(+)-**2,3-Diphenyl-1-iodopropane** (XVII).—A mixture consisting of 7.4 g. (0.02 mole) of (+)-2,3-diphenyl-1-propyl tosylate, 16.5 g. (0.11 mole) of sodium iodide, and 200 ml. of anhydrous acetone was refluxed for 20 hr. with stirring. The precipitated sodium *p*-toluenesulfonate was removed from the cooled mixture by filtration, and the filtrate was evaporated to dryness *in vacuo*. The residual material was suspended in 100 ml. of water, and this mixture was extracted with three 100-ml. portions of ether. The combined ether solution was washed with two 100-ml. portions of water and dried over anhydrous magnesium sulfate. The crystalline product, after two recrystallizations from petroleum ether, melted at 54–55°; 6.35 g. (97%); $[\alpha]^{25}D$ +16.6° (*c* 3.9, ethanol).

Anal. Calcd. for $C_{15}H_{15}I$: C, 55.91; H, 4.69; I, 39.39. Found: C, 56.10; H, 4.72; I, 39.11.

(+)-**2,3-Diphenylpropane** (XVIII).—A mixture composed of 6.35 g. (0.02 mole) of (+)-2,3-diphenyl-1-iodopropane, 3.0 g. of sodium bicarbonate, and 150 ml. of absolute ethanol was hydrogenated at 25° over 5.0 g. of 5% palladium on carbon. Hydrogen absorption ceased after 10 hr. The catalyst was collected on a filter and the filtrate evaporated to dryness *in vacuo*. The residue was suspended in 100 ml. of water and extracted with two 100-ml. portions of ether. The combined ether solution was washed with 100 ml. of water and dried over anhydrous magnesium sulfate. The product distilled at 85° (0.30 mm.); $n^{25}D$ 1.5558; 2.60 g. (68%); $[\alpha]^{25}D$ +76.7° (*c* 2.3, chloroform).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.63; H, 8.29.

The infrared and n.m.r. spectra of this compound were identical with those of (±)-2,3-diphenylpropane [b.p. 119° (2 mm.); $n^{25}D$ 1.5570] prepared by the procedure of Tuot and Guyard.[24]

D-(−)-**1,2-Diphenylpropane**.—A reaction mixture containing 1.4 g. (0.0066 mole) of (−)-*threo*-1,2-diphenyl-1-propanol,[20] 30 g. of hydrogen pretreated W-2 Raney nickel catalyst as used in the preparation of XV, and 100 ml. of absolute ethanol was heated at reflux temperature for 8 hr. The catalyst was collected on a filter and the filtrate concentrated to dryness *in vacuo*. The residual oil in 50 ml. of ether was washed with 50 ml. of water and dried over anhydrous magnesium sulfate. The product distilled at 88° (0.5 mm.); $n^{25}D$ 1.5553; 1.15 g. (89%); $[\alpha]^{25}D$ −76.3° (*c* 2.2, chloroform).

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[24] M. Tuot and M. Guyard, *Bull. soc. chim. France*, 1087 (1947).

A Synthesis of Quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane (Quadricyclene) *via* Photochemical Decomposition of 6,7-Diazaquadricyclo[3.2.1.$1^{3,8}$.$0^{2,4}$]non-6-ene.

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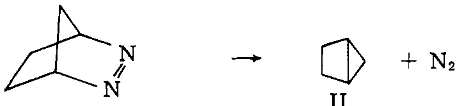
The product of homoconjugate Diels–Alder addition of ethyl azocarboxylate to norbornadiene has been converted by decarboxylation and oxidation to 6,7-diazaquadricyclo[3.2.1.$1^{3,8}$.$0^{2,4}$]non-6-ene (V).[1] The ultraviolet, infrared, and nuclear magnetic resonance spectra of this bridged polycyclic azo compound are discussed, and its thermal conversion to norbornadiene is described. Ultraviolet irradiation of V yielded quadricyclene (VI).[2]

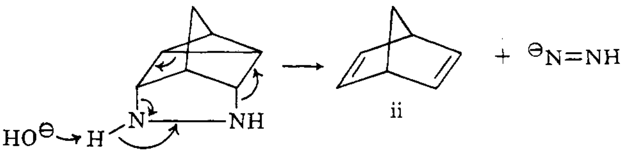
It is known that the thermolysis of cyclic azo compounds proceeds *via* loss of nitrogen with the formation of a diradical.[5] Subsequent reactions of the diradical include fragmentation,[6a] olefin formation,[6b] and intramolecular bond formation.[6c,7] Representative of the last reaction is Criegee's synthesis of bicyclo[2.1.0]pentane (II) from 2,3-diazabicyclo[2.2.1]hept-2-ene (I).[7]



I II

As part of a study aimed at assessing the usefulness of this reaction in the synthesis of other polycyclic fused ring systems, the synthesis of 6,7-diazaquadricyclo[3.2.1.$1^{3,8}$.$0^{2,4}$]non-6-ene (V) was undertaken, and its subsequent conversion to quadricyclene (VI) was investigated.

The starting point for synthesis of V was the formation of ethyl 6,7-diazaquadricyclo[3.2.1.$1^{3,8}$.$0^{2,4}$]nonane-6,7-dicarboxylate (III) from the homoconjugate Diels–Alder addition of ethyl azocarboxylate to norbornadiene. It was found in the present study, and also by Cristol, *et al.*,[8] that this reaction yields a 1:1 mixture of adducts III and IIIa which are separable by chromatography on alumina. Decarboxylation of III in methanolic potassium hydroxide gave a low yield (*ca.* 30%) of the corresponding hydrazine IV. Difficulties inherent in this decarboxylation step arose from the instability of the product as evidenced by the concomitant formation of nonnitrogenous hydrocarbons,[9] and from the unfavorable properties of hydrazine IV (it is water soluble, readily air oxidized, and is absorbed on the potassium carbonate formed as the decarboxylation proceeds). Compound IV was characterized as the crystalline N,N-diacetyl derivative IVa. Oxidation of IV was effected either by means of cupric chloride or, more conveniently, by mercuric oxide. With



i ii

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[1] For nomenclature, see S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958).

[2] The direct photochemical transformation of norbornadiene into quadricyclene has been reported by Dauben and Cargill[3] and also by Hammond, *et al.*[4]

[3] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

[4] G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

[5] S. G. Cohen and C. H. Wang, *ibid.*, **77**, 3628 (1955).

[6] (a) M. G. Kuzmin, Abstract, Ph.D. thesis, State University of Moscow, U.S.S.R., 1959; (b) S. G. Cohen, S. Hsiao, E. Saklad, and C. H. Wang, *J. Am. Chem. Soc.*, **79**, 4400 (1957); (c) S. G. Cohen, R. Zand, and C. Steel, *ibid.*, **83**, 2895 (1961).

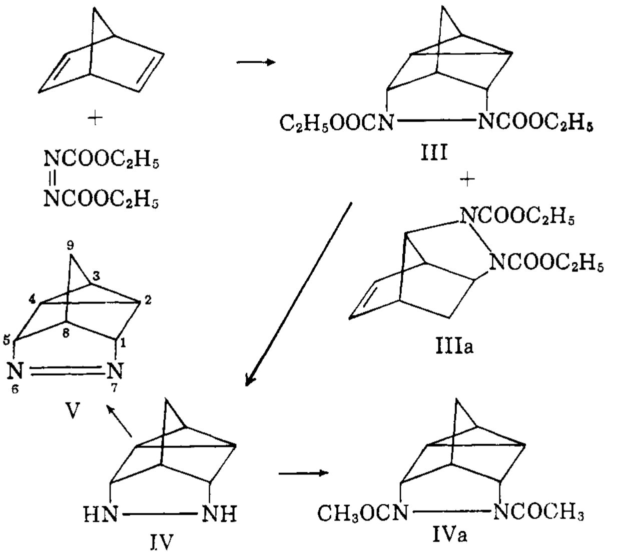
[7] R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).

[8] S. J. Cristol, E. L. Alfred, and D. L. Wetzel, *J. Org. Chem.*, **27**, 4058 (1962). The structures of III and IIIa are treated in this paper.

[9] The destruction of hydrazine IV in base may involve generation of the diimide anion and norbornadiene (i → ii).

cupric chloride, the cuprous complex of azo compound V was obtained. Purification of V by sublimation or recrystallization yielded material of m.p. 98–99°.

Structure of 6,7-diazaquadricyclo[3.1.1.1^{3,8}.0^{2,4}]non-6-ene (V) is based upon its composition, spectra, thermal conversion to norbornadiene, and photochemical conversion to quadricyclene (VII). The infrared spectrum (carbon tetrachloride) shows absorption bands of about equal intensity at 3.18 and 3.39 μ. A strong band occurs at 6.69 μ which is characteristic of the azo stretching vibration in cyclic azo structures.[10] No cisoid disubstituted olefinic absorption was observed at 13.80 μ.[11] The ultraviolet spectrum (n-hexane) shows sharp peaks at 3413 Å., ϵ 565; 3364 Å., ϵ 312; 3270 Å., ϵ 137; 3226 Å., ϵ 79. This pattern of position, intensity, and spacing is also characteristic of bridged cyclic azo compounds.[6c] A spacing of about 390 cm.$^{-1}$ between these peaks suggested the presence of a vibrationally related band in the far infrared near 25 μ. In agreement with this inference, absorption was noted at 27 μ (thallium(II) bromide, thallium(II) iodide cell).



Additional convincing evidence for the structure of V was provided by its n.m.r. spectrum.[14] Absence of vinylic resonance absorption and the presence of peaks at 4.77 τ (2H), quartet ($J \sim 1$ c.p.s.); 7.85 τ (1H), singlet; 8.13 τ (3H), multiplet; and 8.47 τ (2H), doublet ($J \sim 4$ c.p.s.) were observed. The assignments are given in Fig. 1. The bridgehead protons in 2.3 diazabicyclo[2.2.1]hept-2-ene (I) appear at 4.93 τ.[10] The corresponding assignment of 4.77 τ in V is due to extra deshielding by the cyclopropyl ring. The methine proton at 7.85 τ in V is not coupled with the adjacent methylene at C-9 due to unfavorable geometry.[15] The position of cyclopropyl protons resonance in nortricyclene derivatives is highly dependent upon deshielding effects arising from anisotropic groups within the molecule. The cyclopropyl absorption varies with 8.99 τ in nortricyclene to 7.48–7.82 τ in quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane dicarboxylic acid.[2] The assigned position of 8.47 τ to the C-2 and C-4 cyclopropyl protons is reasonable, since they are deshielded by the azo group relative to their positions in nortricyclene.

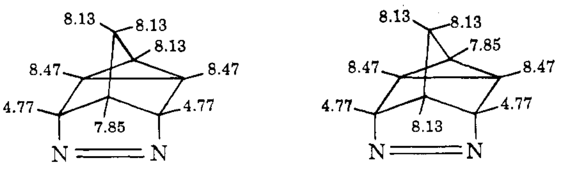
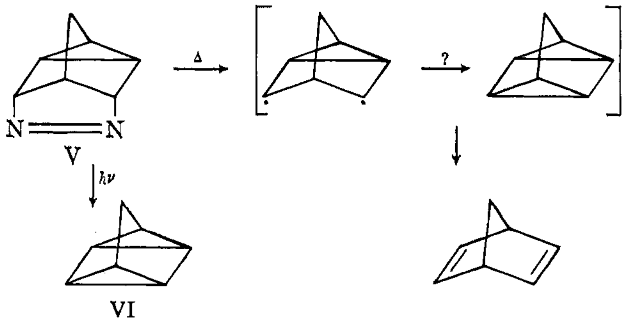


Fig. 1. Possible n.m r. assignments for 6,7-diazaquadricyclo-[3.2.1.1^{3,8}0^{2,4}]non-6-ene (τ-values).

The final confirmatory evidence for the structure of compound V was provided by its pyrolysis to norbornadiene, which was carried out by heating V at 140° for fourteen hours in a sealed tube in a nitrogen atmosphere. This result does not preclude the intermediate formation of quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (quadricyclene) (VI), since this compound rearranges to norbornadiene under these conditions.[3]



Irradiation of an ethereal solution of V with a Hanau Q-81 immersion lamp led to a loss of the azo ultraviolet absorption and an increase in the end absorption. A total yield of 35% of quadricyclene (VI) was obtained in this reaction. Its identity was proven by comparison with an authentic sample prepared by Dauben.[2] Vapor phase chromatographic analysis, infrared and nuclear resonance spectral examination formed the basis of comparison.

The possibility that the azo compound first forms norbornadiene, which then rearranges to quadricyclene, was ruled out by the fact that no conversion of norbornadiene to quadricyclene takes place under the reaction conditions employed.

It may be concluded that the above synthesis *via* Diels–Alder addition, decarboxylation, and oxidation (III → IV → V → VI) is not an economical route to quadricyclene compared to the direct synthesis from norbornadiene.[2] This work does illustrate, however, the possibility of synthesizing other strained polycyclic bridged hydrocarbons *via* a final step involving bond formation by photochemically induced loss of nitrogen from an azo compound.[16]

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[10] S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956.

[12] Cesium bromide optics were used.

[13] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[14] N.m.r. spectra were determined in 25% carbon tetrachloride solution with tetramethylsilane as internal standard.

[15] P. Yates and S. Danishefsky, *J. Am. Chem. Soc.*, **84**, 879 (1962); *cf.* H. Conroy in "Advances in Organic Chemistry," Vol. II, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York N. Y., 1960, p. 265.

[16] Cohen and Zand have reported the preparation of 2,3-diazabicyclo-[2.2.2]-2-octene, starting from the reaction of ethyl azocarboxylate and 1,3-cyclohexadiene, and its thermal decomposition to 1.5-hexadiene without formation of bicyclo[2.2.0]hexane;[10] B. Franzus and J. H. Surridge [*J. Org. Chem.*, **27**, 1951 (1962)] reported the formation of diethyl 2,5-cyclohexadien-1-yl bicarbamate from the initial reaction instead of the Diels–Alder adduct.

Experimental[17]

Norbornadiene was supplied by the Shell Development Company, Emeryville, California, and freshly distilled prior to use.

Ethyl Azocarboxylate was prepared according to the method of N. Rabjohn.[18]

Reaction of Norbornadiene with Ethyl Azodicarboxylate.—Ethyl azodicarboxylate (17.4 g., 0.1 mole), norbornadiene (10 g., 0.109 mole), and 0.05 g. of hydroquinone were heated at 130° in a sealed Pyrex tube for 12 hr. The resulting viscous product was dissolved in ether and washed first with a saturated solution of sodium sulfite and then with 5% sodium carbonate solution. The ether solution was dried with anhydrous magnesium sulfate and concentrated to dryness *in vacuo*. The crude product was distilled in a short path still, and 20 g. of clear viscous distillate was collected at a bath temperature of 120–130° and 0.001 mm. The presence of two components in about 1:1 ratio was indicated by v.p.c.[19] and n.m.r. Chromatography on 1000 g. of Merck neutral alumina gave IIIa, eluted with benzene–ether, 1:1, and III, eluted with chloroform–methanol, 1:1. The first fraction, IIIa, was purified by distillation and had b.p. 130–131° (0.4 mm.); the second fraction (III) had b.p. 125° (0.1 mm.). The infrared spectrum (neat) of III had a doublet carbonyl absorption at 5.70 and 5.80 μ, a pattern typical of N,N-bishydrazides.[21] The above properties are in agreement with those reported by Cristol, *et al.*,[8] for these two adducts.

Decarboxylation of III.—To a solution of 5 g. (0.019 mole) of III in 100 ml. of methanol was added 10 g. (0.18 mole) of potassium hydroxide. The reaction was kept at reflux under nitrogen for 5 hr., and precipitated potassium carbonate was separated by filtration. The potassium carbonate was dissolved in water and combined with the methanol solution and refluxed an additional 5 hr. under nitrogen. After removal of most of the methanol *in vacuo* the resulting deep brown aqueous part was extracted with cold chloroform. Concentration of the dried chloroform solution *in vacuo* yielded a brown oil (2.5 g.), presumably hydrazine IV.

Acetylation of a portion of IV with acetic anhydride in pyridine yielded the bisamide IVa, m.p. 138–139°; infrared (carbon tetrachloride), C=O at 5.88 and 5.95 μ (doublet).

Anal. Calcd. for $C_{11}H_{14}N_2O_2$: C, 64.44; H, 6.85. Found: C, 64.10; H, 6.71.

6,7-Diazaquadricyclo[3.2.1.1^{3,8}.0^{2,4}]non-6-ene (V).—A solution of 1 g. (0.008 mole) of IV in 50 ml. of distilled water and 0.81 g. (0.008 mole) of cupric chloride was stirred for 2 hr. at room temperature. The bright red cuprous complex of the azo compound (1.5 g.) was precipitated and collected. A suspension of this complex yielded the free azo compound upon treatment with excess sodium hydroxide. The azo compound was isolated by extraction with ether. Concentration of the dried ether extracts followed by short path distillation at a bath temperature of 95° (12 mm.) yielded a solid, which was then sublimed at 95° (10 mm.) yielding a sublimate, m.p. 95–97°. Recrystallization from pentane yielded 0.600 g. of material of m.p. 98–100°.

Anal. Calcd. for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.32. Found: C, 69.78; H, 6.71; N, 23.32.

Mercuric Oxide Method.—Excess freshly prepared mercuric oxide was added to a solution of 0.100 g. of IV in 8 ml. of dry ether. An exothermic reaction commenced immediately, and the reaction mixture was shaken at room temperature for 6 hr. After filtration, the ether solution was washed with water, dried, and concentrated *in vacuo*. The product, 0.070 g., was isolated by distillation as previously described and was identical with the material obtained by cupric chloride oxidation.

Thermal Decomposition of V.—A 0.50-g. sample of V was sealed under nitrogen in a Pyrex tube and heated at 140° for 14 hr. After cooling, infrared examination of the liquid product showed it to be essentially pure norbornadiene. Shorter reaction times, *i.e.*, 3 hr., led to incomplete decomposition and much unchanged azo compound.

Quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (Quadricyclene) (VI).—A solution of 0.50 g. of V in 100 ml. of dry ether in a Pyrex flask was externally irradiated under nitrogen at reflux temperature for 8.5 hr. with an uncooled Hanau Q81 immersion lamp. At the end of this period, the ether solution was concentrated to about 15 ml. at a bath temperature of 50°, and washed with a saturated solution of silver nitrate followed by washing with water. The solution was dried and distilled at a bath temperature of 50° to remove the ether. The resulting yellow oil was distilled in a micro distillation apparatus at 95° and the center cut of five fractions was taken for spectral examination. The infrared spectrum in carbon tetrachloride solution was essentially identical with that of an authentic sample of quadricyclene prepared by Dauben.[2] V.p.c. analysis showed one peak after the ether peak (DC silicone grease, 6-ft. column, 75°). Mixture with authentic quadricyclene yielded only one peak under these same chromatographic conditions.

Acknowledgment.—We wish to thank Professor Rolf Huisgen, Institute of Organic Chemistry, Munich, for suggesting this problem and also for his continued interest. We also wish to thank Professor W. G. Dauben, University of California, Berkeley, for supplying us with a sample of quadricyclene.

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(17) All melting points are uncorrected. Microanalyses were performed by George Robertson, Florham Park, N. J. Infrared curves were determined on a Perkin-Elmer Model 137 Infracord recording infrared spectrophotometer and on a Perkin-Elmer Model 21 using cesium bromide optics. Proton n.m.r. spectra were obtained using a Varian A-60 high-resolution spectrophotometer operating at 60.0 Mc. V.p.c. measurements were made on an F & M Model 500 gas chromatograph. Irradiations were carried out with a Hanau Immersion Model Q81 supplied by Quartzlampen Gesellschaft, Hanau, distributed by Ostwald Kerber, Harmon, N. Y.

(18) N. Rabjohn, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 375.

(19) Using a 10-ft. tricyanoethoxypropane[20] column (25% on Chromosorb).

(20) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943).

(21) This observation is based upon the infrared spectra of a number of compounds of this type both published and measured in the author's laboratory.