m.p. 312–315° dec.; λ_{max}^{EtOH} 220, 255, 320 and 400 mμ (ε 24,500, 11,100, 17,400 and 13,500, resp.); ν_{max}^{KBr} 1675, 1640, 1615, 1555, 1500, 1450, 1420, 1380, 1365, 1330, 1285, 1245, 1220, 1180, 1145, 1125, 1085, 1065, 900, 765, 750 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{18}ON_3Br$: C, 58.07; H, 4.87; N, 11.29. Found: C, 58.25; H, 4.97; N, 11.22.

Dehydrogenation and Hydrolysis of the Condensation Product 17.—A solution of the condensation product (110 mg.) and tetrachloro-*o*-benzoquinone (460 mg.) in ethanol (10 ml.) was heated under reflux for 20 hr. and the solvent subsequently evaporated. Recrystallization of the residue from methanol–ethyl acetate yielded 85 mg. of a crystalline product which was heated under reflux for 1 day in methanol (5 ml.) and concentrated hydrochloric acid (4 ml.). The solution was concentrated and diluted with water to give 70 mg. of a crystalline hydrochloride salt which, after two recrystallizations from methanol–ethyl acetate, had m.p. 300–301° dec. pure and mixed with authentic flavocarpine hydrochloride (m.p. 301–302° dec.). (Conversion to flavocarpine seems to have occurred.) Its infrared spectrum was almost identical with that of authentic flavocarpine hydrochloride. The synthetic hydrochloride salt was converted to the acetate salt on a column of Rohm and Haas IR-4B anion exchange resin on the acetate cycle. Recrystallization of the crude product from glacial acetic acid gave a pure product, m.p. 306–307° pure, and mixed with authentic flavocarpine, m.p. 307–308°. The infrared spectra (in KBr) and the ultraviolet spectra (in 0.01 *N* hydrochloric acid in ethanol, in 0.01 *N* sodium hydroxide in ethanol and in ethanol) of the natural and synthetic products were identical.

7H-Pyrido-[2,3-c]-carbazole (8), $\lambda_{max}^{0.01\ N\ HCl-MeOH}$ 227, 252, 258, 303 and 391 mμ (ε 22,000, 30,500, 28,000, 20,000 and 8500); $\lambda_{max}^{0.01\ N\ NaOH-MeOH}$ 225, 245, 280 and 342 mμ (ε 27,000, 30,000, 32,000 and 9,000).

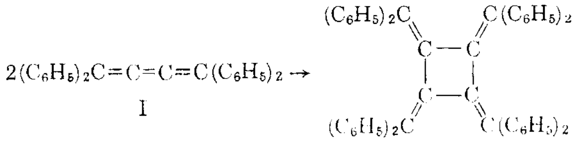
7H-Pyrido-[3,4-c]-carbazole (9), $\lambda_{max}^{0.01\ N\ HCl-MeOH}$ 232, 252, 295, 390 and 408 mμ (ε 21,000 33,000, 25,000, 8,000, 8,500); $\lambda_{max}^{0.01\ N\ NaOH-MeOH}$ 227, 238, 270, 283, 335, 362 and 375 mμ (ε 44,000, 38,000, 34,000, 23,000, 10,000, 9,000, 5,000).

COMMUNICATIONS TO THE EDITOR

THE PHOTODIMER OF TETRAPHENYLBUTATRIENE; DERIVATIVES OF TETRAMETHYLENECYCLOBUTANE

Sir:

Tetraphenylbutatriene (I) is dimerized[1] by solar irradiation in the solid state. It is now reported that the photodimer is tetrakis-(diphenylmethylene)-cyclobutane (II)[2] and thus is derived from center to center dimerization of I.



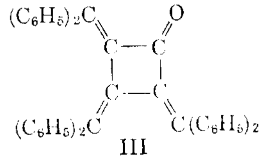
I

II

The structure of II[3] is based on physical evidence and the structural assignments made for its ozonolysis and derived products. Photodimer II is a stable derivative of tetramethylenecyclobutane[4]; because of its simple preparation and the structures of its oxidation products, it also serves as a source of tetramethylenecyclobutanoid derivatives.

Photodimer II[5] is obtained preparatively by sunlamp irradiation (4–5 days) of I.[6] Its infrared absorption is similar to that of I with the exception of new absorption at 13.9μ; absorptions for allenic, acetylenic, or polysubstituted phenyl groups are absent. Photodimer II exhibits n.m.r. absorption for its phenyl groups only at ~ 3.0τ.[7] The shielding in II apparently stems from interactions of the phenyl groups which are prevented sterically from being totally coplanar. Partial conjugation in II is indicated, however, by its extensive ultraviolet absorption: $\lambda_{(CHCl_3)}$ 274 (ε = 18,300), λ_{max} 307–308 (ε = 39,500).[8]

Photodimer II decomposes to I on melting; it does not form adducts with maleic anhydride or tetracyanoethylene. Ozonolysis of II in chloroform yields benzophenone and tris-(diphenylmethylene)-cyclobutanone (III).[9] The n.m.r. of the hydrogens (2.85 τ) in III indicates that there is less overlapping of the phenyl groups in III than in II.



III

Monoketone III does not form a semicarbazone or a 2,4-dinitrophenylhydrazone even under forcing conditions; reduction of III, how-

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[1] K. Brand, *Ber.*, **54**, 1947 (1921).

[2] From the Ph.D. dissertation of R. O. Uhler, The Ohio State University, 1960; R. O. Uhler and H. Shechter, 138th Meeting of American Chemical Society, New York, N. Y., Sept. 14, 1960, Abst. 70-P.

[3] The following head to head, head to tail, head to center, center to ends, and ends to ends photodimers (and their isomeric transannular derivatives) are discarded because they do not accommodate the experimental results: 1,2-bis-(diphenylvinylidene)-3,3,4,4-tetraphenylcyclobutane, 1,3-bis-(diphenylvinylidene)-2,2,4,4-tetraphenylcyclobutane, 1,2-bis-(diphenylmethylene)-3-diphenylvinylidene-4,4-diphenylcyclobutane, 4,5-bis-(diphenylmethylene)-3,3,6,6-tetraphenylcyclohexyne, and 3,3,4,4,7,7,8,8-octaphenyl-1,5-cycloöctadiyne.

[4] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952), predict that tetramethylenecyclobutane has considerable delocalization energy and exists in the singlet state.

[5] Yellow-green fluorescent crystals, m.p. (uncorr.) 290–293°, lit.[1] m.p. 280–281°; *anal.* calcd. for $C_{56}H_{40}$: C, 94.34; H, 5.66; mol. wt., 713. Found: C, 94.14; H, 5.47; mol. wt. (camphor), 695.

[6] J. Wolinski, *Roczniki Chem.*, **29**, 23 (1955).

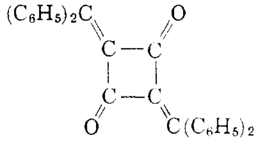
[7] The n.m.r. absorption for the phenyl groups in tetraphenylbutatriene and other non-shielded derivatives occurs at ~2.68 τ. Shielded phenyl absorption has been observed[7c] at ~3.0 τ for *cis*-1,2-diphenylcyclobutanes; absorption is normal in *trans*-1,2- and *cis*-1,3-diphenylcyclobutanes (W. J. Link, Ph.D. dissertation, The Ohio State University (1960)).

[8] (a) 1,1-Diphenylethylene[8b] and 1,2-bis-(diphenylmethylene)-cyclobutane[8c] absorb at 250 (11,000)[8b] and 351 mμ (21,400),[8c] respectively; (b) E. A. Braude, *Ann. Rep. Progr. Chem.*, **42**, 105 (1945); (c) K. B. Alberman and F. B. Kipping, *J. Chem. Soc.*, 779 (1951).

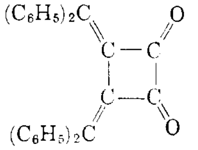
[9] Polymorphs: white plates, m.p. 171.5–172.0°; white needles, m.p. 184.0–185°; *anal.* calcd. for $C_{43}H_{30}O$: C, 91.78; H, 5.37. Found: C, 91.54; H, 5.57. >C=O stretching, 5.6μ; λ_{UV} and ϵ_{UV} (95% methanol); 279, 16,300; 287, 16,100; and 295, 14,500.

ever, by lithium aluminum hydride yielded tris-(diphenylmethylene)-cyclobutanol (IV).[10]

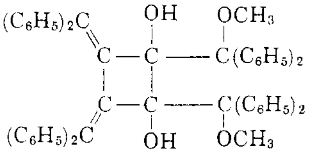
Diozonolysis of II in chloroform–methanol at −55° gave 2,4-bis-(diphenylmethylene)-1,3-cyclobutanedione (V, 10–12%), 3,4-bis-(diphenylmethylene)-1,2-cyclobutanedione (VI, 2%), benzophenone, and 3,4-bis-(diphenylmethylene) - 1,2 - bis - (methoxydiphenylmethyl) - 1,2 - cyclobutanediol (VII, 35%). The structure of V[11] is based on its analysis, the normal n.m.r. of its phenyl groups (2.68τ), its *unsplit* carbonyl absorption (5.73μ), its intense ultraviolet absorption, and its stability to semicarbazide, 2,4-dinitrophenylhydrazine, hydrogen peroxide, *o*-phenylenediamine, and heat. Reduction of V by lithium aluminum hydride gave 2,4-bis(diphenylmethylene)-1,3-cyclobutanediol (VIII, 43%).[12]



V



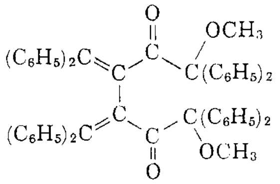
VI



VII

Vicinal diketone VI[13] is a yellow fluorescent solid which exhibits split carbonyl absorption (5.78 and 5.88 μ) as do related *cis*-α-diketones.[14] The instability of VI as compared to II is indicated by its reactivity with ethanol at 25–30° and its decomposition upon recrystallization from hexane or ethyl acetate. Additional study of VI has been limited by its unavailability.

Dimethoxydiol VII is the principal product (35%) of diozonolysis of II in methanol–chloroform; VII apparently is formed *via* epoxidation and methanolysis at two benzhydrylidene centers.[15a] The structure of VII is based on its analysis, methoxyl content and its oxidative-cleavage by lead tetraacetate to 3,4-bis-(diphenylmethylene)-1,6-dimethoxy-1,1,6,6-tetraphenyl-2,5-hexanedione (IX, 51%).[15b] The positions of the *vicinal* hydroxyl groups in VIII agree with the observation that benzophenone is not obtained from the oxidation. The structure assigned to X is consistent with its analysis, methoxyl content, and spectra.



IX

Synthesis of II[16,17] and photochemical reactions of other butatrienes are being studied.[17]

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[10] White crystals, m.p. 205–206°; *anal.* calcd. for $C_{43}H_{32}O$: C, 91.49; H, 5.68. Found: C, 91.54; H, 5.78.

[11] White crystals, m.p. 252.5–253°; *anal.* calcd. for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89. Found: C, 87.50; H, 4.76. Strong infrared absorption of V occurs at 13.9 μ (analogous to that in III; there was no absorption for ketene or allene groups); its ultraviolet absorption (cyclohexane) occurred at 224 (32,500), 256 (5,220), 308 (230), 324 (300) and 362 (280).

[12] White needles, m.p. 285.5–286.5°. *Anal.* Calcd. for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.50; H, 6.10; ultraviolet absorption (95% ethanol) at 201 (1330), 264 (1300) and 272 (870).

[13] M.p. 182–183°; *anal.* calcd. for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89. Found: C, 87.21; H, 5.19; ultraviolet absorption (cyclohexane) at 258 sh (11,000), 307 (5,540), 376 max. (7,300) and 392 sh (6,780).

[14] (a) Bicyclo[2.2.1]heptane-2,3-dione,[14b] 3,*n*-dibenzylidene-1,2-cycloalkanediones (*n* = ring size of 7 to 14),[14c] diphenylcyclobutadienoquinone[14d] and benzocyclobutadienoquinone[14e] are yellow and exhibit split carbonyl absorption whereas biacetyl shows only an unsplit sharp peak. (b) K. Alder, H. K. Schafer, H. Esser, H. Krieger and R. Reubke, *Ann.*, **593**, 23 (1955). (c) N. J. Leonard, J. C. Little and A. J. Kresge, *J. Am. Chem. Soc.*, **79**, 6436 (1957). (d) A. T. Blomquist and E. A. LaLancette, *ibid.*, **83**, 1387 (1961). (e) R. Pohl, private communication. (f) The carbonyl stretching frequencies in V and VI are at 5.73 and 5.78–5.88 μ, respectively, whereas that of diphenylcyclobutadienoquinone, benzocyclobutadienoquinone and related cyclobutenones occur at ~5.6 μ. One wonders if there are 1,3- and 2,4-transannular interactions in V and VI (and in II) giving them tetrahedronic character.

[15] (a) White crystals, m.p. 256–259°; *anal.* calcd. for $C_{54}H_{48}O_4$: C, 86.11; H, 5.98; CH_3O, 7.67. Found: C, 86.10; H, 6.01; CH_3O, 7.54. Ultraviolet absorption (cyclohexane): 245 sh (18,500), 265 sh (10,000). (b) White plates, m.p. 196–197°; *anal.* calcd. for $C_{58}H_{46}O_4$: C, 86.36; H, 5.78; CH_3O, 7.69. Found: C, 86.34; H, 5.93; CH_3O, 7.79; >C=O stretching, 5.84 μ; ultraviolet absorption (cyclohexane): 315 (1030).

[16] Private communication from Dr. G. W. Griffin, Yale University, New Haven, Conn.

CHEMISTRY DEPARTMENT R. O. UHLER
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO H. SHECHTER[17]
CENTRAL RESEARCH DEPARTMENT G. V. D. TIERS
MINNESOTA MINING AND MANUFACTURING CO.
ST. PAUL, MINN.

RECEIVED JULY 9, 1962

THE CHEMISTRY OF PHOTODIMERS OF MALEIC AND FUMARIC ACID DERIVATIVES. IV.[1] TETRAMETHYLENECYCLOBUTANE

Sir:

We wish to report the successful formation of tetramethylenecyclobutane (Ia) from a variety of precursors. This hydrocarbon has been predicted by the HMO treatment to possess substantial delocalization energy[2] and represents a possible precursor for substituted cyclobutadienes.[3] Only one previous description of a compound related to Ia, namely, octaphenyltetramethylenecyclobutane (Ib) is recorded. The latter compound was prepared by photodimerization of tetraphenylbutatriene.[4]

Pyrolysis of the amine oxide IIb (*cis*, *trans*, *cis*) at 250° (1 mm. nitrogen) affords Ia which was collected in hexane at −70°. The hexane solution of Ia then was distilled (< 0°, 0.02 mm.)[5] to remove polymers and incompletely pyrolyzed products such as IVa retaining polar amine oxide groups.

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[1] For the last two papers in this series see G. W. Griffin, R. B. Hager and D. F. Veber, *J. Am. Chem. Soc.*, **84**, 1008 (1962), and G. W. Griffin, J. E. Basinski and L. I. Peterson, *ibid.*, **84**, 1012 (1962).

[2] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *ibid.*, **74**, 4579 (1952).

[3] A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

[4] H. Shechter and R. O. Uhler, *Dissertation Abstr.*, **21**, 765 (1960)

[5] Prior to distillation this solution was washed with 0.5 *N* HCl to remove dimethylhydroxylamine formed during pyrolysis.