analysis now revealed that the reaction was 80% complete. After the product was resubmitted to the reaction conditions for a further 24 hr, the starting material Ib was not detectable by nmr. The product (3.02 g), which was very unstable and liberated iodine on standing or heating, had an nmr spectrum as follows: τ 8.77, 8.69 (3 H each, C-5 Me's), 7.77 (3 H, d, J = 1 Hz, C-3 Me), 7.75 (2 H, broad s, C-6 H's), 5.53 (1 H, d, J = 1 Hz, C-2 H), 4.13 (1 H, p, J = 1 Hz, C-4 H). Peaks for small amounts of contaminants could be observed in the upfield region in all preparations of IIe, but the compound could not be purified, so it was used immediately in subsequent reactions. In one run the reaction was allowed to proceed for 2 weeks, but a 40:60 ratio of IIe to Ib remained.

An 0.0413-g sample of IIe, when treated with excess $AgNO_3$, gave 0.0219 g of AgI (calcd 0.0224 g).

Reaction of Iodide IIe with NaOH.—To a stirred solution of 0.32 g of NaOH in 10 ml of H_2O was added 1.0 g of freshly prepared IIe. After 15 min at room temperature, the reaction mixture had become almost neutral. Analysis of the product by vpc and nmr revealed 70% 3,4,5-trimethylphenol (XI) and 25% diosphenol IIIc and small amounts of isophorone and unidentified substances. 2,3,5-Trimethylphenol (XII) was shown to be absent.

Reaction of Iodide IIe with AgOAc.—To a stirred solution of 2.51 g of AgOAc in 20 ml of glacial HOAc was added 2.0 g of freshly prepared IIe. The reaction mixture, protected from light and air, was stirred for 15 min at room temperature, then heated to 80° for 20 min. Filtration and ether extraction gave 0.80 g of material which was separated into base-soluble (0.40 g) and neutral (0.37 g) fractions. Gas chromatographic analysis revealed that the neutral layer contained 45% of the allylic acetate IId, 15% of isophorone, and 40% of an unidentified product. The base-soluble material was 3,4,5-trimethylphenol (70%) and diosphenol IIc (30%).

Registry No.—Ib, 16004-91-4; IId, 34638-12-5; IIe, 34638-13-6; IIIc, 34638-14-7; IV, 34638-15-8; V, 34638-16-9; VI, 34638-17-0; VII, 34638-18-1; VIII, 34638-19-2; IX, 34638-20-5; X, 34638-21-6; X diacetate, 34638-22-7.

Acknowledgment.—We wish to thank the Robert A. Welch Foundation for support of this work.

The Chemistry of the *trans*-Trimethylenenorbornene Ring System. I. A General Synthesis of 9,9-Disubstituted *trans*-5,6-Trimethylene-2-norbornene Derivatives[1a,b]

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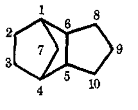
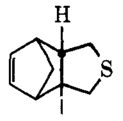
Condensation of *trans*-5,6-dimethylol-2-norbornene ditosylate and diethyl malonate with potassium *tert*-butoxide in *tert*-butyl alcohol afforded a mixture of cyclized products from which 9,9-dicarbo-*tert*-butoxy-*trans*-5,6-trimethylene-2-norbornene was readily separable. Saponification of the remaining ester mixture then gave the corresponding dicarboxylic acid. Attempts to prepare related *trans*-trimethylenenorbornenes by Dieckmann cyclization of *trans*-5,6-dicarbethoxymethyl-2-norbornene or the corresponding dimethyl ester and by Thorpe–Ziegler cyclization of *trans*-5,6-dicyanomethyl-2-norbornene were unsuccessful. Infrared and nmr spectra of the cyclized products were interpreted in terms of a high degree of internal strain associated with the *trans*-trimethylene bridge. It was concluded that unusually large distortions of the norbornyl cage occur in these compounds and that the norbornyl cage shows an unexpectedly high capability of accommodating strain.

The dicyclopentadienes[2,3] are known to exist in two distinct isomeric modifications (**1a** and **1b**) having either the endo,cis or exo,cis ring junction.[4] The possibility that similar derivatives containing a trans ring junction might also be prepared was first considered in 1932 but was rejected at that time on steric grounds.[4] A trans structure was later proposed[5] for a product obtained from the isomerization of tetrahydro-*endo*-dicyclopentadiene, but this was subsequently shown to be incorrect.[6] In 1965, however, Wilder and Feliu-Otero reported[7] the sulfide **2**, an heterocyclic derivative of dicyclopentadiene which incorporates a trans five-membered ring. Bachman[8] had previously suggested the *trans*-trimethylenenorbornane **3** as one of several products obtained from the decomposition of certain



1a, endo, cis
b, exo, cis



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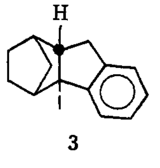

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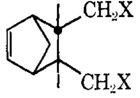

4, X = OTs
5, X = CN
6, X = COOH
7, X = $COOCH_3$
8, X = $COOC_2H_5$

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[1] (a) Grateful acknowledgment is made to the Petroleum Research Fund administered by the American Chemical Society for partial support of this work. (b) Presented in part at the 3rd Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, June 1971. (c) Taken in part from the M.A. Theses of M. N. E. and R. L. T., Bowling Green State University, Bowling Green, Ohio, 1970–1971.

[2] Of the several systems of nomenclature that have been applied to compounds in this series, the semitrivial *trans*-trimethylenenorbornene system based on that proposed by Schleyer and Donaldson[3] for the corresponding norbornanes will be used throughout the remainder of this report to emphasize the close structural relationship between these compounds and norbornene. The numbering is as in **1**.

[3] P. v. R. Schleyer and M. M. Donaldson, *J. Amer. Chem. Soc.*, **78**, 5702 (1956).

[4] K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **496**, 204 (1932).

[5] G. Egloff, G. Hulla, and V. I. Kormarewsky, "Isomerization of Pure Hydrocarbons," Reinhold, New York, N. Y., 1942, p 122, and references cited therein.

[6] P. v. R. Schleyer and M. M. Donaldson, *J. Amer. Chem. Soc.*, **82**, 4645 (1960).

[7] P. Wilder and L. Feliu-Otero, *J. Org. Chem.*, **30**, 2560 (1965).

[8] G. L. Bachman, Ph.D. Dissertation, Washington University, St. Louis, Mo., 1964.

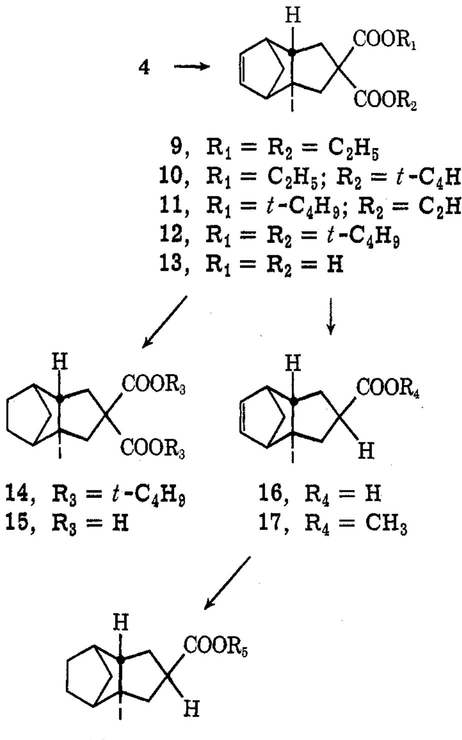
diazonorbornanes, but the structure of this product apparently was not established conclusively.

These results suggested that attachment of a *trans*-5,6-trimethylene bridge to a norbornyl cage was indeed feasible, in spite of the evident increase in strain that this would entail.[6] Although related trans-fused systems have been reported (see discussion below), ring closure to the *trans*-trimethylenenorbornene structure would seem to be especially difficult in view of the anticipated rigidity of the norbornyl cage. Such derivatives would, however, be of considerable interest for defining the limits of the ability of the norbornyl cage to accommodate strain and in studying the effects of strain on this interesting ring structure.

Results and Discussion

Three different approaches to the *trans*-trimethylenenorbornene ring system were investigated. The attempted Thorpe–Ziegler cyclization[9] of the dinitrile **5** and the Dieckmann condensation[9] of the diesters **6** and **7** were unsuccessful, the results in each case (see Experimental Section) indicating that intermolecular reaction remained competitive with intramolecular cyclization even at high dilution and that ring closure was quite slow, as expected. The direct condensation of the ditosylate **4** with diethyl malonate, however, afforded several cyclized products (**9–12**) having the trans ring junction (Scheme I). The most efficient procedure for effecting this conversion was the slow addition of 2 equiv of potassium *tert*-butoxide to a solution of both reactants in *tert*-butyl alcohol. Although a total reaction time of 1 week was required, the yield of cyclized material was surprisingly high and approached 70%. Because of the extended reaction time, partial ester exchange occurred. The major product of the reaction was the di-*tert*-butyl ester **12**, but the nmr spectrum of the crude product indicated that unexchanged and mixed products (**9–11**) were also present. The di-*tert*-butyl ester **12** was readily separable from the mixture by crystallization from ethanol. Separation of the remaining products was not attempted, and the ester mixture was saponified to the common diacid **13**.

Scheme I



9, $R_1 = R_2 = C_2H_5$
10, $R_1 = C_2H_5$; $R_2 = t\text{-}C_4H_9$
11, $R_1 = t\text{-}C_4H_9$; $R_2 = C_2H_5$
12, $R_1 = R_2 = t\text{-}C_4H_9$
13, $R_1 = R_2 = H$

14, $R_3 = t\text{-}C_4H_9$
15, $R_3 = H$

16, $R_4 = H$
17, $R_4 = CH_3$

18, $R_5 = H$
19, $R_5 = CH_3$

The above structural assignments are based on both chemical and spectroscopic evidence. As expected for a substituted malonic acid, the diacid **13** smoothly decarboxylated at elevated temperatures[10] to afford a mixture of isomeric monoacids **16**. The same products were also obtained by decarbalkoxylating the di-*tert*-butyl ester **12** with lithium iodide in collidine[11] and saponifying the intermediate monoesters. Esterification of the acids **16** in methanol then yielded the methyl esters **17**. That this product was a mixture was clearly evident from its nmr spectrum, which contained two methoxyl singlets at 3.77 and 3.65 ppm.

Catalytic hydrogenation of **12**, **13**, or **16** proceeded readily at atmospheric pressure and room temperature with the absorption of 1 equiv of hydrogen to yield the corresponding derivatives of the *trans*-trimethylenenorbornane system (**14**, **15**, and **18**). Esterification of **18** in methanol then yielded the saturated monoester **19**.

In addition to correct elemental analyses for all cyclized products isolated, the neutralization equivalents[12] of the diacid **13** and the monoacid **14** were in satisfactory agreement with those calculated from the indicated formulae. The possibility that a dimeric product has been formed *via* intermolecular condensation was considered unlikely and was excluded by cryoscopic estimation of the molecular weight[12] of the di-*tert*-butyl ester **12**. The value obtained (see Experimental Section) was consistent only with a monomeric product.[13]

Another possibility considered was that of rearrangement during cyclization to afford the isomeric endo,cis or exo,cis products.[10] These structures were, however, clearly excluded by the nmr spectra of the isolated materials. All showed absorptions arising from distinctly nonequivalent vinyl hydrogens, an observation inconsistent with symmetrical structures of the type **1**.

Some insight into the nature of strain effects in the *trans*-trimethylenenorbornene system may be gained by comparison with related systems. Meinwald and coworkers have shown[14] that *trans*-1,2-dibromomethylcyclobutane (**20**) condenses with diethyl malonate to yield derivatives of the strained *trans*-bicyclo[3.2.0]heptane system (**21**) in good yield. However, the

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[9] Both of these procedures have successfully been used in this laboratory for the preparation of the corresponding endo,cis derivatives: (a) R. A. Bell, M. A. Thesis, Bowling Green State University, Bowling Green, Ohio, 1970; (b) Y. K. Chan, M.A. Thesis, Bowling Green State University, Bowling Green, Ohio, 1971.

[10] C. F. Culberson and P. Wilder, *J. Org. Chem.*, **26**, 4289 (1961).

[11] F. Elsinger, *Org. Syn.*, **45**, 7 (1965).

[12] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd ed, Interscience, New York, N. Y., 1958.

[13] This determination has been subsequently confirmed by mass spectrometric measurement. The authors are indebted to Ms. W. V. Jones and the Department of Chemistry, Iowa State University, for this analysis.

[14] (a) J. Meinwald, J. J. Turariello, and J. J. Hurst, *J. Org. Chem.*, **29**, 2914 (1964); (b) J. Meinwald, P. Anderson, and J. J. Tufariello, *J. Amer. Chem. Soc.*, **88**, 1301 (1966).

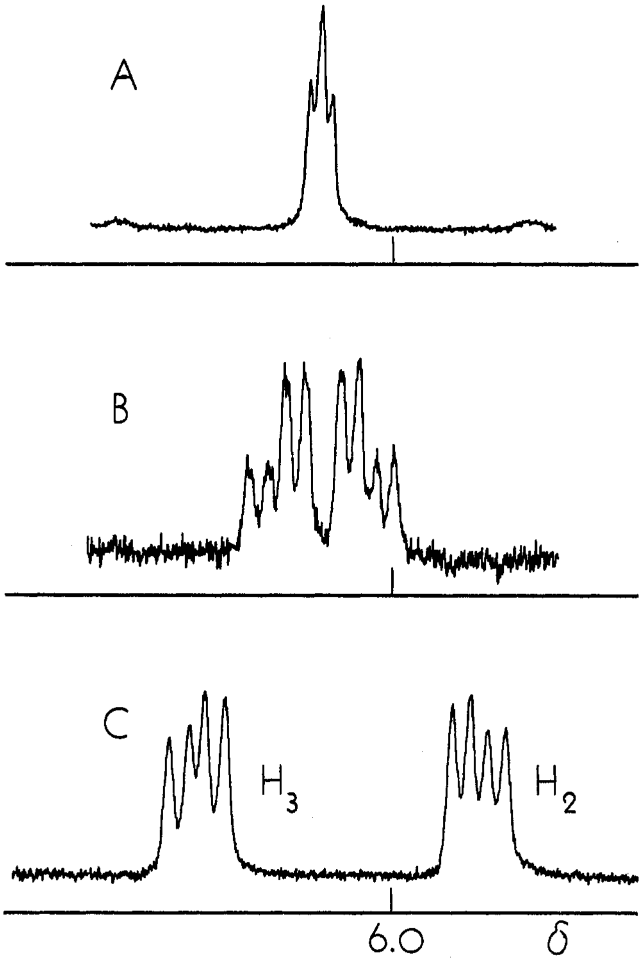
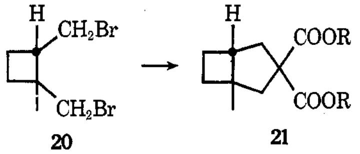


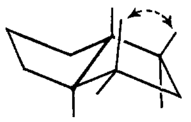
Figure 1.—60-MHz nmr spectra of the vinyl hydrogen region of (a) *endo,cis*-5,6-dicarbethoxymethyl-2-norbornene in $CDCl_3$; (b) **8** in $CDCl_3$; (c) **17**, neat.

puckering of the cyclobutane ring[15] in **20** permits a significant reduction of the dihedral angle between the two groups that must be joined, thus facilitating an otherwise very difficult ring closure. An equal reduction of the dihedral angle in the ditosylate **4** would not be anticipated (see below), and, in fact, cyclization appears to take place less readily than in the case of **20**.



20 **21**

The *trans*-trimethylenenorbornenes may also be viewed as derivatives of the *trans*-bicyclo[3.3.0]octane (*trans*-pentalane) system (**22**) in which positions 2 and 4 are joined by an ethynyl bridge. The *trans*-pentalane system is reported[16] to be about 6 kcal/mol less stable than the cis. This value may, however, be taken as a lower limit for the difference in strain between the *trans*-trimethylenenorbornenes and their cis counterparts (**1**), because the ethynyl bridge in the former requires a considerable twisting of the *trans*-pentalane moiety (**23**) that is not present in the parent trans system **22**.[17] It may thus be concluded that significant strain is introduced into the molecule on cyclization of **4**.



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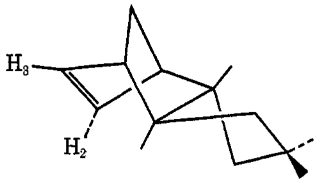

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In contrast to this conclusion, neither the olefin stretching frequencies nor the vinyl coupling constants (J_{23}) of the cyclized products obtained in the present study showed evidence[18-20] of an increase in internal strain, the values observed (see Experimental Section) being essentially identical with those reported[18,21] for norbornene itself.[22] It therefore appeared that the strain associated with the *trans*-trimethylene bridge was not effectively transmitted through the norbornyl cage to the 2,3 double bond.

However, a large increase in the separation of the vinyl hydrogen resonances was found in the nmr spectra of these compounds compared to that observed for related disubstituted norbornenes (see Figure 1).[23] That this shift was not the result of substituent effects was evident from the fact that these signals were found at exactly the same positions regardless of the nature of the substituents at position nine. It was therefore concluded that the effect was a characteristic of the ring structure itself.

Wiberg and Nist[19] have observed large downfield shifts of vinyl hydrogen absorptions with increasing bond angle compression in cyclic olefins. In the present system attachment of the *trans*-trimethylene bridge causes a severe twisting of the norbornyl portion of the molecule (**23**). As a result, the $C_2{=}C_3{-}C_4$ bond angle is slightly compressed and the $C_1{-}C_2{=}C_3$ angle is slightly expanded.[24] In norbornene the corresponding angles are equal and are compressed to about 109°.[25,26] Further compression of the $C_2{=}C_3{-}C_4$ angle by the *trans*-trimethylene bridge would then produce the observed downfield shift of the H_3 resonance, while expansion of the $C_1{-}C_2{=}C_3$ angle would produce the shift of the H_2 resonance in the opposite direction. Since these bond angle deformations are mutually compensating, the overall strain applied to the double bond is essentially unchanged, a conclusion consistent

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[15] J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3884 (1965).

[16] J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).

[17] An additional factor involved here is that the *endo*-dicyclopentadienes are approximately 3 kcal/mol less stable than the exo isomers (see ref 6 and references cited therein).

[18] (a) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958); (b) R. C. Lord and R. W. Walker, *ibid.*, **76**, 2518 (1954).

[19] K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

[20] (a) O. L. Chapman, *ibid.*, **85**, 2014 (1963); (b) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); (c) P. Laszlo and P. v. R. Schleyer, *ibid.*, **85**, 2017 (1963).

[21] P. Laszlo and P. v. R. Schleyer, *ibid.*, **86**, 1171 (1964).

[22] For norbornene these values are as follows: ν_{C-C} 1568 cm^{-1} (ref 18); J_{23} = 5.80 Hz (ref 20).

[23] The sulfide **2** exhibited similar shifts of the vinyl hydrogen absorptions. The authors are indebted to Mr. D. M. Jacobson for preparing[7] a sample of this compound and obtaining its nmr spectrum.

[24] The remaining bond angles of the norbornyl cage are distorted accordingly.

[25] W. G. Woods, R. Carboni, and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 5653 (1956).

[26] The bond angles of **8** and *endo,cis*-5,6-dicarbethoxymethyl-2-norbornene are assumed to be the same as those of norbornene (see ref 28).

with the infrared and coupling constant data presented above.[27]

Similar twisted conformations resulting from nonbonded repulsions have been observed in certain substituted norbornanes.[28] In at least one case a torsional angle about the 2,3 bond as large as 9° was observed in a trans 2,3-disubstituted derivative. Such deformations were not found in substituted norbornenes, and, indeed, they would be less likely because of the restricted rotation about the double bond.[29] Nonetheless, the cylization of the ditosylate **4** and the stability of the products thus formed[30] reveal a surprising capacity on the part of the norbornene ring system to minimize internal strain. It is evident that the geometric requirements of the *trans*-trimethylene bridge in the compounds reported here are satisfied only by a considerable distortion of the norbornenyl cage even at relatively remote positions in the molecule. Because of their greater flexibility, the corresponding saturated compounds would be expected to show even greater deviations from normal geometry. We are currently attempting to define more precisely the limits of the conformational mobility of the norbornene and norbornane ring systems.

Experimental Section

General.—Infrared spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer equipped with a Varian Model V-6058A spin decoupler and a Varian Model V-6057 variable temperature accessory. Chemical shifts (δ) are reported downfield relative to tetramethylsilane as internal reference in the indicated solvents. Coupling constants (J) are reported in hertz. All melting points and boiling points are uncorrected. Microanalyses are by M-H-W Laboratories, Garden City, Mich.

***trans*-5,6-Dicyanomethyl-2-norbornene** (**5**).—An adaptation of the method of Smiley and Arnold[31] was used for the preparation of this compound. A slurry of 10.8 g (0.22 mol) of sodium cyanide in 100 ml of dimethyl sulfoxide was heated over steam, and a solution of 25.0 g (0.054 mol) of the *trans*-ditosylate **4**[32] in 200 ml of dimethyl sulfoxide was added over 15 min. The resulting mixture was then heated over steam for 19 hr, cooled, and diluted with 50 ml of saturated brine and 50 ml of water. The aqueous mixture was extracted with chloroform, and the combined organic extracts were washed five times with water, dried ($MgSO_4$), and concentrated to afford 10.4 g (110%) of a yellow liquid. This material was fractionated at reduced pressure, and after a forerun of dimethyl sulfoxide the trans dinitrile **5** was collected as a colorless oil (8.6 g, 92%) which crystallized slowly on cooling: bp 126–130° (0.3 mm); mp 37.5–38.5°; ir (neat) 2240 (CN), 1590 cm^{-1} (C=C); nmr ($CDCl_3$) δ 6.37 (d, d, 1, J = 6 and 3 Hz, HC=C), 6.15 (d, d, 1, J = 6 and 3 Hz, C=CH).

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.73; H, 7.07; N, 16.41.

***trans*-5,6-Dicarboxymethyl-2-norbornene** (**6**).—A mixture of 41.0 g (0.20 mol) of the trans dinitrile **5** and 55 g of potassium hydroxide in 125 ml of water was refluxed until the evolution of ammonia ceased (*ca.* 45 hr). The solution was then cooled and extracted with ether (no residue on concentration). The aqueous phase was acidified with concentrated hydrochloric acid, and the resulting white solid precipitate was extracted into ether. The combined ether extracts were washed with saturated brine, dried ($MgSO_4$), and concentrated to yield 33.0 g (80%) of the crude acid **6**, which was recrystallized from ethyl acetate to afford 27.3 g (62%) of the pure product as white needles: mp 155–160°; ir (Nujol) 3350–2500 (OH), 1720 cm^{-1} (C=O); nmr (acetone-d_6) δ 5.67 (d, d, 1, J = 6 and 3 Hz, HC=C), 5.48 (d, d, 1, J = 6 and 3 Hz, C=CH), 5.25 (s, 2, COOH).

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.68; H, 6.61.

***trans*-5,6-Dicarbethoxymethyl-2-norbornene** (**8**).—A solution of 27.3 g (0.13 mol) of the trans diacid **6** and 1.0 g of *p*-toluenesulfonic acid in 950 ml of ethanol was refluxed for 20 hr. Sodium acetate (1.0 g) was added, and the bulk of the solvent was removed by distillation at reduced pressure. The residue was taken up in ether and was washed with water, saturated sodium bicarbonate, and saturated brine. The resulting ether solution was dried ($MgSO_4$) and concentrated to afford the crude diethyl ester **8** as a yellow oil. This material was fractionated at reduced pressure, and after a small forerun the pure product was collected as a colorless oil (29.5 g, 85%): bp 120–128° (0.6 mm); ir (neat) 1750 (C=O), 1590 cm^{-1} (C=C); nmr ($CDCl_3$) δ 6.27 (d, d, 1, J = 6 and 3 Hz, HC=C), 6.08 (d, d, 1, J = 6 and 3 Hz, C=CH), 4.32 (q, 2, J = 7 Hz, OCH_2CH_3), 4.30 (q, 2, J = 7 Hz, OCH_2CH_3), 1.25 (t, 6, J = 7 Hz, OCH_2CH_3).

Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.45; H, 8.27.

***trans*-5,6-Dicarbomethoxymethyl-2-norbornene** (**7**).—A solution of 6.65 g (0.025 mol) of the trans diethyl ester **8** and 0.5 g of *p*-toluenesulfonic acid in 350 ml of methanol was refluxed for 68 hr. Sodium acetate (0.5 g) was added, and the solvent was removed by distillation at atmospheric pressure. The residue was taken up in ether and was washed with saturated aqueous sodium bicarbonate and saturated brine. The resulting ether solution was dried ($MgSO_4$) and concentrated to afford 6.20 g of crude product. This material was distilled at reduced pressure to yield 3.80 g (64%) of the pure dimethyl ester **7** as a colorless oil: bp 107–108° (3.0 mm); ir (neat) 1750 (C=O), 1580 cm^{-1} (C=C); nmr ($CDCl_3$) δ 6.28 (d, d, 1, J = 6 and 3 Hz, HC=C), 6.13 (d, d, 1, J = 6 and 3 Hz, C=CH), 3.66 (s, 3, OCH_3), 3.65 (s, 3, OCH_3).

Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.26; H, 7.55.

Attempted Thorpe–Ziegler Cyclization of the Dinitrile 5. Method A.—The procedure of Bloomfield and Fennessy[33] was modified as follows. A slurry of 1.5 g (0.03 mol) of sodium cyanide in 30 ml of dimethyl sulfoxide was heated over steam, and 4.6 g (0.01 mol) of the trans ditosylate **4** was added over 0.5 hr. The mixture was stirred over steam for 3.0 hr, and 0.48 g of a 50% dispersion of sodium hydride in mineral oil (0.01 mol NaH) was added rapidly. Heating was continued for 70 hr, and the resulting mixture was poured onto ice. The mixture was extracted with ether, and the combined organic extracts were washed five times with water, dried ($MgSO_4$), and concentrated to yield 0.35 g of a mixture of the starting dinitrile **5** and dimethyl sulfoxide identified by its nmr spectrum.

Method B.[34]—A mixture of 172 mg (1 mmol) of the dinitrile **5** and 48 mg of a 50% dispersion of sodium hydride in mineral oil (1 mmol of hydride) was heated at 130° for 90 hr. The mixture was then cooled and diluted with 15 ml of saturated brine. The aqueous mixture was treated with ether, and a brown solid that precipitated at the interface was collected. This material was dried to yield 149 mg (81%) of a brown solid: mp 145° dec; ir (KBr) 3456 and 3345 (NH_2), 3046 (vinyl H), 2245 (isolated C≡N), 2190 (conjugated C≡N), 1680, 1614, 1541 cm^{-1}; nmr ($CDCl_3$) δ 6.30 (d, d, vinyl H), 6.08 (d, d, vinyl H). The alkaline aqueous layer obtained above was acidified with concentrated hydrochloric acid and extracted with

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[27] That the vinyl coupling constant is not altered by these bond angle changes follows from the theoretical conclusion of Karplus that the coupling constant across a cis ethylenic system should depend on the sum of the HC=C bond angle deformations for most dihedral angles. Since in the present system these angles would change in the opposite directions, the effects would again tend to cancel. See M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963). We are investigating this point further.

[28] C. Altona and M. Sundaralinam, *ibid.*, **92**, 1995 (1970).

[29] Dreiding molecular models clearly reveal the greater mobility of the saturated system.

[30] As indicated, for instance, by the fact that the diacid **13** may be decarboxylated at 185° without noticeable loss due to rearrangement or decomposition.

[31] R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960).

[32] For the sequence of reactions used to prepare this compound, see (a) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 98 (1928); (b) M. S. Morgan, R. S. Tipson, A. Lowy, and W. E. Baldwin, *J. Amer. Chem. Soc.*, **66**, 404 (1944); (c) L. Baur and C. Nambury, *J. Org. Chem.*, **26**, 1106 (1961); (d) K. Alder and W. Roth, *Ber.*, **87**, 161 (1954).

[33] J. J. Bloomfield and P. V. Fennessey, *Tetrahedron Lett.*, 2273 (1964).

[34] The authors are indebted to Mr. Richard L. Hutchens for carrying out this reaction and obtaining the infrared spectrum of the product.

ether. No residue was obtained on concentration of this extract.

Attempted Dieckmann Cyclization of the Trans Diesters 7 and 8.—Of the several procedures used in attempts to cyclize these two compounds, the following modification of the method of Linstead and Meade[35] is representative. A mixture of 0.71 g (0.003 mol) of the trans dimethyl ester **7**, 0.11 g (0.005 g-atom) of sodium, and one drop of ethanol in 5 ml of xylene was refluxed under dry nitrogen for 16 hr. The resulting mixture was taken up in ether and saturated brine and made acid to litmus with concentrated hydrochloric acid. The organic layer was extracted with 5% sodium hydroxide. No residue was found on concentration of the ether solution. The combined alkaline extracts were acidified with concentrated hydrochloric acid and extracted with ether. The combined ether extracts were washed with saturated brine, dried ($MgSO_4$), and concentrated to yield 0.62 g (98%) of the crude trans diacid **6** identified by its nmr spectrum.

9,9-Dicarbo-*tert*-butoxy-*trans*-5,6-trimethylene-2-norbornene (12) and 9,9-Dicarboxy-*trans*-5,6-trimethylene-2-norbornene (13).—A solution of 3.9 g (0.10 g-atom) of potassium in 200 ml of *tert*-butyl alcohol was added over 10.0 hr to a solution of 46.2 g (0.10 mol) of the trans ditosylate **4** and 16.0 g (0.10 mol) of diethyl malonate in 300 ml of *tert*-butyl alcohol refluxed under dry nitrogen. The resulting mixture was refluxed for 12.0 hr, and a solution of 5.8 g (0.15 g-atom) of potassium in 200 ml of *tert*-butyl alcohol was added over 12 hr. Reflux was then continued for 5 days, and the mixture was poured onto 750 ml of saturated aqueous sodium chloride (brine) and extracted with four 100-ml portions of ether. The combined extracts were washed once with saturated brine, once with 10% hydrochloric acid, once with saturated aqueous sodium bicarbonate, and finally once with saturated brine. The ethereal solution was dried ($MgSO_4$) and concentrated to yield 30.9 g of a pale yellow, semisolid mixture of the esters **9–12**. Crystallization from ethanol afforded 13.6 g (41%) of the di-*tert*-butyl ester **12** as white needles: mp 166–167°; ir (KBr) 3053 (C=CH), 1721 (CO), 1399 and 1371 (C_4H_9), 749 cm^{-1} (C=CH); nmr ($CDCl_3$) δ 6.58 (d, d, 1, J = 6 and 3 Hz, vinyl H), 5.82 (d, d, 1, J = 6 and 3 Hz, vinyl H), 1.47 (s, 9, C_4H_9), 1.45 (s, 9, C_4H_9).

Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04; mol wt, 334. Found: C, 71.97; H, 8.84; mol wt,[12,13] 329.

The combined mother liquors of the above crystallization were concentrated and treated with 3.5 g of potassium hydroxide in 50 ml of water, and the mixture was refluxed for 12.0 hr. The resulting solution was washed once with chloroform (no residue on concentration), and the aqueous layer was made acid to litmus with concentrated hydrochloric acid. The precipitated solid was extracted into chloroform, and the organic phase was washed with saturated brine, dried ($MgSO_4$), and concentrated to yield 5.6 g (25%) of the diacid **13** as a white solid. A small portion of this material was recrystallized from ethyl acetate for analysis: mp 211–212°; ir (KBr) 3350–2300 (OH), 1704 (C=O), 1568 (C=C), 952 (OH), 745 cm^{-1} (vinyl H); nmr (acetone-d_6) δ 8.33 (s, 2, OH), 6.57 (d, d, 1, J = 5.5 and 3 Hz, vinyl H), 5.82 (d, d, 1, J = 5.5 and 3 Hz, vinyl H).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; neut equiv, 111. Found: C, 64.99; H, 6.43; neut equiv,[12] 115.

9-Carboxy-*trans*-5,6-trimethylene-2-norbornene (16). Method A.—A procedure similar to that of Culberson and Wilder[10] for a similar reaction was used for the decarboxylation of the diacid **13**. A mixture of 3.0 g (0.014 mol) of **13** and 50 ml of phenyl ether was immersed in an oil bath preheated to 135°, and the bath temperature was slowly raised to a maximum of 185° over 0.5 hr, by which time the evolution of carbon dioxide had ceased. The resulting solution was cooled, diluted with 100 ml of ether, and extracted with two 20-ml portions of 5% aqueous sodium hydroxide. The combined alkaline extracts were washed once with ether (no residue on concentration) and acidified with 20 ml of 10% hydrochloric acid. The precipitated solid was taken up in ether, and the ethereal solution was washed with saturated brine, dried ($MgSO_4$), and concentrated to afford the monoacid mixture **16**. This material was sublimed at reduced pressure (1.0 mm at 100°) to afford the pure product as white needles (2.0 g, 83%): mp 69°; ir (KBr) 3053 (vinyl H), 3200–2400 (OH), 1714 (C=O), 1567 (C=C), 898 (OH), 720 cm^{-1} (vinyl H); nmr ($CDCl_3$) δ 10.88 (s, 1, OH), 6.57 (d, d, 1, J = 5.5 and 3 Hz, vinyl H), 5.82 (d, d, 1, J = 5.5 and 3 Hz, vinyl H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; neut equiv, 178. Found: C, 74.29; H, 7.98; neut equiv,[12] 173.

Method B.[11]—A solution of 6.7 g (0.02 mol) of the di-*tert*-butyl ester **12** in 50 ml of collidine was added to a solution of 11.3 g (0.06 mol) of lithium iodide trihydrate in 15 ml of collidine, and the mixture was refluxed for 24 hr. The reaction mixture was then poured onto ice and made acid to litmus with concentrated hydrochloric acid. The aqueous solution was extracted with ether, and the combined extracts were washed with 10% hydrochloric acid, 10% sodium bisulfite, and saturated brine. The crude product was extracted with three 10-ml portions of 5% sodium hydroxide, and the extracts were combined and retained (solution A). The ether phase was dried ($MgSO_4$) and concentrated to afford 2.5 g of a red-black oil. This material was dissolved in 25 ml of ethanol and 5 ml of water, and 5 g of sodium hydroxide was added. The solution was then refluxed for 24 hr and diluted with 50 ml of saturated brine. The aqueous solution was washed with ether (no residue on concentration) and made acid to litmus with concentrated hydrochloric acid. The precipitated solid was taken up in ether, and the ether solution was washed with saturated brine, dried ($MgSO_4$), and concentrated to yield 1.5 g (42%) of a black oil. Sublimation of this material at reduced pressure afforded the monoacids **16** as white needles, mp 59–60°. The nuclear magnetic resonance spectrum of this product was identical with that of the product obtained by the thermal decarboxylation of the diacid **13**.

The combined alkaline extracts obtained above (solution A) were acidified with concentrated hydrochloric acid, and the precipitated solid was extracted into ether. The ether solution was washed with saturated brine, dried ($MgSO_4$), and concentrated to give 2.0 g (45%) of the diacid **13**, identified by its nuclear magnetic resonance spectrum.

9-Carbomethoxy-*trans*-5,6-trimethylene-2-norbornene (17).—A solution of 360 mg (2.0 mmol) of the monoacids **16** and 36 mg of *p*-toluenesulfonic acid in 30 ml of methanol was stirred at room temperature for 16 hr. Sodium acetate (100 mg) was added, and the bulk of the solvent was distilled. The residue was diluted with an equal volume of saturated brine and extracted with ether. The combined ether extracts were washed with saturated brine and saturated sodium bicarbonate, and were dried ($MgSO_4$) and concentrated to afford 423 mg of a yellow oil. This material was evaporatively distilled at reduced pressure to yield the methyl esters **17** as a colorless oil (285 mg, 74%): ir (neat) 3049 (vinyl H), 1734 (C=O), 1567 cm^{-1} (C=C); nmr ($CDCl_3$) δ 6.57 (d, d, 1, J = 5.75 and 3.35 Hz, H_3), 5.82 (d, d, 1, J = 5.75 and 2.85 Hz, H_2), 3.67 (s, OCH_3), 3.65 (s, OCH_3), 3.20 (m, H_9), 2.72 (m, H_1), and 2.52 (m, H_4).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.88; H, 8.49.

9-Carboxy-*trans*-5,6-trimethylenenorbornane (18).—To a solution of 2.41 g (0.014 mol) of unsaturated acid **16** in 30 ml of ethyl acetate a few milligrams of 30% palladium on carbon was added, and the mixture was subjected to hydrogen at atmospheric pressure and room temperature until the absorption of hydrogen ceased. A total volume of 307 ml of hydrogen was taken up (theoretical, 302 ml). The catalyst was removed by filtration, and the filtrate was concentrated at reduced pressure to afford 2.1 g (87%) of the saturated acid **18**. Sublimation of this material at reduced pressure yielded the pure product: mp 45–47°; ir (KBr) 2850–2450 (COOH), 1700 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.41; H, 9.01.

9,9-Dicarbo-*tert*-butoxy-*trans*-5,6-trimethylenenorbornane (14).—The diester **12** was hydrogenated by the same procedure used for the hydrogenation of **16**. The saturated diester **14** was obtained as white needles from ethyl acetate in 70% yield: mp 123–125°; ir (KBr) 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.45 (s, 9, *t*-C_4H_9).

Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.39; H, 9.59. Found: C, 71.41; H, 9.58.

9,9-Dicarboxy-*trans*-5,6-trimethylenenorbornane (15).—This compound was obtained from the unsaturated diacid **13** by the hydrogenation procedure described above. The product **15** was obtained in 80% yield as white needles from ethyl acetate: mp 214–215°; ir (KBr) 3200–2900 (COOH), 1700 cm^{-1} (C=O); nmr (acetone-d_6) δ 7.58 (s, 1, COOH).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.48; H, 7.32.

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(35) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 940 (1934).

9-Carbomethoxy-*trans*-5,6-trimethylenenorbornane (19).—The saturated acid **18** was esterified in methanol by the same procedure used for the preparation of the ester **17**. The product **19** was obtained in 89% yield as a colorless oil: bp 126–127°; ir (neat) 1750 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.68 (s, 3, OCH_3).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.17; H, 9.35. Found: C, 74.18; H, 9.51.

Registry No.—**5**, 34561-91-6; **6**, 34561-92-7; **7**, 34561-93-8; **8**, 34561-94-9; **12**, 34561-95-0; **13**, 34561-96-1; **14**, 34561-97-2; **15**, 34561-98-3; **16** isomer a, 34599-26-3; **16** isomer b, 34599-27-4; **17** isomer a, 34561-99-4; **17** isomer b, 34562-00-0; **18** isomer a, 34562-01-1; **18** isomer b, 34562-02-2; **19** isomer a, 34562-03-3; **19** isomer b, 34562-04-4.

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Studies on Reactions of Isoprenoids. XVII.[1] The Cycloaddition Reactions of Norbornadiene with Some Unsymmetrically Substituted Dienophiles. Competitive Ionic Additions with Homo-Diels–Alder Reactions

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The reactions of norbornadiene (1) with unsymmetrically substituted acetylenic and heterodienophiles were investigated. Cyanoacetylene and *N-tert*-butylpropiolamide as acetylenic dienophiles gave only homo-Diels–Alder adducts **3a** and **3b**, respectively, while chlorocyanoacetylene afforded 2 + 2 cycloadduct **4** and its skeletal rearrangement product **5** *via* an ionic intermediate **7** together with homo-Diels–Alder adduct **3c**. Phenylacetylene, chloropropiolamide, and dimethylaminocyanoacetylene did not afford any isolable adducts. The reaction of **1** with methylenebisurethane in the presence of boron trifluoride etherate afforded 8-aza-δ-cyclane (**10**) and the 3-aminonortricyclene derivative **11**, while that with benzalbisurethane gave only 3-nortricyclylurethane (**12**). Anhydrochloralurethane did not afford any adduct.

We have previously reported 1,4-cycloaddition reactions of some monoterpenoid diene and triene systems.[1,2] As an extension of these studies, this paper deals with cycloaddition of homoconjugated norbornadiene (**1**) and unsymmetrically substituted acetylenic and heterodienophiles. It is well known that **1** gives δ-cyclane derivatives *via* the homo-Diels–Alder (${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$ cycloaddition) reaction,[3,4] and quadricyclane (**6**) affords tricyclo[4.2.1.0^{2,5}]non-7-ene derivatives *via* the bishomodiene addition (${}_{\pi}2_s + {}_{\sigma}2_a + {}_{\sigma}2_a$ cycloaddition)[5] as the thermally allowed process under the Woodward–Hoffmann orbital symmetry rules.[6] However, only reactions of **1** with symmetrically substituted active acetylenes such as dimethyl acetylenedicarboxylate and dicyanoacetylene seem to have been studied.[4] In order to know the chemical behavior of the homoconjugated diene system of **1** with dienophiles that are strongly perturbed by substituents, we have investigated the reactions of **1** with cyanoacetylene (**2a**), *N-tert*-butylpropiolamide (**2b**), chlorocyanoacetylene (**2c**), phenylacetylene (**2d**), chloropropiolamide (**2e**), and dimethylaminocyanoacetylene (**2f**) as well as those with the heterodienophiles *N*-ethoxycarbonylimines **9a**, **9b**, and **9c**.

Results and Discussion

An equimolar mixture of **1** and **2a** was heated under the conditions shown in Table I. The product **3a** was isolated as a colorless liquid by distillation. The best yield was obtained by heating the reactants without solvent or any addenda at 145–160°, while the presence of aluminum chloride or copper(II) bromide lowered the yields considerably.[7,8]

TABLE I

THE YIELD OF **3a** UNDER VARIOUS CONDITIONS

Solvent	Addenda	Temp, °C	Time, hr	Yield,[a] %
None	None	160	28	31
None	None	145	40	31
Benzene	None	90	69	26
None	$AlCl_3$[b]	80	70	9
Benzene	$CuBr_2$[b]	80	240	Trace

[a] Isolated yield. [b] Trace–0.3 molar equiv amounts were examined but the results were similar.

The structure of **3a** was determined as 8-cyano-δ-cyclene (8-cyanotetracyclo[4.3.0.0.^{2,4}0^{3,7}]non-8-ene)[9] on the basis of analytical and spectral data. The nmr spectrum (CCl_4, 60 MHz) revealed a doublet at τ 3.15

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[9] For the nomenclature, see footnote 3 in P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).