are given in Table I. The infrared spectra exhibited bands characteristic of a vinyl ether group (1150–1240 cm^{-1}) and of a trimethylene oxide ring (995, 980 cm^{-1}).[8] The separation of the two adducts formed from benzophenone and 2,4-dimethylfuran was achieved by washing the crude product with carbon tetrachloride: the1,4-dimethyl-6,6-diphenyl-2,7-dioxabicyclo[3.2.0]-Δ^3-heptene (III) remained on the filter and the other adduct dissolved in the carbon tetrachloride.

Nmr spectra were measured at approximately 30° with a Varian A-60 nmr spectrometer; tetramethylsilane was used as an external standard. The long distance coupling (J = 1.2 cps) between the C-5 and the 4-methyl group in 1,4-dimethyl-6,6-diphenyl-2,7-dioxabicyclo[3.2.0]-Δ^3-heptene (III) was determined by the usual decoupling techniques.

Registry No.—Benzophenone, 119-61-9.

[8] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, pp 117–119.

2,3-Dicyanoquadricyclane. Synthesis and Isomerization

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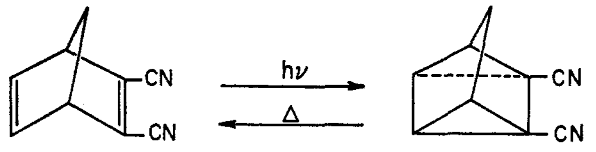
The first isomerization of a norbornadiene to a quadricyclane was that of norbornadiene-2,3-dicarboxylic acid.[1] Since then, the isomerizations of norbornadiene and a number of other substituted norbornadienes have been reported.[2] Although the reverse thermal reaction has frequently been observed, the only kinetic work in this area was done by Frey.[3] He studied the isomerization of quadricyclane to norbornadiene in the vapor phase and pointed out that the Arrhenius parameters he obtained were more closely related to those of the cyclobutene to diene[4] rearrangements than the cyclobutanes to two molecules of olefin rearrangements.[5] The only photosensitized isomerization reported is that of quadricyclane to norbornadiene.[6]

Analogous to norbornadiene-2,3-dicarboxylic acid,[1] we find that 2,3-dicyanonorbornadiene (2,3-dicyanobicyclo[2.2.1]hepta-2,5-diene)[7] (**1**) isomerizes cleanly to 1,5-dicyanotetracyclo$[3.2.0.0.^{2,7}0^{4,6}]$heptane[8] (2,3-dicyanoquadricyclane) (**2**) when irradiated in ether without a sensitizer.



1 2

In contrast to compound **1**, compound **2** is a stable white solid which can be stored at room temperature for at least 1 year. Its structure was verified by spectroscopic[9] and analytical data. The nmr spectrum consists of a multiplet with peaks at 147, 144, and 137 cps and an integrated intensity of 2 and a second multiplet with peaks at 165 and 159 cps and an integrated intensity of 1. The infrared spectrum exhibits cyclopropyl C–H stretching at 3070 and 3080 cm^{-1}, $-C{\equiv}N$ at 2220 cm^{-1}, and no HC=CH stretching. The ultraviolet spectrum shows only end absorption with a shoulder at 2070 A (ϵ 1140).

When attempts were made to react dicyanoquadricyclane with various dienophiles,[10] the observed product was **1**. This was true for electron-rich and electron-poor olefins and for acetylenes in polar and nonpolar solvents. Since the thermal isomerization of **2** to **1** appeared to go quite readily (80–100°) and could be followed by nmr, it seemed of interest to examine it more closely. The isomerization was studied at three temperatures and plots of ln (C_0/C) (C, concentration of quadricyclane as determined by integration of the nmr spectrum) *vs.* time gave straight lines from which the rate constants in Table I were calculated. An Arrhenius plot of these data gave a good straight line from which the activation energy (E_a = 33.8 kcal) and entropy ($\Delta S^{\ddagger}$ = +8.5 eu) were calculated. In order to compare these results with quadricyclane,[11] we determined E_a and $\Delta S^{\ddagger}$ for the isomerization of quadricyclane to norbornadiene in deuterioacetonitrile. The values obtained were E_a = 38.3 kcal and $\Delta S^{\ddagger}$ = +7.5 eu. We feel the decrease in activation energy in going from quadricyclane to 2,3-dicyanoquadricyclane and the positive $\Delta S^{\ddagger}$ values are more consistent with the known isomerizations of cyclobutanes to two molecules of olefin[5] than with the isomerizations of cyclobutenes to dienes.[4] However, any attempt to define a reaction mechanism on the basis of existing data seems premature. Additional work should be done with substituted quadricyclanes in various solvents and the vapor phase.

TABLE I

ISOMERIZATION OF DICYANOQUADRICYCLANE

	Temperature, °C		
	123	111	101
10^4k, sec^{-1}	3.8	0.97	0.30

The similarity in behavior of the thermal isomerization of 2,3-dicyanoquadricyclane to that of quadricyclane prompted an investigation of the possible photoisomerization of 2,3-dicyanoquadricyclane. Hammond, Wyatt, DeBoer, and Turro[6] report that benzophenone (T_1 = 68.5 kcal), 2-naphthaldehyde (T_1 = 59.5 kcal), and benzil (T_1 = 53.7 kcal) sensitize the isomerization of quadricyclane to norbornadiene. In substantiating this point, we find that pyrene (T_1 = 48.7 kcal) and anthracene (T_1 = 42.5 kcal) also work

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(1) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958).

(2) J. R. Edman, *ibid.*, **88**, 3454 (1966). See ref 1 for a partial listing of work in this area.

(3) H. M. Frey, *J. Chem. Soc.*, 365 (1964).

(4) (a) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958); (b) H. M. Frey, *Trans. Faraday Soc.*, **58**, 957 (1962).

(5) M. Zupan and W. D. Walters, *J. Am. Chem. Soc.*, **86**, 173 (1964), and references cited therein.

(6) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964).

(7) (a) A. T. Blomquist and A. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945); (b) we appreciate the generous gift by Dr. E. Ciganek of the 2,3-dicyanonorbornadiene used in this work.

(8) Named in accordance with IUPAC rules as suggested by J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).

(9) Nmr spectrum run in $CDCl_3$–TMSi on a Varian A-60 spectrometer. Infrared spectrum run in Nujol on Perkin-Elmer 237. Ultraviolet spectrum run in acetonitrile.

(10) C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966).

(11) Frey[3] obtained E_a = 33.5 kcal and $\Delta S^{\ddagger}$ = −2.6 eu (calculated from his data) for the vapor phase reaction.

very well while azulene is ineffective. The results of a run using filtered light (see Experimental Section) are summarized in Table II.

TABLE II

PHOTOISOMERIZATION OF QUADRICYCLANES

Compound[a]	Sensitizer	Result[b]
Quadricyclane[c]	Pyrene	3.7% conversion to norbornadiene
Quadricyclane	Anthracene	9.4% conversion to norbornadiene
2,3-Dicyanoquadricyclane	Pyrene	No detectable reaction
2,3-Dicyanoquadricyclane	Anthracene	No detectable reaction[d]
2,3-Dicyanonorbornadiene	Pyrene	Trace of **2**
2,3-Dicyanonorbornadiene	Anthracene	Trace of **2**

[a] Concentration = 50 mg/0.3 ml of CD_3CN. Degassed and sealed in nmr tubes. [b] Quadricyclane and norbornadiene concentrations determined by glpc. Concentrations of **1** and **2** determined by nmr. [c] Kindly supplied by Dr. C. D. Smith. [d] Excluding the dimerization of anthracene.

We conclude that under conditions where the sensitized isomerization of quadricyclane to norbornadiene takes place, there is no evidence for a similar sensitization of 2,3-dicyanoquadricyclane. We cannot rule out the possibility, however, that some sensitized isomerization does take place. The isomerization of **1** to **2** is always observed under all conditions tried and if the sensitized isomerization of **2** to **1** is extremely slow compared to the isomerization of **1** to **2**, then any **1** formed will be converted back to **2**. This could lead to an undetectable concentration of **1**.

Experimental Section[12]

2,3-Dicyanoquadricyclane.—2,3-Dicyanonorbornadiene[7] (500 mg) dissolved in 20 ml of oxygen-free ether was irradiated for 18 hr at 32° in a cylindrical photoreactor.[13] The solution was then filtered to remove a trace of insoluble residue, diluted with petroleum ether (bp 60°), and cooled in a Dry Ice chest. The resulting slurry was filtered to give 370 mg of analytically pure leaflets melting at 74–76°. One recrystallization from ether gave 2,3-dicyanoquadricyclane melting at 76.5–77°.

Anal. Calcd for $C_9H_6N_2$: C, 76.12; H, 4.20. Found: C 75.97; H, 4.37.

Kinetic Runs.—A 15% solution of 2,3-dicyanoquadricyclane in deuterioacetonitrile was sealed in thin-walled nmr tubes. The nmr spectra of the solutions were recorded and integrated on a Varian A-60 spectrometer. The tubes were then submerged in constant-temperature baths ($\pm 0.1°$), removed after a given time, and cooled with ice water. The nmr spectra were determined as soon as possible and the per cent of 2,3-dicyanoquadricyclane was calculated from the integration. The tubes were protected from light as much as possible and the total product area remained constant within experimental error as determined by comparison with the solvent peak in the deuterioacetonitrile.

Solutions of quadricyclane in deuterioacetonitrile (~15%) were sealed in melting point capillary tubes. The tubes were immersed in a constant-temperature bath and then withdrawn at various intervals, cooled, and analyzed by glpc (Dow 200 silicone oil on 60–80 Chromosorb W at room temperature). The per cent of quadricyclane was calculated from the peak areas.

Photoisomerizations.—Solutions were prepared for photolysis by placing 50 mg of the appropriate acceptor (see Table II), 5 mg of sensitizer, and 0.3 ml of deuterioacetonitrile in thin-walled, Pyrex nmr tubes. The tubes were degassed by three freeze–thaw cycles and then sealed. Three tubes, one containing 2,3-dicyanoquadricyclane, one 2,3-dicyanonorbornadiene, and one quadricyclane, were irradiated with a sensitizer for 18 hr with a 450-w Hanovia high-pressure lamp using a cupric sulfate pentahydrate solution (400 g/600 ml) and Corning 7-39 filter between the tubes and the light source. This combination of sensitizer, light source, and filters gave the smallest conversion of 2,3-dicyanonorbornadiene to 2,3-dicyanoquadricyclane of any tried, while still effecting the isomerization of quadricyclane to norbornadiene.

Registry No.—**2**, 13283-33-5.

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[12] Melting points are corrected and were taken on a Mel-Temp apparatus.

[13] Rayonet Srinivasan-Griffin photochemical reactor equipped with 16 F8T5 BLB bulbs.

Steroids. CCCV.[1] Synthesis of 11-Hydroxy-1-methyl-19-norretrotestosterone[2]

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With few exceptions,[3] most retro $(9\beta,10\alpha)$ steroids have so far been obtained by photochemical reactions.[4] In this note, the chemical synthesis is reported of a retro steroid presenting the *anti,cis,anti,trans* stereochemistry at the ring junctions. Reduction of the aromatic ring of estrone methyl ether with metals in amines, followed by subsequent mild acid treatment, is known[5] to afford 19-nortestosterone, with the "natural" $9\alpha,10\beta$ stereochemistry. However, examination of molecular models and conformational considerations suggested that an analogous reduction of ring A aromatic steroids with the 9β-H configuration should lead, after acid treatment, to 19-nor-Δ^4-3-keto steroids with the $9\beta,10\alpha$ (retro) stereochemistry.

Aromatization of prednisone acetate (I) by the method of Bailey, *et al.*,[6] afforded the $\Delta^{9(11)}$-aromatic

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[1] Part CCCIV: I. T. Harrison and S. Harrison, *Chem. Commun.*, No. 20, 752 (1966).

[2] A preliminary communication of this work has already appeared; see J. A. Edwards, P. Crabbé, and A. Bowers, *J. Am. Chem. Soc.*, **85**, 3313 (1963).

[3] (a) L. Velluz, G. Nominé, R. Bucourt, A. Pierdet, and J. Tessier, *Compt. Rend.*, **252**, 3903 (1961); L. Velluz, J. Valls, and G. Nominé, *Angew. Chem. Intern. Ed. Engl.*, **4**, 181 (1965); L. Velluz, J. Mathieu, and G. Nominé, *Tetrahedron Suppl.*, **8**, Part II, 495 (1966), and references therein; (b) J. A. Edwards, H. Carpio, and A. D. Cross, *Tetrahedron Letters*, 3299 (1964); (c) J. M. H. Graves, G. A. Hughes, T. Y. Jen, and H. Smith, *J. Chem. Soc.*, 5488 (1964).

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[6] E. J. Bailey, J. Elks, J. F. Oughton, and L. Stephenson, *J. Chem. Soc.*, 4535 (1961); see also, E. Caspi, P. K. Grover, and Y. Shimizu, *J. Am. Chem. Soc.*, **86**, 2463 (1964), and related papers.