ml. of petroleum ether gave 75 mg. of starting material. Elution with 100 ml. of 9:1 petroleum ether–benzene gave 27 mg. of material, $[\alpha]_D$ +105°. Two recrystallizations of this from methanol gave m.p. 73.5–74.5° (reported[7] for 3-keto-A-norcholestane, m.p. 73–74°), $\lambda_{\max}^{\mathrm{CS_2}}$ 5.76 μ.

The semicarbazone had m.p. 267–268° (reported[17] m.p. 268–270°).

Determination of the Ratio of Ester I to Ester II.—A sample of the mixed methyl esters from the Favorskii reaction, from which none of ester I had been removed by crystallization, was chromatographed to remove the diester III. The remaining combined esters I and II were then converted to the mixed diphenylethylenes as described above in 83% over-all yield. This material had $[\alpha]_D$ −27° and from this and the rotations of the pure diphenylethylenes IV and VI it was calculated that the ratio of esters I and II was 54 to 46% respectively.

Identification of Methyl 2,3-*seco*-Cholestane-2,3-dioate (III).—The material from the original chromatogram designated as fraction II had $[\alpha]_D$ +19°, $\lambda_{\max}^{\mathrm{CS_2}}$ 5.80 μ. Three recrystallizations from methanol gave m.p. 59–60°; two more recrystallizations gave m.p. 60–60.3°.

Anal. Calcd. for $C_{29}H_{50}O_4$: C, 75.28; H, 10.89. Found: C, 75.33, 75.57; H, 10.81, 11.16.

Heating the diester III with 0.04 *N* sodium hydroxide in ethylene glycol resulted in only partial saponification.

The diester III (70 mg.) in 10 ml. of acetic acid and 10 ml. of 48% hydrobromic acid was heated under reflux overnight, the resulting solution was then cooled, poured into water, and the resultant mixture extracted with an ether-benzene mixture. The ether and benzene were evaporated and the residue recrystallized from methanol–water and then petroleum ether–ether to give 10 mg., m.p. 196–197°, mixture m.p. with an authentic sample (reported[8] m.p. 196°) of 2,3-*seco*-cholestane-2,3-dioic acid, 196–197°.

A sample of the authentic acid was esterified with methanolic hydrogen chloride and the diester had m.p. 59–60°, $[\alpha]_D$ +20° (reported[8] m.p. 67°). A mixture m.p. with the diester III was 59–60°, and the infrared spectra of the two samples were identical.

Reduction of 2-Carbomethoxy-A-norcholestane (I) to 2-Hydroxymethyl-A-norcholestane (VIII).—To a stirred slurry of 0.5 g. of lithium aluminum hydride in 25 ml. of anhydrous ether was added 200 mg. (0.48 millimole) of crystalline ester I. The mixture was stirred for 1.5 hours, the addition complex was then decomposed by the slow addition of dilute sulfuric acid, and the resulting mixture was extracted with benzene. The extract was washed with water, dried over anhydrous sodium sulfate, the benzene evaporated, and the residue (169 mg.) taken up in petroleum ether and chromatographed on 20 g. of alumina. Elution with benzene gave 158 mg. of alcohol VIII (85%), which, after four recrystallizations from 95% methanol, had m.p. 118–118.5°, $[\alpha]_D$ +32°. $\lambda_{\max}^{\mathrm{CS_2}}$ 2.85 μ.

Anal. Calcd. for $C_{27}H_{48}O$: C, 83.43; H, 12.47. Found: C, 83.17; H, 12.60.

Cathylation of 2-Hydroxymethyl-A-norcholestane (VIII).—To a solution of 156 mg. (0.4 millimole) of the alcohol VIII in 5 ml. of pyridine cooled to 0° was added dropwise 0.5 ml. of ethyl chlorocarbonate. After the mixture had stood overnight at room temperature, it was diluted with 50 ml. of benzene, washed twice with water, twice with dilute hydrochloric acid, and twice with water, and then the benzene was evaporated. The residue was taken up in petroleum ether and passed over a column containing 5 g. of alumina to give 164 mg. (88%) of the cathylate. Two recrystallizations from acetone–ethanol gave material with m.p. 60.5–61.5°, $[\alpha]_D$ +34°, $\lambda_{\max}^{\mathrm{CS_2}}$ 5.67 μ.

Anal. Calcd. for $C_{30}H_{52}O_3$: C, 78.20; H, 11.38. Found: C, 77.99; H, 11.37.

Pyrolysis of 85 mg. in a sealed evacuated Pyrex tube at 300° for 2.5 hours, followed by chromatography of the residue, gave 69 mg. of starting material, and intractable oils. Longer periods of heating and higher temperatures resulted in decomposition and only oils could be isolated.

Providence 12, R. I.

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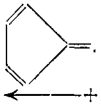
[17] H. Lettre, *Z. physiol. Chem.*, **221**, 73 (1933).

[Contribution from the Chemical Laboratories of the Polytechnic Institute of Brooklyn]

The Reaction of 1,2,3,4-Tetraphenylfulvene with Grignard Reagents

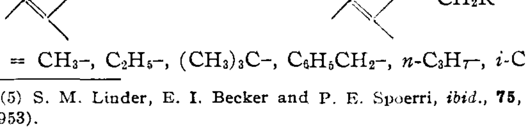
By Anthony G. Bonagura,[1] Martin B. Meyers,[1] Stanley J. Storfer[1] and Ernest I. Becker[2]

Received June 28, 1954

Ethyl-, *n*-propyl- and isopropylmagnesium halides have been newly added to 1,2,3,4-tetraphenylfulvene and the reported additions of benzyl-, *t*-butyl- and methylmagnesium halides have been verified to give the corresponding 5-(RCH_2)-1,2,3,4-tetraphenylcyclopentadienes. The dienes, where R = CH_3–, C_2H_5–, *n*-C_3H_7– and $(CH_3)_3C$–, have been synthesized by the addition of RCH_2– organometallic derivatives to tetracyclone and reducing the intermediates to the dienes. The correspondence of the dienes prepared by both routes is interpreted to be in accord with the dipolar character of fulvene .

Recently Fuson and York[3] and Taber, *et al.*,[4] have reported that 1,2,3,4-tetraphenylfulvene (I) reacts with benzyl,[3] *t*-butyl[3] and methyl[4] Grignard reagents at the 6-position to give 5-alkyl-1,2,3,4,-tetraphenylcyclopentadienes. However, Taber, *et al.*, had raised a question concerning the course of the addition depending upon the purity of the magnesium. Elucidation of this point was of interest in connection with related studies here on the reactions of dipolar hydrocarbons.[4,5] This investigation was, therefore, designed to prove unequivocally the course of the reaction and to extend the reaction to other organometallic compounds.

The previously reported experiments were repeated using sublimed magnesium with essential accord in all important features. Then, the addi-



(1)

R = CH_3–, C_2H_5–, $(CH_3)_3C$–, $C_6H_5CH_2$–, *n*-C_3H_7–, *i*-C_3H_7–

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[1] Taken from the theses of A.G.B., M.B.M. and S.J.S. presented to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Bachelor of Science degree in Chemistry, 1954.

[2] To whom inquiries should be sent.

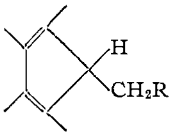
[3] R. C. Fuson and O. York, Jr., *J. Org. Chem.*, **18**, 570 (1953).

[4] D. Taber, E. I. Becker and P. E. Spoerri, This Journal, **76**, 776 (1954).

[5] S. M. Linder, E. I. Becker and P. E. Spoerri, *ibid.*, **75**, 5972 (1953).

TABLE I

5-ALKYL-1,2,3,4-TETRAPHENYLCYCLOPENTADIENES FROM GRIGNARD REAGENTS AND 1,2,3,4-TETRAPHENYLFULVENE (I)



Starting mater.,		Grignard reagent		Temp.,	Time,	Products		
g.	Mole	Structure	Mole	°C.	hr.	No.	M.p., °C. (solvent)	Yield of pure prod., %
6.0	0.016	$(CH_3)_3CMgCl$	0.028	120–125	1.0	II	137–139[a] (abs. ethanol)	22
4.0	.010	$C_6H_5CH_2MgCl$	.011	120–125	0.5	III	135.2–136.4[b] (ethanol–chloroform)	8
6.3	.0165	CH_3MgI	.053	100	2.0	IV	178–179[c] (benzene–hexane)	41
5.0	.013	C_2H_5MgBr	.042	120	0.5	V	140–142 (benzene–hexane)	27
5.0	.013	*n*-C_3H_7MgBr	.038	120	.75	VI	159–160 (ethanol–EtAc)	26[d]
5.0	.013	*i*-C_3H_7MgI	.029	120	.5	VII	155.5–156.0 (ethanol–EtAc; acetonitrile)	9.3[e]

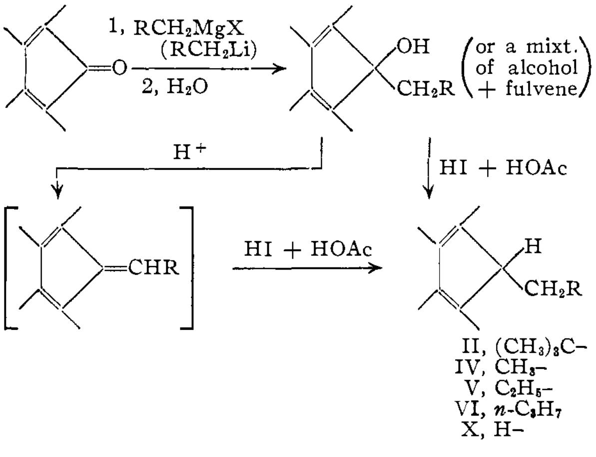
[a] Reported m.p. 135.5–136.0°.[3] [b] Reported m.p. 138–139°.[3] [c] Reported m.p. 179–180°.[4] [d] *Anal.* Calcd. for $C_{33}H_{30}$: C, 92.91; H, 7.09. Found: C, 92.65; H, 7.31. [e] *Anal.* Calcd. for $C_{33}H_{30}$: C, 92.91; H, 7.09. Found: C, 92.66; H, 7.19.

tion of ethylmagnesium bromide and iodide, *n*-propylmagnesium bromide and isopropylmagnesium iodide were added to I affording the corresponding dienes (see equation 1 and Table I).

All of the reactions were carried out in anisole at 100–120°.[4] It is interesting that under these conditions the saturated, aliphatic organometallic compounds react with I. On the other hand, these are not reactive in refluxing ethyl ether, conditions which are satisfactory for the reaction of benzyl- and *t*-butylmagnesium chlorides. The addition of ethylmagnesium iodide to I did not afford a pure product, but under the same conditions ethylmagnesium bromide afforded the diene in 27% yield.

In order to prove the structures of the dienes obtained, the two-step path *via* tetracyclone (VIII) was selected: namely, (a) the addition of the appropriate organometallic compound to VIII followed by hydrolysis to the tertiary alcohol or to an alcohol–fulvene mixture; and (b) the reduction or dehydration and reduction, of the product(s) of (a) to the desired diene[5] (see Chart I).

CHART I



It was originally presumed that all of the intermediate alcohols might be prepared by the addition of the organometallic compound to VIII as is the case with 5-methyl-(IX)-[6] and 5-ethyltetraphenylcyclopentadien-5-ol.[6] However, with *n*-propylmagnesium iodide only 1.7% of the corresponding dienol was isolated. Since it is feasible that the Grignard reagent was reducing VIII, a hindered ketone, recourse was had to the lithium derivative. Substituting *n*-propyllithium in ether gave an alcohol-fulvene mixture in 34% yield, while *n*-propyllithium in pentane gave a 36% yield. Therefore, with *n*-butyl also the lithium derivative was used. With neopentyl the magnesium derivative was employed because this Grignard cannot have any reducing action.

In the attempted preparation of the *n*-propyl- and *n*-butyldienols another difficulty was encountered. These alcohols apparently dehydrated to the dark-colored fulvenes even under conditions designed to prevent this and, therefore, were not characterized. However, model experiments carried out on I and on IX to give 5-methyl-1,2,3,4-tetraphenylcyclopentadiene (X) showed that a higher yield could be obtained from the fulvene (I) than from the dienol (IX). Therefore, the crude reaction mixtures obtained from the addition of *n*-propyl- and *n*-butyllithium were subjected directly to the action of hydriodic acid in acetic acid.

The dienes prepared in this sequence of reactions did not depress the melting points of the corresponding dienes prepared by the addition of Grignard reagents to I.

The structure of III has not been established unequivocally and is most probably a compound other than the β-phenethyldiene. A band at 1380 cm.$^{-1}$ in the infrared absorption spectrum indicates the presence of a CH_3-group. Thus, III is most likely 5-*o*-tolyl-1,2,3,4-tetraphenylcyclopentadiene and not the β-phenethyl isomer.[7]

It has thus been substantiated that organomagnesium halides and organolithium compounds add as reported to give 5-alkyl-1,2,3,4-tetraphenylcyclopentadienes in accord with the dipolar nature of fulvene.

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(6) W. Dilthey and P. Huchtemann, *J. prakt. Chem.*, **154**, 238 (1940).

(7) Professor R. C. Fuson and Dr. O. York have privately informed us of the following: (1) that no depression is observed on admixture of our product prepared in anisole with that prepared in ether; (2) that an independent unequivocal preparation of 1-(β-phenethyl)-2,3,4,5-tetraphenylcyclopentadiene, m.p. 138–139°, depressed the melting point of the product prepared *via* I to 126–130°; (3) on long standing the melting point of III changes from 138–139° to 130–131°.

Experimental[8–10]

Grignard Reagents and Tetracyclone.—The addition of Grignard reagents to VIII was carried out by titrating it in benzene with standardized Grignard reagents. At a 1:1 molar ratio a sharp color change occurred from deep red to yellow or green. Nevertheless, a 2–3 fold excess of Grignard reagent was employed since, when it was not, small quantities of unreacted tetracyclone remained. Excesses probably as high as 10-fold[6] were found not to be required.

IX.—Under nitrogen a solution of 20 g. (0.052 mole) of tetracyclone in 400 ml. of benzene was added with stirring to 0.090 mole (60 ml. of 1.5 *M*) methylmagnesium iodide in ether during 15 minutes. After heating the reaction flask an additional 10 minutes, a solution of 10 ml. of concentrated sulfuric acid in 400 ml. of ice-water was added and stirring was recommenced until the two layers were clear. The organic layer was washed twice with 2% aqueous potassium carbonate and then dried over anhydrous calcium chloride.

After removing the benzene and ether at the aspirator at 50°, the residue was dissolved in 500 ml. of boiling ethanol. Water was added to incipient crystallization and cooling gave 15.6 g. (0.039 mole, 75%) of a light yellow, crystalline product, m.p. 195–196° (reported m.p. 195°[6]).

I.—To a solution of 20 ml. of concentrated sulfuric acid in 450 ml. of acetic acid was added 15 g. (0.037 mole) of IX. The mixture was heated on a steam-bath with constant swirling and under an ultraviolet light. In from 5–10 minutes the blue fluorescence of the solution changed to a green fluorescence. The mixture was heated for an additional five minutes and then chilled in an ice-bath. Filtration gave 13.4 g. (0.035 mole, 94%) of orange I, m.p. 205–206°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) (60:40) afforded 12.9 g. (0.034 mole, 89%) of orange needles, m.p. 208–209° (reported m.p. 211–212°[6]).

5-Alkyl-1,2,3,4-tetraphenylcyclopentadienes by Addition of Grignard Reagents to I.—The procedure was similar in each case and so the preparation of 1-*n*-butyldiene (VI) is described here as typical. See Table I for variations.

In a 250-ml. three-necked flask set up for a Grignard reaction under nitrogen and arranged with the condenser set for distillation, there were placed 0.038 mole (30 ml. of 1.27 *M* solution) of *n*-propylmagnesium bromide. Five grams (0.013 mole) of I in 100 ml. of anisole was added while raising the temperature to 120°. Stirring was commenced and the temperature was held at 120° for 45 minutes.

After pouring the contents into a mixture of cracked ice and dilute hydrochloric acid, the separated organic layer was washed with water and then dried over anhydrous calcium chloride. The benzene and anisole were removed at the water aspirator and the residue was recrystallized from 50 ml. of boiling ethanol to give 2.78 g. of yellow product, m.p. 156–158°. Recrystallization from ethanol–ethyl acetate afforded 1.50 g. (0.0047 mole, 26%) of light yellow needles of VI, m.p. 159–160°. This product did not depress the melting point of VI prepared by alkylating 1,2,3,4-tetraphenylcyclopentadiene with 1-butanol and sodium 1-butoxide.[11]

5-Methyl-1,2,3,4-tetraphenylcyclopentadiene. A. From IX.—To a refluxing solution of 2.0 g. (5.2 mmoles) of IX in 100 ml. of acetic acid, 1.3 ml. (10.4 mmoles) of 57% hydriodic acid was added. Immediate darkening due to the formation of free iodine took place. After cooling, a solution of stannous chloride in concentrated hydrochloric acid was added until the iodine color disappeared. The solution was poured into 300 ml. of water. Extraction with four 25-ml. portions of benzene and washing the combined extracts with water, 5% sodium bisulfite and finally water gave an organic layer which was dried over anhydrous magnesium sulfate, filtered and distilled to dryness at reduced pressure to give 0.04 g. (1.1 mmoles, 21%) of crude X, m.p. 173.5–176.0°. Recrystallization three times from petroleum ether (b.p. 90–100°) and twice from a 1:1 mixture of ethanol–ethyl acetate raised the melting point to 178.5–179.5°. A mixture with a sample supplied by Ochek (m.p. 178.5–179.5°) melted at 178.0–179.0°.

B. From I.—To a refluxing solution of 0.96 g. (2.5 mmoles) of I in 75 ml. of acetic acid, 0.6 ml. (5.0 mmoles) of 57% hydriodic acid was added. Iodine appeared as above and the product was isolated as above. Distillation of the benzene gave a pale yellow compound, m.p. 172–173° (uncor.). Recrystallization from petroleum ether (b.p. 90–100°) afforded 0.58 g. (1.5 mmoles, 60%) of X, m.p. 176.5–177.5°. Recrystallization once from each solvent as in A raised the melting point to 178.0–179.0°. No depression was observed with Ochek's compound.

C. From IX by Dehydration and Reduction.—A solution of 2.0 g. (5.0 mmoles) of IX and one drop of 85% phosphoric acid in 11.2 g. of acetic anhydride was refluxed for 15 minutes. The solution gradually became dark red and then did not darken further. At this point 1.3 ml. (10 mmoles) of 57% hydriodic acid, dissolved in 1.7 ml. of acetic acid was added dropwise with shaking. A vigorous reaction took place and iodine formed. The product was isolated as in A affording 1.07 g. (2.7 mmoles, 54%) of X, after crystallization of the crude product from ethanol–ethyl acetate, m.p. 175.5–177.5° (uncor.). Three additional recrystallizations from this solvent and one from acetonitrile raised the melting point to 179–180° and no depression was observed with Ochek's sample.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.79; H, 6.24.

Organolithium Compounds.—*n*-Butyllithium was prepared according to Gilman, Zoellner and Selby.[12] A similar procedure was used for *n*-propyllithium with the exception that petroleum ether (b.p. 30–40°) was substituted for ether. In both cases, 0.15 mole of the alkyl chloride, dissolved in 45 ml. of the solvent, was added to 0.33 mole of lithium in 45 ml. of the solvent. The filtered alkyllithium solutions were used within one-half hour of their preparation.

5-*n*-Propyl-1,2,3,4-tetraphenylcyclopentadiene.[2,4]—Under nitrogen 60 ml. of 0.74 *M* *n*-propyllithium (0.044 mole) was added to 7.7 g. (0.020 mole) of VIII dissolved in 140 ml. of hot benzene. After 28 ml. of the alkyllithium compound had been added, the solution was dark green and the addition of the excess did not further change the color. The solution was hydrolyzed with 300 ml. of saturated aqueous ammonium chloride and crushed ice. The organic layer, combined with a pentane washing of the aqueous layer, was washed with saturated ammonium chloride and finally three times with water and then dried over anhydrous magnesium sulfate. Distillation of the pentane and benzene at reduced pressure was followed by recrystallization of the residue from acetonitrile to give 3.1 g. (0.0072 mole, 36%) of a brown solid, m.p. 149.5–153.0°.

To a refluxing solution of 1.07 g. (2.5 mmoles) of the above product in 50 ml. of acetic acid was added dropwise 0.64 ml. (5.0 mmoles) of 57% hydriodic acid. Iodine darkened the solution and the product was isolated as described earlier. Crystallization from acetonitrile gave 0.37 g. (0.90 mmole, 36%) of V, m.p. 128.0–131.0°.

For analysis the compound was recrystallized twice from ethanol–ethyl acetate, m.p. 141.6–142.6°. No depression was observed with V, m.p. 141.0–143.0°, prepared by adding ethylmagnesium bromide to I, m.p. 141.6–143.0°.

Anal. Calcd. for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found: C, 93.01; H, 7.05.

5-*n*-Butyl-1,2,3,4-tetraphenylcyclopenta-2,4-diene (VI).—A hot solution of 3.84 g. (10.0 mmoles) of VIII in 80 ml. of benzene was added under nitrogen to a solution of *n*-butyllithium in ether (from 0.15 mole of *n*-butyl chloride) changing the color of the solution to chartreuse. The addition complex was hydrolyzed and worked up similarly to that in the third paragraph preceding and the tan solid obtained after removing the benzene–ether solvent was recrystallized from acetonitrile affording 2.1 g. of brown crystals, m.p. 164.5–169.5°.

The entire quantity of the brown crystals obtained was dissolved in 100 ml. of refluxing acetic acid, and 1.2 ml. (9.4 mmoles) of 57% hydriodic acid in 1.2 ml. of glacial acetic acid was added dropwise. The solution, which darkened in the expected manner, was worked up in the usual fashion. A dark-colored oil, remaining after the removal of the benzene, was redissolved in benzene and chromatographed through alumina. A yellow band which

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(8) All melting points are corrected.

(9) Analyses were performed by Dr. K. Ritter, Microanalytisches Laboratorium, Basel 2, Switzerland.

(10) All Grignard reagents were prepared using sublimed magnesium (see footnote 4).

(11) G. Ochek, M.S. thesis, Polytechnic Institute of Brooklyn, 1953.

(12) H. Gilman, E. A. Zoellner and W. M. Selby, THIS JOURNAL, **55**, 1252 (1933).

fluoresced blue-white under ultraviolet light was eluted, leaving a yellow-fluorescing band at the top of the column. The eluate containing the former band was distilled at reduced pressure, leaving a yellow tar which recrystallized from a mixture of ethanol-ethyl acetate to give 0.3 g. (0.7 mmole, 15%) of yellow crystals melting at 151.5–154.5°. A sample of VI, m.p. 156.5–158.5°, gave a mixture melting point of 154.5–157°.

Neopentyl Alcohol and Neopentyl Iodide.—An ether solution of *t*-butylmagnesium chloride from 247 g. (292 ml., 2.67 moles) of *t*-butylmagnesium chloride and 65 g. (2.67 g. atoms) of magnesium was prepared according to Whitmore and Badertscher.[13] Adapting the procedure of Whitmore and Church[14] for the synthesis of neo-carbon alcohols, 67.5 g. (2.25 moles) of paraformaldehyde was depolymerized with heat and the vapors passed into the Grignard solution, which was cooled in an ice-bath. The Gilman test for Grignard reagent was negative. After hydrolysis, extraction and drying, the product was obtained by distillation at 110–112°, 97 g. (1.10 moles, 49%).

Neopentyl alcohol was converted to neopentyl iodide using methyl iodide and triphenyl phosphite.[15] The reactants were refluxed for 41 hours instead of the prescribed 24, because the temperature of the liquid did not rise as rapidly as that described. The crude product was obtained in 73% yield, b.p. 45–75° (50 mm.), while distillation gave the pure product in 49% yield, b.p. 58–59° (50 mm.), n^{25}_{D} 1.4880, d^{25}_{4} 1.4887, R^{25}_{D} 38.33 (calcd. for $C_5H_{11}I$: R^{25}_{D} 37.95).

5-Neopentyltetraphenylcyclopentadien-5-ol (XI).—A solution of 39.6 g. (0.20 mole) of neopentyl iodide in 50 ml. of absolute ether was added under nitrogen at a rate of one drop per second to 6.1 g. (0.25 g. atom) of sublimed magnesium turnings in 75 ml. of absolute ether. The addition of 40 drops of the iodide solution, accompanied by heating, served to initiate the reaction, and gentle heat was applied throughout the addition to permit a slight reflux. After the addition, the solution was filtered through glass wool. Titration indicated that the solution was 0.54 *M* (34%).

Eighty-five milliliters (0.046 mole) of the above Grignard solution was added to a hot solution of 8.0 g. (0.021 mole) of VIII in 160 ml. of benzene; the addition of 41 ml. served to decolorize VIII. The yellow addition complex was hydrolyzed with an aqueous solution of ammonium chloride and ice with a change in color of the organic layer to brown. The ether–benzene layer was separated, combined with an ether washing of the aqueous layer, washed with water, dried over anhydrous magnesium sulfate, and subjected to distillation at reduced pressure at 40°. A dark yellow solid, m.p. 115–155°, remained. Recrystallization from cyclohexane gave 5.5 g. (0.012 mole, 57%) of XI, m.p. 170–174°.

The tertiary alcohol was recrystallized twice more from cyclohexane and once from acetonitrile, m.p. 175.5–176.5°.

Anal. Calcd. for $C_{34}H_{32}O$: C, 89.43; H, 7.07. Found: C, 89.54; H, 7.13.

5-Neopentyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (II).—A solution of 1.82 g. (4.0 mmoles) of XI in 100 ml. of glacial acetic acid was heated to boiling. The addition of 4.0 ml. of acetic anhydride and one drop of 85% phosphoric acid to the refluxing solution failed to effect any change, indicating that the alcohol did not dehydrate to the fulvene. Iodine was liberated as a side product when 1.0 ml. (8.0 mmoles) of 58% hydriodic acid in 1.2 ml. of glacial acetic acid was added dropwise, darkening the solution. After refluxing one minute longer, the solution was worked up, leaving a yellow oil which was chromatographed in benzene through alumina. A yellow band which fluoresced blue-white under ultraviolet light was eluted with benzene, leaving a green-fluorescing band at the top of the column. The benzene was distilled from the eluted band at reduced pressure and the yellow oil remaining was recrystallized from ethanol, cooling the solution to 0°. A yield of 0.7 g. (1.6 mmoles, 40%) of II was obtained, m.p. 117–129°.

Three recrystallizations from ethanol and one from toluene raised the melting point to 137.0–139.2°. It did not depress the melting point (137.0–139.0°) of the compound prepared in anisole from I, m.p. 137.0–139.0°.

Anal. Calcd. for $C_{34}H_{32}$: C, 92.68; H, 7.32. Found: C, 92.58; H, 7.27.

BROOKLYN 1, NEW YORK

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[13] F. C. Whitmore and D. E. Badertscher, THIS JOURNAL, **55**, 1161 (1933).

[14] F. C. Whitmore and J. M. Church, *ibid.*, **55**, 1121 (1933).

[15] S. R. Landauer and H. N. Ryder, *J. Chem. Soc.*, 2224 (1953).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

1,2,3,4-Tetraphenylfulvalene[1]

BY ERIC C. SCHREIBER[2] AND ERNEST I. BECKER[3]

RECEIVED JULY 9, 1954

1,2,3,4-Tetraphenylfulvalene (I) has been synthesized by the addition of cyclopentadienylmagnesium bromide to tetracyclone and dehydrating the so-formed alcohol (II). The red hydrocarbon was characterized by its method of synthesis, ultimate analysis, color, and exclusion of other possibilities. It forms a 1:1 adduct (IV) with maleic anhydride which is identical with that formed by dehydration of the maleic anhydride adduct (III) of II.

Fulvalene, a previously unknown cyclic system,[4] was predicted by Brown[5] in 1949 to be a stable, aromatic non-benzenoid hydrocarbon. Theoretical interest in this compound has been heightened by the fact that the valence bond method predicts chemical properties somewhat different from those anticipated by the molecular orbital method.[6,7] The first problem was to synthesize a representative fulvalene since none were known.

In the cyclopentadienone group of compounds, four phenyl groups must be attached to the ring before the cyclopentadienone will be completely stable as a monomer.[8,9] Further, tetracyclone has been found not to condense with a variety of active methyl and active methylene compounds,[10] whereas reactions with Grignard reagents have been known for some time.[11,12] With these considerations in mind the reaction between cyclopentadienylmagnesium bromide and tetracyclone was examined as a potentially feasible path to a fulvalene.[13]

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[1] This subject was the basis of a recent, brief Communication, THIS JOURNAL, **76**, 3354 (1954).

[2] From the thesis presented to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the degree of Master of Science in Chemistry, 1954.

[3] To whom inquiries should be sent.

[4] Fused ring fulvalenes such as bifluorenylidene are, of course, well known.

[5] R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949).

[6] R. D. Brown, *ibid.*, **46**, 146 (1950).

[7] R. D. Brown, *Nature*, **165**, 566 (1950).

[8] W. Dilthey and W. Schommer, *J. prakt. Chem.*, **136**, 293 (1933).

[9] C. F. H. Allen and J. A. VanAllan. THIS JOURNAL, **72**, 5165 (1950).

[10] D. Taber, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1953.

[11] K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1925).

[12] A. Löwenbein and G. Ulich, *Ber.*, **58**, 2662 (1925).

[13] E. D. Bergmann, G. Berthier, D. Ginsburg. Y. Hirshberg, D. Lavie. S. Pinchas, B. Pullman and A. Pullman (*Bull. soc. chim. France*, 661 (1951)) have reported that cyclopentadienyllithium gives no well-defined product.