of acetic anhydride was shaken under hydrogen (50 lb.) at room temperature for 6 hr.

The reaction mixture was filtered and the filtrate was distilled under diminished pressure. The residue was washed with water and recrystallized from dilute alcohol to yield 5.01 g. (80.6%) of the diamide XXXIX as white crystals: m.p. 226–227°; λ_{max}^{MeOH} 227 mμ (ε 37,900) and 313 mμ (ε 17,500); λ_{max}^{KBr} 3.06, 6.09, and 6.46 μ.

Anal. Calcd. for $C_{24}H_{28}ClN_3O_4$: C, 63.03; H, 6.16; N, 9.18. Found: C, 62.96; H, 6.16; N, 9.02.

1-Acetyl-2-(*p*-chlorophenyl)-5,6-dimethoxyindole-3-carbonitrile (XL).—A mixture of 5 g. (0.016 mole) of 2-(*p*-chlorophenyl)-5,6-dimethoxyindole-3-carbonitrile in 140 ml. of acetic anhydride was allowed to reflux for 5.5 hr., then stirred at room temperature for 19 hr. The reaction mixture was filtered, and the residue (the starting material and the desired product) was heated with benzene and filtered to separate the benzene-insoluble starting material. The filtrate, was cooled and 1.77 g. (31.2%) of 1-acetyl-2-(*p*-chlorophenyl)-5,6-dimethoxyindole-3-carbonitrile (XL) was obtained as tan plates: m.p. 266–267°; λ_{max}^{MeOH} 218 mμ (ε 10,800), 244 (10,800), and 327 (11,600); λ_{max}^{KBr} 4.42 (—C≡N), 5.83, and 6.22 μ.

Anal. Calcd. for $C_{19}H_{15}ClN_2O_3$: C, 64.32; H, 4.26; N, 7.89. Found: C, 64.43; H, 4.56; N, 7.89.

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Syntheses and Spectra of 7,7'-Bis(2,5-norbornadiene) and 7,7'-Bisquadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane[1,2]

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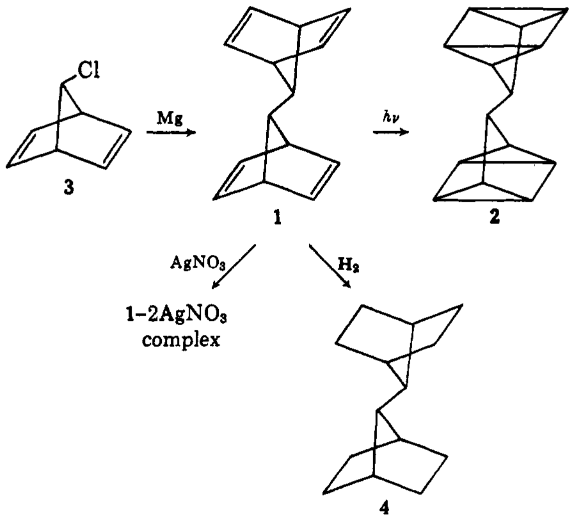
7,7'-Bis(2,5-norbornadiene) (1) and 7,7'-bisquadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane (2) were prepared. The detailed analysis of the first overtones of cyclopropyl CH stretching vibration in the near-infrared spectrum of 2 gave useful information on the structural investigations of cyclopropyl rings.

Whereas the chemistry of norbornadiene and its valence bond isomer, quadricyclene (quadricyclo-[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane),[3] has received considerable attention in recent years, that of their dimer appears to have not. During the course of study of the reactivity at the 7-position of norbornadiene system, we observed that treatment of 7-chloronorbornadiene with magnesium with the purpose of preparation of the Grignard reagent results in the instantaneous formation of the coupling product, 7,7'-bis(2,5-norbornadiene) (1). Preparation of 1 and its photochemical conversion to 7,7'-bisquadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane (2) are a part of this report. On the other hand, in connection with our other work,[6] we desired a powerful tool to demonstrate the presence of tertiary cyclopropyl hydrogens, in the case of which n.m.r. spectra can not usually provide good evidence, because the n.m.r. peaks of tertiary cyclopropyl hydrogens do not appear at high field characteristic of the cyclopropyl methylene protons.[7] It is known that the examination of near-infrared spectra provides a strong evidence for the presence of cyclopropyl hydrogens,[8–10] even in the case of a tertiary cyclopropyl hydrogen. In general, a cyclopropyl hydrogen is evidenced by the presence of carbon–hydrogen stretching vibration bands around 3000 cm.$^{-1}$ in the infrared region and by its first overtones in the near-infrared region. However, to our knowledge the detailed assignments and investigations of intensities of cyclopropyl hydrogens have not been reported so far. Since the compound 2 was purely isolable crystals[11] and thought to be a suitable model compound for the above kinds of investigations owing to the presence of abundant cyclopropyl hydrogens, we performed detailed analysis of the near-infrared spectrum of 2 and obtained useful information about the relative molecular extinction coefficients of aliphatic and cyclopropyl CH stretching vibrations,



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[1] Part IX of a series on Bicyclic Systems. Part VIII: H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965).

[2] Presented, in part, at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1964.

[3] Quadricyclene was obtained in 1961 with the photoisomerization of norbornadiene by the two independent groups of investigators.[4,5]

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

[5] G. S. Hammond, N. J. Turro, and A. Fisher, *J. Am. Chem. Soc.*, **83**, 4674 (1961); see also, G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964).

[6] Part VIII. In this work, we had a compound, 2-cyanotricyclo[4.1.0.$0^{3,7}$]heptane, in which the presence of a cyclopropyl ring was demonstrated by the analysis of the near-infrared spectrum.

[7] L. M. Jackmann, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 52.

[8] W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958).

[9] J. Meinwald, A. Lewis, and P. G. Gassman, *ibid.*, **84**, 977 (1962).

[10] P. G. Gassman, *Chem. Ind.* (London), 740 (1962).

[11] Since the highly strained ring system of quadricyclene is thermodynamically less favored than the ring system of norbornadiene, the facile thermal reversion of quadricyclene to norbornadiene is usually observed.[4,5] Thus due to the labile nature of the ring system and the oily nature, the isolation of a pure sample of quadricyclene and thereby a program in the area of quadricyclene chemistry were often accompanied by some technical difficulties.

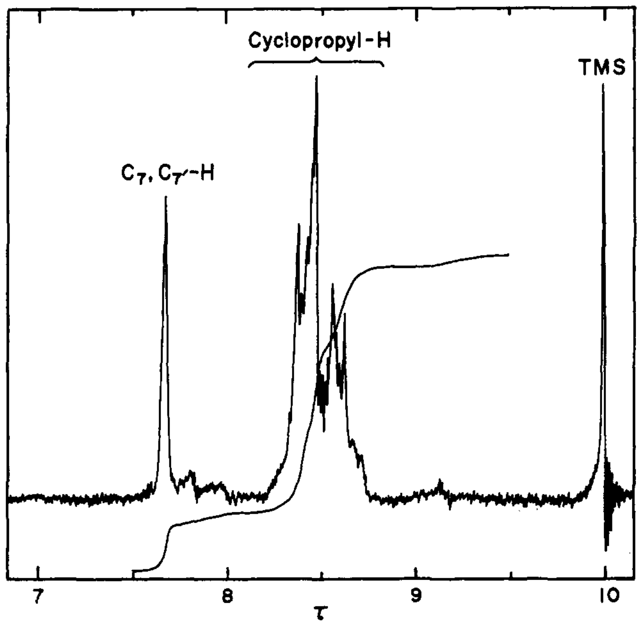

Figure 1.—N.m.r. spectrum of diquadricyclene **2** in deuteriochloroform solution.

which may make an important contribution to structural problems and hence are being reported here.

Preparations.—Carbonation and condensation of acetone with the transient Grignard reagent formed by treatment of 7-chloronorbornadiene (**3**) with magnesium and a small amount of methylmagnesium iodide in ether solution did not yield any expected products and, instead, the work-up procedure resulted in the formation of a dimeric product (**1**), $C_{14}H_{14}$, m.p. 63°. Analogously to that of norbornadiene, its infrared spectrum showed absorption bands at 3070 (olefinic hydrogen stretching), 2975 (saturated carbon–hydrogen), and 1647 cm.$^{-1}$ (olefinic carbon stretching), and also showed a very intense band at 732 cm.$^{-1}$ characteristic of a cisoid disubstituted olefin (see Experimental). The structure of **1** was also supported by the n.m.r. spectrum in deuteriochloroform, which showed two kinds of four each vinyl protons at τ 3.30 and 3.49 as triplets, the four bridgehead protons at τ 6.81 as a multiplet, and the two C-7 protons at τ 7.50 as a singlet. Formation of the 1:2 silver nitrate complex by treatment with 5 *N* silver nitrate solution and conversion into the saturated dimer, 7,7′-bisnorbornane (**4**), with the catalytic absorption of 4 moles of hydrogen were coincidental with the assigned structure of **4**.

When a pentane solution of **1** was irradiated for 12 hr. with a 500-w. high-pressure mercury lamp under cooling with chilled water, there was obtained in 36% yield a photoisomer (**2**), $C_{14}H_{14}$, m.p. 143.5–144°,[12] whose infrared spectrum possessed a band at 3048 (m) and 3072 cm.$^{-1}$ (s) characteristic of either olefinic or cyclopropyl hydrogens, and the intensity of the 3072-cm.$^{-1}$ band was twice that of the 2892-cm.$^{-1}$ band of the saturated carbon–hydrogen absorption. The olefinic carbon stretching at 1647 cm.$^{-1}$ and the cisoid disubstituted olefin band at 732 cm.$^{-1}$ were missing. The best evidence for the structure of **2** was offered by the n.m.r. spectrum. As shown in Figure 1, the spectrum in deuteriochloroform had the peaks at τ 7.67 (singlet) and 8.3–8.7 ($A_2B_2C_2$ system) clearly indicating the absence of any vinyl protons.[13]

The Near-Infrared Spectrum of 2.—The assignments and the determinations of molecular extinction coefficients of carbon–hydrogen stretching vibration bands in the 1–3-μ region were carried out as shown in Figure 2 and Table I. According to Fox and Martin,[14] the peak at 2892 cm.$^{-1}$ (ν_{III}) is attributed to an aliphatic tertiary CH stretching vibration band. The peaks at 3048 (ν_{II}) and 3072 cm.$^{-1}$ (ν_I) at significantly shorter wave length than the above are assigned to cyclopropyl CH stretching vibration. The strong peak at 6020 cm.$^{-1}$ ($2\nu_I$) is thought to be the first overtone of cyclopropyl CH stretching vibration and this assignment is rationalized as follows. The wave number of the *n*th overtone vibration can be calculated by

$$\nu^n = n\nu^1[1 - (n - 1)x] \qquad (1)$$

where ν^n is the *n*th overtone vibration in cm.$^{-1}$, ν^1 is the fundamental vibration in cm.$^{-1}$, and x is anharmonicity. When the values of 3072 and 6020 cm.$^{-1}$ are used for ν^1 and ν^2, respectively, x is obtained as 0.02. By using this x value, eq. 1 gives ν^3 as 8850 cm.$^{-1}$, the value of which is in good agreement with the experimental value of 8844 cm.$^{-1}$. Consequently, it was concluded that the assignments for ν_I, $2\nu_I$, and $3\nu_I$ were reasonable.

TABLE I

FUNDAMENTAL AND OVERTONE BANDS OF THE CH STRETCHING VIBRATIONS OF **2**[a]

Frequency, cm.$^{-1}$	Intensity, ϵ[b]	Assignment
2892	75	Aliphatic CH stretching (ν_{III})
3048	Shoulder	Cyclopropyl CH stretching (ν_{II})
3072	165	Cyclopropyl CH stretching (ν_I)
5635	0.16	1st overtone of ν_{III} ($2\nu_{III}$)
6020	4.4	1st overtone of ν_I ($2\nu_I$)
8850	0.24	2nd overtone of ν_I ($3\nu_I$)

[a] Taken in carbon tetrachloride. [b] ϵ = molecular extinction coefficient.

Examination of molecular extinction coefficients (Table I) indicated that the relative extinction coefficient ratios of the aliphatic and the cyclopropyl CH stretching vibration were 0.45 ($\epsilon\nu_{III}:\epsilon\nu_I$) at the fundamental vibration and 0.04 ($\epsilon 2\nu_{III}:\epsilon 2\nu_I$) at the first overtone. Accordingly, it turned out that the relative intensity of the cyclopropyl CH was much raised at the first overtone.[15] In most cases, even though a cyclopropyl hydrogen band is well separated from

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[12] The structure elucidation of other by-products formed as a complex oily mixture was not undertaken.

[13] Dauben and Cargill[4] reported that the n.m.r. spectrum of quadricyclene in carbon tetrachloride showed only two bands centered at τ 8.01 (triplet) and 8.59 (quintuplet), each of which were assigned to the two C-7 hydrogens and the six cyclopropyl hydrogens, respectively.

[14] J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), **A175**, 226 (1940).

[15] We observed that the spectrum of 3-N-carboethoxyaminotricyclene had the fundamental aliphatic CH stretching at 2866 cm.$^{-1}$ (ϵ 72), 2940 (139), and 2974 (94), and the first overtones of the first two bands at 5731 cm.$^{-1}$ (ϵ 0.42) and 5869 (0.42), respectively; and the fundamental cyclopropyl CH stretching at 3062 cm.$^{-1}$ (ϵ 32), and its first overtone at 6013 cm.$^{-1}$ (ϵ 0.95). We also observed that the spectrum of β-thujone had the fundamental aliphatic CH stretching at 2870 cm.$^{-1}$ (ϵ 111), 2928 (114), and 2958 (238), and the first overtone of the first band at 5914 cm.$^{-1}$ (ϵ 0.60); and the fundamental cyclopropyl CH stretching at 3026 cm.$^{-1}$ (ϵ 17.3) and 3056 (17.3), and the first overtone of the former band at 6068 cm.$^{-1}$ (ϵ 0.25). Accordingly, we obtained that, for 3-N-carboethoxyaminotricyclene, the relative extinction coefficient ratios were 4.34 at the fundamental CH stretching and 0.44 at the first overtone; for β-thujone, they were 13.76 at the fundamental and 2.40 at the first overtone. Therefore, we had the same relationship.

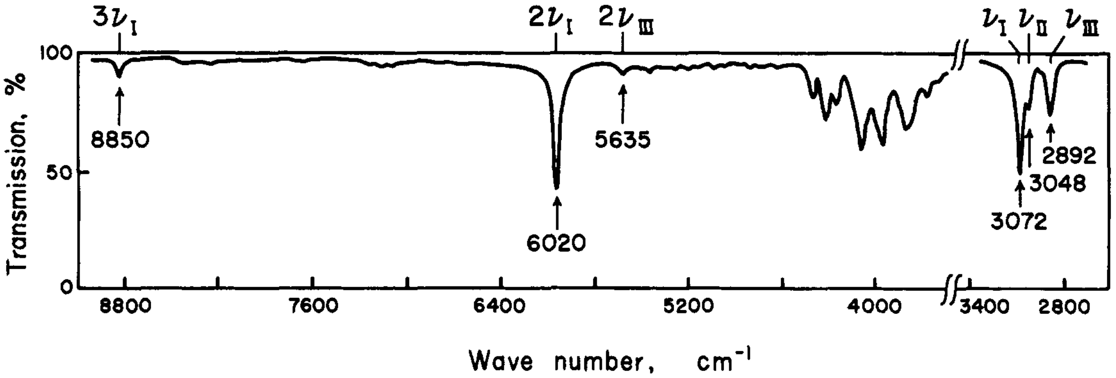

Figure 2.—Near-infrared spectrum of diquadricyclene 2 in carbon tetrachloride solution.

other kinds of bands in the near-infrared region, the measurement of a near-infrared spectrum requires a sample in amounts much greater than those used for the measurement of an infrared spectrum, because the absorptions in the near-infrared region are much weaker than those in the infrared region. Therefore, the above finding will decrease this weak point and, accordingly, in some cases near-infrared spectra will display a more important role for identification of cyclopropyl CH bands than infrared spectra do.

Experimental

Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Ultraviolet spectra were determined with a Beckman DK-2 spectrometer. Infrared spectra were recorded on a Nippon Bunko IR-S spectrometer in carbon tetrachloride and carbon disulfide. N.m.r. spectra were determined at 60 Mc. with a Varian A-60 spectrometer using tetramethylsilane as internal standard.

The near-infrared spectrum of 2 was measured in carbon tetrachloride solution with the following instruments: for around the 3-μ region, a Perkin-Elmer infrared spectrometer Model 12C using LiF prism; and for the 1–2.5-μ region, a Hitachi spectrometer Model EPS-2 using a photoconductive PbS cell as the receiving element.

7,7'-Bis(2,5-norbornadiene) (1).—To a mixture of a few drops of methyl iodide, 1 g. (0.04 g.-atom) of magnesium turnings, and 2 ml. of anhydrous ether there was added under nitrogen atmosphere a solution of 2.5 g. (0.02 mole) of 7-chloronorbornadiene[6,16] in 15 ml. of anhydrous ether at a rate which maintained gentle reflux. After the addition was completed, the mixture was refluxed for 2 hr., cooled, and poured into a cold ammonium chloride solution. The ether layer was separated and the aqueous phase was extracted with ether. The combined ether solution was dried over anhydrous sodium sulfate and filtered, and the ether was removed. Vacuum distillation of the residue gave 430 mg. (24% yield) of the crude 1 at the boiling point of 80° (8 mm.) which was immediately crystallized, m.p. *ca.* 50°. It was recrystallized from a mixed solvent of petroleum ether and ether to give the pure 1 as colorless prisms, m.p. 63°.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74; mol. wt., 182.3. Found: C, 92.51; H, 7.78; mol. wt., 190.0 (vapor phase osmometry, in cyclohexane).

The ultraviolet spectrum in *n*-heptane showed a maximum at 177 mμ (ϵ 14,400) and broad shoulders around 220 (3900) and 240 (390).[17] The infrared spectrum in CCl_4 and CS_2 showed absorption bands at 3070 (s), 2975 (s), 1647 (w), 1305 (s), 1221 (m), 1185 (m), 938 (m), 909 (m), 876 (m), 796 (m), and 732 (vs) cm.$^{-1}$.

The silver nitrate complex of 1 was prepared in quantitative yield by treatment of 1 with 5 *N* silver nitrate solution. Colorless prisms (from methanol) had dec. pt. >200°.

Anal. Calcd. for $C_{14}H_{14}\cdot 2AgNO_3$: C, 32.21; H, 2.70. Found: C, 32.18; H, 2.84.

The infrared spectrum in Nujol showed absorption bands at 1310 (s), 1185 (m), and 861 (m) cm.$^{-1}$. Treatment of this complex with concentrated ammonia solution recovered 1 in quantitative yield.

7,7'-Bisquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (2).—In a 100-ml. quartz flask, a solution of 0.5 g. of 1 in 45 ml. of *n*-pentane was irradiated for 12 hr. with a 500-w. high-pressure mercury lamp under cooling with chilled water around 0°. The solution was filtered to remove amorphous by-products and concentrated. Washing of the residual crystals with methanol gave 180 mg. (36% yield) of the crude 2, m.p. 135.5–138.5°. Recrystallization from carbon tetrachloride followed by sublimation gave pure colorless prisms of 2, m.p. 143.5–144°. All physical measurements were carried out with pure samples of 2.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74; mol. wt., 182.3. Found: C, 92.43; H, 7.76; mol. wt., 185 (vapor phase osmometry, in benzene).

The infrared spectrum in CCl_4 and CS_2 showed absorption bands at 3072 (s), 3048 (m), 1338 (w), 1240 (s), 1075 (m), 961 (m), 911 (m), 800 (s), and 772 (s) cm.$^{-1}$.

7,7'-Bisnorbornane (4).—Catalytic reduction of 1 was carried out over platinum oxide with the absorption of 4 moles of hydrogen. The usual work-up procedure gave colorless crystals, m.p. 118°, in quantitative yield. Crystals purified by sublimation showed the same melting point.[20]

Anal. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65; mol. wt., 190.3. Found: C, 88.69; H, 11.86; mol. wt., 199 (vapor phase osmometry, in benzene).

The infrared spectrum in CCl_4 showed absorption bands at 2970 (s), 2850 (s), 1480 (m), 1461 (m), 1311 (m), 1198 (w), 1169 (w) 1138 (w), and 873 (m) cm.$^{-1}$.

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(16) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

(17) For comparison, the ultraviolet spectrum of norbornadiene is presented. We observed $\lambda_{\max}^{n\text{-heptane}}$ 178 mμ (ϵ 8000) and 186 (7600) and the shoulders around 215 mμ (ϵ 2800, fine structure) and 235 (240).[18,19]

(18) C. F. Wilcox, S. Winstein, and W. G. McMillan [*J. Am. Chem. Soc.*, **82**, 5450 (1950)] observed $\lambda_{\max}^{\text{EtOH}}$ 205 mμ (ϵ 2100), 214 (1480), and 220 (870) and shoulder at 230 mμ (ϵ 200).

(19) R. B. Hermann [*J. Org. Chem.*, **27**, 441 (1962)] observed $\lambda_{\max}^{\text{vapor phase}}$ 188 and 211 mμ, the intensity of the former of which was 1.75 times of that of the latter.

(20) The compound, m.p. 107–109°, prepared by H. Kwart and L. Kaplam [*J. Am. Chem. Soc.*, **76**, 4072 (1954)] by treatment of 7-bromonorbornane with magnesium was assumed to be the same as our compound.