.94; H, 7.80.

Reduction of 1-neopentyl-2,3-diphenylindenol with hydriodic acid. The procedure used here was similar to that described by Vansheidt and Maldovskii (8). To a solution of 0.2 g. of 1-neopentyl-2,3-diphenylindenol in 5 ml. of acetic acid was added 1 ml. of 45% hydriodic acid. The dark red solution was heated for three minutes in a bath at 130°, during which time the color changed to a light yellow. When the solution was cool 10 drops of a 10% solution of stannous chloride in hydrochloric acid was added. The gum which separated was collected and dissolved in ether. The ether solution was washed with water, with sodium hydroxide solution, and again with water. Evaporation of the solvent left a yellow, oily residue which was taken up in 5 ml. of hot acetic acid. A few drops of water were added to the acetic acid solution, and it was then allowed to cool. In the course of several days 0.04 g. of white needles separated; m.p. 95–110°. Concentration of the acetic acid filtrate gave another 0.03 g. of material; m.p. 90–110°. Two recrystallizations of these two fractions from dilute acetic acid gave pure 1-neopentyl-2,3-diphenylindene; m.p. 124–125°. A mixture melting point of the compound obtained from the reaction of *tert*-butylmagnesium chloride and 2,3-diphenylbenzofulvene with this authentic sample of 1-neopentyl-2,3-diphenylindene showed no depression. The infrared absorption spectra of the two products were identical.

Anal. Calc'd for $C_{26}H_{26}$: C, 92.25; H, 7.74.
Found: C, 92.54; H, 7.93.

REACTIONS OF DIBENZOFULVENE WITH GRIGNARD REAGENTS

9-Neopentylfluorene. tert-Butylmagnesium chloride was prepared by adding 4.6 g. of *tert*-butyl chloride, with stirring, to a mixture of 2.4 g. of magnesium in 100 ml. of dry ether and refluxing the resulting solution for two hours. The Grignard reagent was decanted into a flask containing dibenzofulvene, prepared from 3.38 g. of the dibromide as described by Wieland and Krause (2), in 100 ml. of ether. This suspension was stirred for 11 hours under reflux in an atmosphere of nitrogen. The complex was decomposed and the polymerized fulvene which gathered at the ether-water interface (0.4 g.) was collected. The clear ether layer was washed with water and dried. Evaporation of the ether gave a yellow oil which was taken up in 30 ml. of hot acetic acid. When the solution was cooled 0.5 g. of a sticky, crystalline product was obtained; m.p. 60–65°. This material was recrystallized from 20 ml. of methanol to give 0.15 g. (6%) of the crude 9-neopentylfluorene; m.p. 70–74°. Recrystallization of this material from methanol gave the pure hydrocarbon in the form of long needles; m.p. 79–80°.

Anal. Calc'd for $C_{18}H_{20}$: C, 91.47; H, 8.53.
Found: C, 91.32; H, 8.81.

The infrared absorption spectrum had bands characteristic of the *tert*-butyl group at 1364 and 1394 cm^{-1}.

Reaction of benzylmagnesium chloride with dibenzofulvene. A solution of benzylmagnesium chloride, prepared from 12.6 g. of benzyl chloride and 4.48 g. of magnesium, was decanted into a flask containing dibenzofulvene, made from 3.38 g. of the dibromide, in 100 ml. of dry ether. This suspension was stirred overnight under reflux in a nitrogen atmosphere. The complex was decomposed and the polymerized fulvene which gathered at the ether-water interface was collected. The ether layer was then washed with water and dried, and most of the solvents were distilled. When the residue was treated with a little ether and allowed to stand, white crystals separated; yield 0.13 g.; m.p. 203–207°. Recrystallization from an acetic acid-benzene solution gave a product melting at 209–210°. The analysis checked with that calculated for the monobenzyl adduct.

Anal. Calc'd for $C_{21}H_{24}$: C, 93.29; H, 6.71.
Found: C, 93.06; H, 6.48.

The infrared absorption spectrum had bands at 697 and 756 cm^{-1} characteristic of the monosubstituted phenyl group.

The yellow ether solution from which the first crop of crystals was obtained was evaporated and 10 ml. of acetic acid was added to the residue. The small amount of crystalline material which separated (0.1 g.) was recrystallized from 10 ml. of acetic acid to give 0.02 g. of long, rhombic shaped, colorless crystals. The melting point of this material was not sharp and the crystals lost gas at about 110°. After being heated in a vacuum at 100° overnight the crystals were opaque and melted at 185–188°.

SUMMARY

tert-Butylmagnesium chloride reacts with dibenzofulvene and 2,3-diphenylbenzofulvene to produce 9-neopentylfluorene and 1-neopentyl-2,3-diphenylindene, respectively. The neopentylindene has been synthesized from 2,3-diphenylindone and neopentylmagnesium chloride.

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