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.

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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.

The addition of cyclopentadienylmagnesium bromide to tetracyclone in benzene gave 74% of an almost colorless product (II). Ultimate analysis and molecular weight were in support of a 1:1 adduct. That reaction had taken place at the carbonyl group was inferred from the infrared spectrum.[14] The absence of a band at 5.6–6.1 μ (C=O region) and the presence of a definite one at 2.83 μ (OH region) suggested that 1,2-addition had occurred. In the pertinent regions this infrared spectrum is quite comparable to that for pentaphenylcyclopentadienol and 5-methyltetraphenylcyclopentadien-5-ol.[15] Further, the ultraviolet spectrum in methanol is in excellent agreement with that reported for 5-methyltetraphenylcyclopentadien-5-ol.[15,16]

II readily adds one mole of maleic anhydride to give III, a 1:1 adduct. Although two diene systems are available—in the substituted and unsubstituted cycles—even an excess of maleic anhydride failed to effect a second addition. The infrared spectrum of III showed a strong bond at 2.9 μ when taken in a potassium bromide pellet (but not in chloroform), indicative of the hydroxyl group, and also exhibited bands at 5.40 and 5.62 μ characteristic of the anhydride group. The band at 5.40 μ is attenuated with respect to the latter suggesting hydrogen bonding and favoring IIIa for the structure. A lactone (IIIb),[20] which is conceivable for one of the possible structures of III, was ruled out inasmuch as a well-defined single band at 5.48–5.50 μ was absent. A general hypsochromic shift was noted in the ultraviolet as compared with that of II in agreement with the shortened conjugated chain of double bonds. These physical considerations were valuable in assigning a possible structure to III, since it did not undergo an interchange with either phosphorus (III) chloride in pyridine or with thionyl chloride and did not give an acetate with acetyl chloride in pyridine.

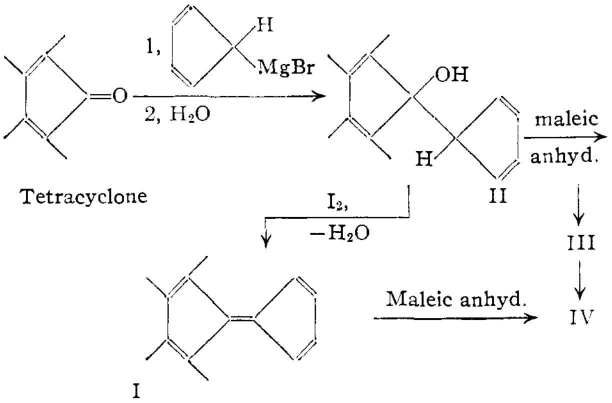
Dehydration of II was accomplished by refluxing it overnight in benzene with iodine.[21] Selection of this procedure was based on knowing that the reaction is a mild one and that the 5,6-double bond of fulvenes does not add iodine.

1,2,3,4-Tetraphenylfulvalene (I) obtained by the dehydration is a brilliant orange-red solid. No hydroxyl band appeared in the infrared region and ultimate analysis was in accord with the expected values.

I readily undergoes the Diels-Alder reaction to give a red compound IV. The red color indicates an intact arylated fulvene system and not an alkyl substituted fulvene system which would be only yellow. Thus, with both I and II the addition of maleic anhydride has taken place across the non-arylated ring. As compared with that for I, the ultraviolet absorption curve of IV is shifted hypsochromically, thus speaking for a shortened system of double bonds. No absorption is apparent in the OH region in the infrared spectrum.

When III is heated at 275° for ten minutes, water is almost quantitatively eliminated with the formation of IV. That IV was the product was evident from the identity of the infrared and ultraviolet spectra, ultimate analysis and no depression of the melting point in admixture with the previously prepared material.

CHART I



The unfavorable reaction of tetracyclone with cyclopentadienyllithium[18] prompted a test of the generality of the addition of lithium derivatives. At least with phenyllithium no particular difficulty was encountered in obtaining pentaphenylcyclopentadienol in 78% yield. Tetracyclone also adds *n*-propyl- and *n*-butyllithium.[22]

Experimental[23]

II.—A solution of 0.10 mole of methylmagnesium bromide in 100 ml. of ether was stirred rapidly while 6.6 g. (0.10

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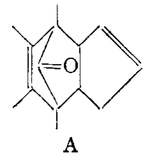
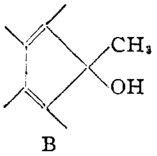
[14] For a possible 1,4-addition which had to be ruled out see C. F. H. Allen and J. A. VanAllan, THIS JOURNAL, **65**, 1384 (1943).

[15] N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, *ibid.*, **75**, 2283 (1953).

[16] Had either cyclopentadiene or methylmagnesium bromide remained in excess in the preparation of cyclopentadienylmagnesium bromide, then the products A[17] or B[18,19] would have formed, respectively. These were eliminated by mixture melting points with authentic samples and by comparison of their infrared spectra.



A



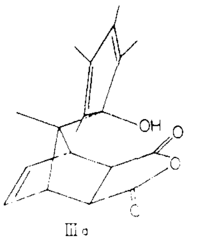
B

[17] O. Grummitt, R. S. Klopper and C. W. Blenkhorn, THIS JOURNAL, **64**, 602 (1942).

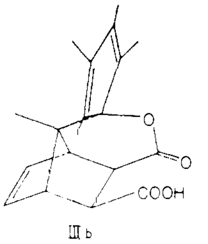
[18] W. Dilthey and P. Huchtemann, *J. prakt. Chem.*, **154**, 238 (1940).

[19] We thank Dr. D. Taber for a sample.

[20] Two possible structures for III are



III a



III b

[21] H. Hibbert, THIS JOURNAL, **37**, 1748 (1915).

[22] A. G. Bonagura, M. B. Meyers, S. J. Storfer and E. I. Becker, *ibid.*, **76**, 6122 (1954).

[23] The infrared and ultraviolet spectra referred to in this paper have been deposited as Document number 4327 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

mole) of cyclopentadiene was added at a rate sufficient to maintain a gentle reflux. After the addition was completed, the mixture was cooled to room temperature and 3.84 g. (0.010 mole) of tetracyclone dissolved in 100 ml. of benzene was added in one portion. Immediate discharge of the purple color took place. After stirring for an additional hour, 1:1 acetic acid–water was added to hydrolyze the mixture. Separation of the organic layer, washing it with water, drying it over anhydrous magnesium sulfate and then distilling the solvent gave 3.9 g. of pale yellow solid. Recrystallization from methanol (Darco G-60) afforded 3.3 g. (0.0073 mole, 74%) of almost colorless II, m.p. 197.6–198.6°. A second recrystallization did not raise the melting point.

Anal. Calcd. for $C_{34}H_{26}O$: C, 90.63; H, 5.82. Found: C, 90.43; H, 6.00.

III.—A solution of 0.45 g. (1.0 mmole) of II and 0.30 g. (3.0 mmoles) of freshly sublimed maleic anhydride in 20 ml. of bromobenzene was refluxed for one-half hour. After removing the solvent at reduced pressure and washing the residue with water and then methanol, the residue was recrystallized twice from nitromethane to give 0.28 g. (0.55 mmole, 55%) of colorless III, m.p. 251.0–252.5° dec.

Anal. Calcd. for $C_{38}H_{28}O_4$: C, 83.2; H, 5.1. Found: C, 82.9; H, 5.4.

I.—One-tenth gram (0.22 mmole) of II and 0.02 g. of iodine in 50 ml. of benzene was refluxed overnight. Distillation of the benzene at reduced pressure gave an olive residue which was washed with water, taken up in petroleum ether (b.p. 30–60°) and chromatographed on 3 g. of alumina. The eluate of the lowest band gave, on concentration, a brilliant, orange-red solid. Recrystallization from a mixture of petroleum ether, methanol and ether gave 0.028 g. (0.050 mmole, 27%) of orange-red, dendritic crystals, m.p. 201.0–202.1°.

Anal. Calcd. for $C_{34}H_{24}$: C, 94.41; H, 5.59. Found: C, 94.04, 94.43; H, 5.51, 5.81.

Pyrolysis of III to Give IV.—One-tenth gram (0.182 mmole) of III was heated at 275° for ten minutes. During this time nitrogen was swept through the reaction vessel and into a train consisting of silica gel, 5% palladium(II) chloride solution and saturated barium hydroxide. The silica gel gained 3.22 mg. (0.179 mmole, 98%) of water. No palladium was formed and no barium carbonate precipitated. The product was a dark red oil which crystallized on trituration with ether. Recrystallization from ethanol afforded 0.020 g. (0.038 mmole, 21%) of red IV, m.p. 177–181°.

Anal. Calcd. for $C_{38}H_{26}O_3$: C, 86.01; H, 4.94. Found: C, 85.93; H, 4.6.

IV from I.—One-tenth gram (0.23 mmole) of I was refluxed for 15 minutes with 0.3 g. (3 mmoles) of maleic anhydride in 15 ml. of toluene. The solvent was removed at reduced pressure, and the excess maleic anhydride was sublimed out of the product. Two recrystallizations from methanol gave 0.040 g. (0.075 mmole, 33%) of red adduct, m.p. 178–179°. A mixture melting point with the previous product melted at 178–181°.

Pentaphenylcyclopentadienol.—A solution of 3.84 g. (0.010 mole) of tetracyclone in 100 ml. of benzene was added to phenyllithium (from 7.8 g. (0.050 mole) of bromobenzene and 0.70 g. (0.10 atom) of lithium in 100 ml. of ether). The dark color of the tetracyclone was immediately discharged to give a clear yellow solution. After stirring for one hour, 100 ml. of 1:1 aqueous acetic acid was added. The organic layer was washed throughly with water, dried over anhydrous magnesium sulfate and distilled to give a brown oil. Trituration with methanol gave a solid which, upon recrystallization from methanol, afforded 3.6 g. (0.0078 mole, 78%) of pale yellow product, m.p. 176–177° (reported m.p. 175–176°[11]).

Ultraviolet Absorption Spectra.—The spectra were taken in methanol using a Cary spectrophotometer, model 11.

Acknowledgment.—The authors hereby express their appreciation to Charles Pfizer and Co., in whose laboratories this work was done, for their coöperation.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF WISCONSIN]

The Organic Acids of *Narcissus poeticus*[1]

BY R. R. SMEBY, V. ZBINOVSKY, R. H. BURRIS AND F. M. STRONG

RECEIVED JULY 1, 1954

Several closely related organic acids have been obtained in crystalline form from *Narcissus poeticus* bulbs. Because of changes occurring during recrystallization it is not certain whether the isolated acids are the same as those originally existing in the plant. The isolated acid which appears to be the native form apparently changes into a more stable compound on mild alkaline treatment. This acid has the molecular formula $C_{11}H_{12}O_7$, and appears to contain one phenolic hydroxyl, two alcoholic hydroxyl and two carboxyl groups.

Vickery, *et al.*,[2] found that about half of the organic acids of *Narcissus poeticus* appeared to be of unknown constitution. They speculated that the main component of the unidentified acids might be isocitric acid, and expressed the opinion that the unknown acids play "a large and important part in the general organic acid metabolism of this species of plant."[2]

In the present work, the acids from the bulbs of this species were separated by partition chromatography.[3] Two peaks were observed which could not be attributed to any of the common plant acids (Fig. 1, peaks 1 and 2). Two others (peaks 3 and 4, Fig. 1) are due to malic and citric acids, respectively. The peak 1 acid has been isolated

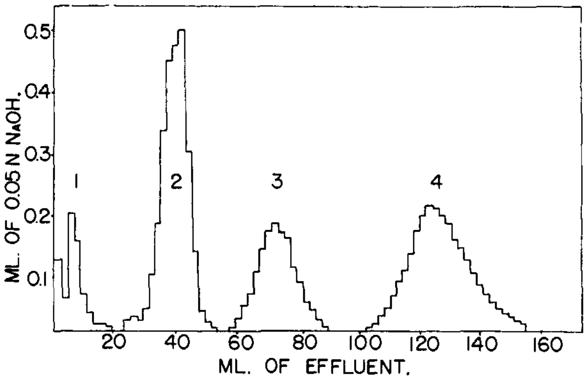

Fig. 1.—Chromatographic separation of organic acids from *Narcissus poeticus* bulbs.

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[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station. Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

[2] H. B. Vickery, G. W. Pucher, A. J. Wakeman and C. S. Leavenworth, *Bull. Conn. Agr. Exp. Sta.*, No. 496 (1946).

[3] F. A. Isherwood, *Biochem. J.*, **40**, 688 (1946).