Regio- and Stereospecific $[2_\pi + 2_\sigma + 2_\sigma]$ Cycloaddition Reaction of Quadricyclane

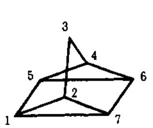
Iwao Tabushi,* Kazuo Yamamura, and Zen-ichi Yoshida

Contribution from the Department of Synthetic Chemistry, Kyoto University, Kyoto 606, Japan. *Received May 7, 1971*

Abstract: $[2_\pi + 2_\sigma + 2_\sigma]$ cycloaddition reaction of cis- or trans-disubstituted olefinic dienophiles (**4a–4f**) to tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (quadricyclane) was found to be regio- and stereospecific, giving *exo*-tricyclo[4.2.1.0^{2,5}]-7-nonene derivatives (**5a–5f**), which conserved the original stereochemistry in the dienophiles. A "maximal overlap rule," extended from that in the Diels–Alder reactions, is presented in order to explain endo selectivity of the dienophiles' substituents at C_3 and C_4 in most cycloadducts from quadricyclane and cis disubstituted olefins. In nmr studies of the cycloadducts, a general trend was observed for protons at C_3 or C_4 in that the endo-proton signal appeared at *ca.* 0.8 ppm lower field than the exo-proton signal regardless of the substituents. As to the coupling constants of protons on the cyclobutane ring ($C_2C_3C_4C_5$), J_{cis} was found to be appreciably larger than J_{trans}.

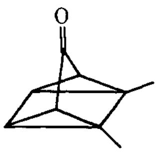
The electronic state and chemical reactivity of cyclopropane have attracted the continuous attention of organic chemists. Its uniqueness has been assigned to the sp^5 hybrid orbital and the in-plane mobile electrons.[1]

The interaction of two cyclopropane rings is of considerable theoretical interest. Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane or quacricyclane (hereafter abbreviated as Q) seems to be a good model for this purpose in which the two cyclopropane rings are fixed nearly parallel and in close proximity to allow a strong interaction between them. The strong interaction may afford an unique electronic state (another unique hybridization) in Q. The experimental observation obtained so far, which suggests the interaction of the two cyclopropane rings in Q, is the reported cycloaddition reaction.[2-4] Smith reported cycloaddition reactions of Q with some dienophiles such as tetracyanoethylene, dimethyl acetylenedicarboxylate, or dicyanoacetylene, giving the tricyclo[4.2.1.0^{2,5}]-7-nonene derivatives (**1**) or -3,7-nonadiene derivatives (**2**). More recently Prinzbach, *et al.*, reported that dimethyl acetylenedicarboxylate or methyl acetylenecarboxylate added to 3-methylenequadricyclanes[3] (methylene-Q) and 3-oxoquadricyclanes[3,4] (oxo-Q) to give 9-methylene and 9-oxo derivatives of **2**, respectively. These characteristic cylcoaddition reactions of Q exhibit a striking contrast to cycloaddition reactions of norbornadiene with some dienophiles,[5] and these are most easily understood by applying the principle of orbital symmetry conservation,[6] if these reactions are concerted ones.

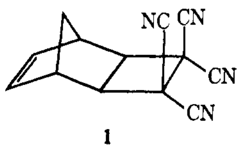


Q

methylene-Q



oxo-Q



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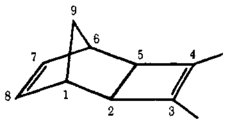

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In this article the authors report the cycloaddition reactions of Q with cis- or trans-disubstituted olefinic dienophiles. These cycloaddition reactions were concluded to be completely stereospecific from the chemical and the spectroscopic studies of the adducts, therefore it seems to be concerted, suggesting that the interaction of bonding electrons in the four-membered ring in Q is important. This (to the authors' knowledge) seems to

Table I. Mass Spectra of the Cycloadducts[a]

Adduct	m/e
5a	p 190 (19), 118 (65), 117 (100), 115 (62), 92 (70), 91 (88), 66 (100)
5b	p + 2 226 (4), p 224 (13), 189 (5.5), 117 (98), 115 (54), 92 (44), 66 (100)
5c	p 236 (13), 205 (46), 177 (64), 171 (45), 139 (93), 117 (100), 115 (61), 111 (93), 92 (57), 91 (77), 66 (88)
5d	p 236 (12), 205 (24), 177 (20), 171 (79), 139 (30), 117 (95), 115 (95), 111 (96), 92 (45), 91 (82), 66 (100)
5e	p 170 (12), 117 (16), 116 (13), 104 (68), 92 (62), 91 (97), 66 (100)
5f	p 170 (6), 117 (9), 116 (8), 104 (84), 92 (49), 91 (93), 66 (100)

[a] Relative intensities are in parentheses.

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(1) (a) The bathochromic effect of the cyclopropane ring in electronic spectra was the first indication that cyclopropane might have conjugation ability: M. T. Rogers, *J. Amer. Chem. Soc.*, **69**, 2544 (1947); (b) J. D. Roberts and V. C. Chambers, *ibid.*, 5030 (1951); (c) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965); (d) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956); H. J. Bernstein, W. G. Schneider, and J. A. Pople, *Proc. Roy. Soc., Ser. A*, **236**, 515 (1956).

(2) C. D. Smith, *J. Amer. Chem. Soc.*, **88**, 4273 (1966).

(3) (a) H. Prinzbach and J. Rivier, *Angew. Chem., Int. Ed. Engl.*, **6**, 1069 (1967); (b) H. Prinzbach, *Pure Appl. Chem.*, **16**, 17 (1968).

(4) 9-Oxo derivatives of **2** were, without isolation, decarboxylated to cyclooctatetraenes.

(5) Cycloaddition reactions of norbornadiene with dienophiles are known to be homo-Diels–Alder reactions in a few cases, giving tetracyclic compounds of the type (**3**): (a) H. K. Hall, *J. Org. Chem.*, **25**, 42 (1960); (b) A. T. Blomquist and Y. C. Meinwald, *J. Amer. Chem. Soc.*, **81**, 667 (1959); (c) E. F. Ullman, *Chem. Ind. (London)*, 1173 (1958); (d) R. C. Cookson, J. Dance, and J. Hudec, *J. Chem. Soc.*, 5614 (1964).

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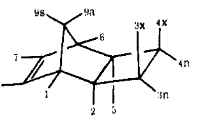
(6) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

Table II. Chemical Shifts[a] of the Protons of the Cycloadducts



	5a[b]	**5b**[b]	**5c**[c]	**5d**[c]	**5e**[b]	**5f**[b]
$H_{7,8}$	3.91 (t)	3.83 (t)	4.04 (3.97) (t)	4.04 (3.97) (t)	3.92 (t)	3.90 (t)
$H_{1,6}$	6.94	6.80	7.24	7.18	7.04 6.92	6.93
H_2	7.63	7.67	7.68 (d)	7.96 (q)	7.52	7.63 (d)
H_5	7.63	7.45	7.68 (d)	7.74 (q)	7.59	7.63 (d)
H_{3n}						6.29 (m)
H_{3x}	7.00	6.87	7.35 (q)	7.24 (q)	7.22	
H_{4n}				6.47 (q)	6.41 (q)	6.29 (m)
H_{4x}	7.00		7.35 (q)			
H_{9s}[d]	8.45	8.40	8.60 (8.54)	8.71 (8.65)	8.38	8.34
H_{9a}[d]	8.45	8.20	8.45 (8.45)	8.51 (8.50)	8.19	7.84

[a] τ values. [b] $CDCl_3$. [c] CCl_4 (τ values in $CDCl_3$ are in parentheses). [d] The signal of H_{9s} and H_{9a} form AB quartet with a coupling constant J_{sa}.

be the first concrete evidence for the concerted $[2_\pi + 2_\sigma + 2_\sigma]$ cycloaddition reactions.

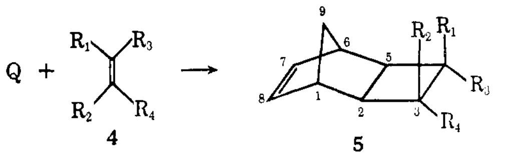
Results and Discussion

Determination of the structure of the products was made chemically (*vide infra*) and spectroscopically (Tables I, II, and III). The mass spectrum of each adduct showed molecular peak and characteristic fragment peaks (*m*/*e* 66 and 92) of retrocycloaddition reactions[7] (Table I). Nmr spectra showed the presence of two nearly symmetrical olefinic protons and bridgehead protons at C_1 and C_6 (Table II), excluding the rearranged structure (**6**).[8] The chemical shifts of the olefiinc protons in *exo*- (7_X) and *endo*-tricyclo[4.2.1.0^{2,5}]-7-nonene (7_N) were τ 4.11 and 3.66, respectively,[9] and the downfield shift in the absorption of the olefinic protons in 7_N relative to 7_X of *ca.* 0.5 ppm has been attributed to the interaction between C_3–H and a double bond in 7_N (within a van der Waals radii).[9,10] A similar characteristic was also observed for some norbornadiene dimers.[10] Therefore, if our adducts have the endo configuration **8**, the substituent X or Y should cause a large chemical shift difference between the two olefinic protons[11] in the adduct from Q and a trans-disubstituted olefin. But the observed maximum splitting of the absorption of the two olefinic protons in each of our adducts was only 0.05 ppm; therefore, this

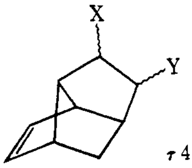
Table III. Coupling Constants[a]

	5a	**5b**	**5c**	**5d**	**5e**	**5f**
J_{23x}	∼2	∼3	4	4.6	∼4	
J_{23n}						9
J_{4x5}	∼2		4			
J_{4n5}				9.8	∼9	9
J_{3x4n}				7.8	∼7	
J_{25}		5		6.8	6	
J_{sa}[a]		11	10	10	11	12

[a] These coupling constants are the splitting observed, although real gem coupling constants are negative. *J* is given in hertz.



a, $R_1 = R_2 = H$; $R_3R_4 =$ —COOOC—
b, $R_1 = H$; $R_2 = Cl$; $R_3R_4 =$ —COOOC—
c, $R_1 = R_2 = H$; $R_3 = R_4 = CO_2CH_3$
d, $R_2 = R_3 = H$; $R_1 = R_4 = CO_2CH_3$
e, $R_2 = R_3 = H$; $R_1 = R_4 = CN$
f, $R_1 = R_2 = CN$; $R_3 = R_4 = H$



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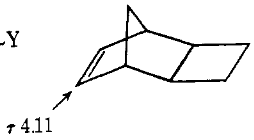
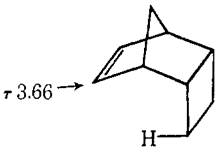


7X



7N

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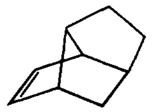
[7] (a) S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2738 (1966); (b) K. Bieman, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 102.

[8] The unsubstituted hydrocarbon was formed in a thermal isomerization of a C_9H_{12} tetracyclic compound: H-D. Scharf and G. Weisgerber, *Tetrahedron Lett.*, 1567 (1967).

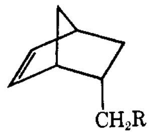


nmr τ 4.1 (2 H, quartet); 7.1 (1 H, multiplet); 7.7 (3 H, multiplet); 8.3–9.0 (6 H, multiplet)

[9] R. R. Saurs, S. B. Schlosberg, and P. E. Pfeffer, *J. Org. Chem.*, **33**, 2175 (1968).

[10] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965).

[11] The substituents R in **9** cause chemical shift differences (0.16



9, R = H, OH, Cl, CN, CO_2H, or CO_2CH_3

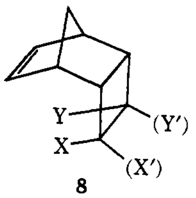
∼ 0.24 ppm) between the two olefinic protons. (a) E. Pretsch, H. Immer, C. Pascual, K. Schaffner, and W. Simon, *Helv. Chim. Acta*, **50**, 105 (1967); (b) R. V. Moen and H. S. Makowski, *Anal. Chem.*, **39**, 1860 (1967).

Table IV. Yields,[a] Melting Points,[b] and Elemental Analyses

Adduct	Yield, %	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found
5a	89	122	69.46	69.74	5.29	5.40
5b	91	130–131	58.80	58.45	4.01	4.31
5c	28 (91)	91.5–92.5	66.08	66.20	6.83	7.01
5d	83 (93)	84.0–84.5	66.08	65.92	6.83	6.95
5e	97	83.0–84.0	77.62	77.38	5.92	6.03
5f	96	172.5–173.0[c]	77.62	77.46	5.92	6.03

[a] Yields based upon dienophiles reacted are in parentheses. [b] Uncorrected. [c] In part sublimes at 163°.

means that the two olefinic protons are nearly equivalent. Furthermore, the chemical shifts of these equivalent olefinic protons (Table II) were observed to be nearly independent of the substituents at C-3 and C-4,



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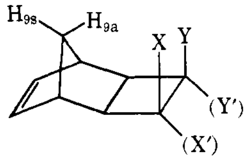

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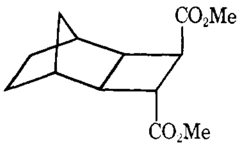
and were close to the chemical shift of the olefinic protons of the unsubstituted hydrocarbon 7_X, strongly indicating that C_2–C_3 and C_5–C_4 bonds were to be exo (**10**). The exo configuration of the cyclobutane ring in **5d** was supported by the catalytic hydrogenation of **5d** to the trans diester (**11**). The diester **11** showed the same nmr and ir spectra as the reported trans diester[12] in every detail. The exo configuration of the cyclobutane ring in **11** had been ascertained by the degradation of **11** to the known *exo*-2,3-bishydroxymethylbicyclo[2.2.1]heptane (**12**), so that the exo cyclobutane ring juncture in **5d** was evident. That the other cycloadducts (**5a–f**) have the same exo configuration of the cyclobutane ring as **5d** was shown from the study of chemical conversion of the cycloadducts.



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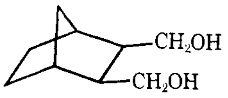

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Chemical Conversion of the Cycloadducts. Cis- and trans-disubstituted olefins (**4a** ~ **4f**) gave different cycloadducts (**5a**~**5f**) in nearly quantitative yields (Table IV). Acid-catalyzed esterification[14] of **5a** and **5e** led to **5c** and **5d**, respectively, and base-catalyzed isomerization–hydrolysis followed by esterification converted **5d**, **5e**, or **5f** to the same cis diester **5c**. The base-catalyzed conversion of **5d**, **5e**, or **5f** to **5c** seems to be attained as follows. An equilibrium between the thermodynamically more stable trans diester **5d** and the less stable cis diester **5c** was at first attained by treating **5d** with sodium methoxide in methanol[13,15] (**5c**, *ca.* 20% and **5d**, *ca.* 80%). But a trace of sodium hydroxide produced from sodium and *wet* methanol readily converted **5c** to the monosodium salt of the cis-endo dicarboxylic acid (**13**) and the precipitation of **13** enabled the selective conversion of **5d** to **13**. The sodium salt **13** was easily hydrolyzed and esterified giving **5c**, and this is a convenient method to convert the 1,2-trans diester to the cis diester. The precipitation of **13** also enabled the practically selective conversion of the nitrile **5e** or **5f** to the cis diester **5c**, although it remained to be clarified whether isomerization preceded hydrolysis or *vice versa*.

On the basis of the chemical conversion cited above, cycloadducts **5a**–**5f** were concluded to differ only in substitutents or in stereochemistry at C_3 and C_4. Thus the present cycloaddition reaction was concluded to be stereospecific (to confirm the stereospecificity, additional evidence from the nmr coupling constants will be shown later). The structural correlation of the cycloadducts was shown in Scheme I.

Stereochemistry and Chemical Shifts. An examination of the chemical shift data in Table II reveals a very characteristic trend: the τ values of the endo protons at C_3 (C_4) were much lower than those of the exo protons at C_3 (C_4). For example, in **5d** (**5e**), the chemical shift of H_{4n} was τ 6.47 (τ 6.41) and that of H_{3x} was τ 7.24 (τ 7.22). The chemical shift difference between the exo and endo protons amounted to 0.77 ppm (0.81 ppm).

A similar trend is well known in norbornanes[16] or norbornenes.[17] In these cases the resonances of endo protons were observed at somewhat higher field than those of exo protons, and these were mainly explained as the result of C–C shielding effect.[18]

The relation between the stereochemistry and the chemical shifts, mentioned above for **5d** and **5e**, is also applicable to other cycloadducts. The nmr spectrum of cis diester **5c** displayed a quartet at τ 7.35 assigned to protons α to the carbomethoxy groups, indicating that these were the exo protons (H_{3x} and H_{4x}). Protons α to cyano groups of **5f** showed a multiplet at τ 6.29 and were at slightly lower field than the endo proton H_{3n} (τ 6.41) of the trans dinitrile **5e**. Therefore these α protons in **5f** were assigned to the endo protons (H_{3n} and H_{4n}). In the case of **5b**, the chemical shift of exo proton (H_{3x}) was τ 6.87, close to the chemical shift

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(12) The photoaddition reaction of norbornadiene with dimethyl maleate was reported to give cis-endo isomer of **11** [H. Hara, Y. Odaira, and S. Tsutsumi, *Tetrahedron*, **22**, 95 (1966)], but the cis structure of the product was later corrected to be the trans diester (**11**) by R. L. Cargill, *et al.*[13]

(13) R. L. Cargill and M. R. Willcott, *J. Org. Chem.*, **31**, 3938 (1966).

(14) Acid-catalyzed hydrolysis of the cis dinitrile **5f** was attempted but only one of the two cyano groups was hydrolyzed. The tentative structure of **5f** was strongly supported by the nuclear magnetic resonance spectrum data.

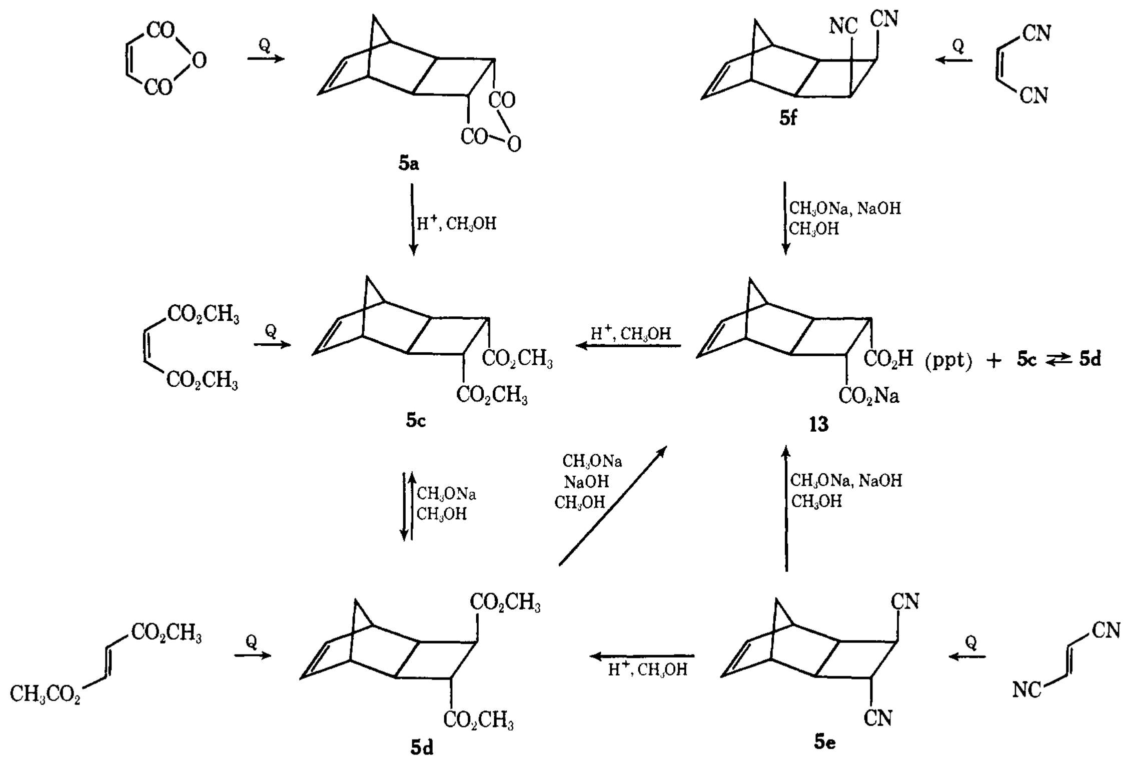
(15) *Ca.* 80% of **11** and *ca.* 20% of the cis-endo diester isomer were involved in the equilibrium mixture attained by base-catalyzed isomerization of **11**, and the same isomer distribution was obtained from the cis-endo diester isomer (see ref 13).

(16) W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).

(17) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 2709 (1963).

(18) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, pp 78, 79.

Scheme I



(τ 7.00) of the exo protons in **5a**, indicating that this downfield shift of 0.13 ppm of H_{3x} was derived from the vic chloro substituent.

Furthermore, the chemical shift of H_{9a} is very sensitive to C_3 and C_4 substituents, while that of H_{9s} is rather insensitive to the substituents. Since the chemical shift variation of H_{9a} is considered as the result of the magnetic anistotropic effect of C_3 and C_4 substituents, the chemical shift of H_{9a} and $\Delta\tau = \tau_{H_{9s}} - \tau_{H_{9a}}$ give information about the stereochemistry at C_3 and C_4 to some extent. In **5e**, which has one exo and one endo cyano group, the chemical shift of H_{9a} was τ 8.19 and was somewhat lower than that in **5a**, **5c**, or **5d**. But the signal of H_{9a} in **5f** was observed at much lower field (τ 7.84) than those, and $\Delta\tau$ in **5f** was remarkably large (0.50 ppm), whereas $\Delta\tau$ in **5e** was 0.19 ppm. This, therefore, indicates that **5f** has two exo cyano groups. While two carbomethoxy groups arranged as trans (**5d**) and cis (**5c**) at C_3 and C_4 had nearly the same effect upon the chemical shift of H_{9a}, little chemical shift change was observed for H_{9s} (Table II). But it is beyond our reach to elucidate the complicated effects of the two carbomethoxy groups on the chemical shifts of H_{9a} and H_{9s} in more detail.

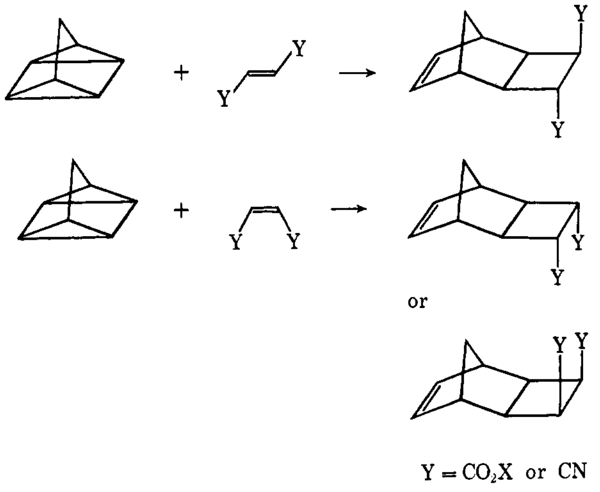
The stereochemistry was also supported by the observed spin–spin coupling constants on a cyclobutane ring in the adducts described in the next paragraph.

Coupling Constants of Protons on the Cyclobutane Ring. Nmr decoupling experiments of cycloadducts were carried out by means of a 100-MHz nmr spectrometer. Irradiation on H_3, H_4, or H_2 in **5d** or **5e** made it possible to calculate $J_{2,5}$, $J_{2,3n}$, $J_{3x,4n}$, or $J_{2,3x}$ and these values are summarized in Table III.

These coupling constants were confirmed to be appropriate by calculations of theoretical spectra of 6 spin system (H_2, H_3, H_4, H_5, H_{9s}, and H_{9a}). Apparently there is a general trend that J_{cis} is somewhat larger than J_{trans}. This trend had been also observed in rigid cyclobutane systems such as coumarin dimers,[19a] a cyclopentadienone dimer,[19b] a 2,4-cyclooctadienone dimer,[19c] or 3,4-dihalocyclobutane-1,2-dicarboxylic acids.[19d] All of the J values observed are consistent with the assigned stereochemistry.

Stereospecificity and Regiospecificity of the Cycloaddition and Strong σ-Bond Interaction in Quadricyclane. It is concluded from the assigned structures of the cycloadducts that the reaction is completely stereospecific as shown in Scheme II. This implies that the reaction is concerted and allowed. The other interesting point to note is the stereoselectivity of the present cycloaddition reactions. Most of the cis and trans disubstituted olefinic dienophiles added to Q in a way of "maximal overlap"[20] as in the case of Diels–

Scheme II



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(19) (a) L. Paolillo, H. Ziffer, and O. Buchardt, *J. Org. Chem.*, **35**, 38 (1970); (b) P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962); (c) T. S. Cantrell and J. S. Solomon, *ibid.*, **92**, 4656 (1970); (d) V. Georgian, L. Georgian, and A. V. Robertson, *Tetrahedron*, **19**, 1219 (1963).

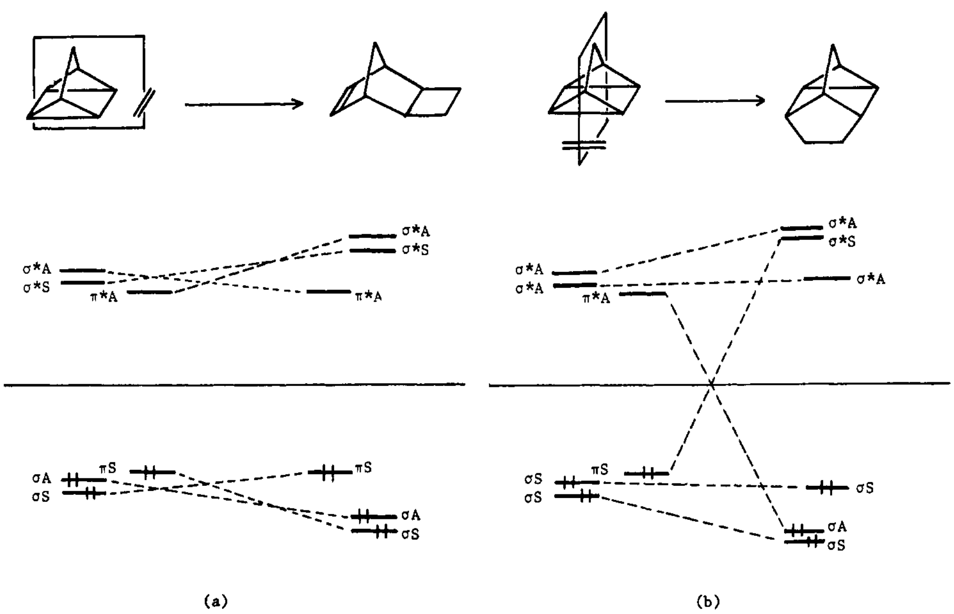
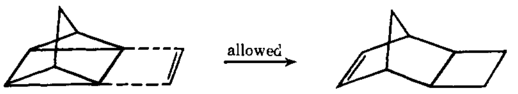


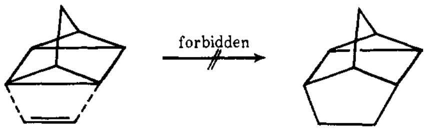
Figure 1. Orbital correlation diagram: (a) exo-type cycloaddition; (b) homo-endo-type cycloaddition.

Alder cycloadditions. Consideration of the usual orbital correlation diagram (Figure 1) suggests that the exo-type cycloaddition to Q is allowed, whereas the homo-endo-type cycloaddition to Q, shown in Scheme III, is forbidden. Thus experimental results are in good agreement with symmetry considerations. On the other hand, for norbornadiene, exo-type cycloaddition is forbidden and homo-endo-type cycloaddition is allowed (Scheme IV). Again, experimental results in literature[5] are in good agreement with the prediction (from the orbital symmetry consideration). The concertedness and regiospecificity of the cycloaddition of Q to dienophiles require the presence of some strong interaction between the two σ bonds[21] (C_1–C_7 and C_5–C_6) in order to allow such a remarkable specificity.[22]

Scheme III

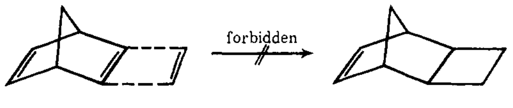


exo-type cycloaddition

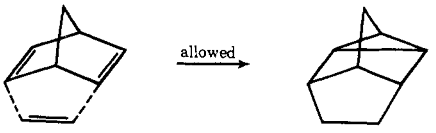


homo-endo-type cycloaddition

Scheme IV



exo-type cycloaddition



homo-endo-type cycloaddition

Experimental Section

Spectral data, except infrared spectra, are listed in Tables I–III, and yields, uncorrected melting points, and elemental analyses are listed in Table IV.

Preparation of Quadricyclane (Q). Quadricyclane (Q)[23] was prepared from norbornadiene by acetophenone- or benzophenone-sensitized irradiation and purified by fractional distillation: bp 45° (80 mm); ν_{max} (corrected) 3075, 3055, 2935, 2865, 1260, 1241, 909, 896, 800, and 770 cm^{-1} (lit.[23c] 3050 and 2990 cm^{-1}). The nuclear magnetic resonance spectrum of Q was in accord with the reported one.[23b,c]

Reaction of Q with Maleic Anhydride. A mixture of 1.0 ml (*ca.* 9.0 mmol) of Q and 0.53 g (5.55 mmol) of maleic anhydride in a 20-ml microflask equipped with a refluxed condenser was heated to 90° for 24 hr and, after evaporation of excess Q, a slightly yellow solid was obtained. Recrystallization from petroleum ether yielded 881 mg (89%) of colorless needles, tricyclo[4.2.1.0^{2,5}]-7-nonene-3,4-*cis*-*endo*-dicarboxylic anhydride (**5a**): ν_{max} (KBr) 2985, 1850, 1774, 1464, 1329, 1201, 1068, 918, 735, and 719 cm^{-1}.

Reaction of Q with Monochloromaleic Anhydride. A mixture of 1.0 ml (*ca.* 9.0 mmol) of Q and 0.80 g (6.00 mmol) of monochloromaleic anhydride was heated to 90° for 1 hr and, after evaporation of excess Q, 1.22 g (91%) of a white solid, tricyclo[4.2.1.0^{2,5}]-7-nonene-3-*exo*-chloro-3,4-*cis*-*endo*-dicarboxylic anhydride (**5b**), was obtained. Recrystallization from methylene chloride gave 981 mg of pure white solid, **5b**: ν_{max} (KBr) 2995, 1865, 1788, 1250, 1222, 1092, 928, 738, and 720 cm^{-1}.

Reaction of Q with Dimethyl Maleate. A mixture of 2.0 ml (*ca.* 18.0 mmol) of Q and 1.10 g (7.70 mmol) of dimethyl maleate in 3 ml of chloroform was heated to 90° for 40 hr. After 1.5 ml of chloroforom was evaporated; the residual solution was kept for a day. Precipitated colorless crystals were filtered and washed with a small amount of methanol. The colorless crystals of dimethyl tricyclo[4.2.1.0^{2,5}]-7-nonene-3,4-*cis*-*endo*-dicarboxylate (**5c**)

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(20) Maximal overlap means that besides the overlap between the dienophiles' π electrons and the reaction center of Q, there is additional overlap of the π electrons of the dienophiles' substituents (CN or COOX) with four-membered ring electrons of Q.

(21) This interaction must be recognized at least in the perturbed state of Q, which is derived from the interaction between Q and a dienophile. And the interaction seems to become stronger and stronger, as the system approaches the transition state.

(22) The reactivity of Q to dienophiles was observed to be much higher than that of norbornadiene to dienophiles.

(23) (a) G. S. Hammond, O. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964); (b) G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, **83**, 4673 (1961); (c) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

amounted to: 551 mg (28%, 91% based upon the dimethyl maleate reacted); ν_{max} (KBr) 2980, 1745, 1719, 1423, 1362, 1349, 1220, 1200, 1181, 722, and 710 cm^{-1}.

Reaction of Q with Dimethyl Fumarate. A solution of 1.5 ml (*ca.* 13 mmol) of Q and 0.78 g (5.4 mmol) of dimethyl fumarate in 2 ml of chloroform was heated to 90° for 2 days. After evaporation of chloroform, the solid residue was recrystallized from petroleum ether, giving 1.05 g (83%) of colorless crystals of tricyclo[4.2.1.0^{2,5}]-7-nonene-3,4-*trans*-dicarboxylate (**5d**): ν_{max} (KBr) 2975, 1730, 1720, 1310, 1256, 1200, 1180, 1018, 800, and 710 cm^{-1}.

Reaction of Q with Fumaronitrile. A solution of 1.5 ml (*ca.* 13 mmol) of Q and 0.78 g (10 mmol) of fumaronitrile in 2 ml of 1,2-dichloroethane was heated to 90° for a day. Evaporation of excess Q and 1,2-dichloroethane gave a white solid. Recrystallization of the solid from chloroform yielded 1.65 g (97%) of tricyclo-[4.2.1.0^{2,5}]-7-nonene-3,4-*trans*-dinitrile (**5e**). For further purification, recrystallization from 1,2-dichloroethane and petroleum ether (1:1) was carried out: ν_{max} (KBr) 2965, 2940, 2340, 1260, 1121, 1080, 1024, 795, 728, and 696 cm^{-1}.

Reaction of Q with Maleonitrile. A solution of 1.25 ml (*ca.* 11.3 mmol) of Q and 0.681 g (8.75 mmol) of maleonitrile in 1 ml of 1,2-dichloroethane was heated to 90° and, in about 5 min, a white solid precipitated. Heating was continued for a further 60 min with addition of 1 ml of 1,2-dichloroethane. The removal of the solvent under reduced pressure yielded 1.42 g (96%) of tricyclo[4.2.1.0^{2,5}]-7-nonene-3,4-*cis-exo*-dinitrile (**5f**). For further purification, recrystallization from 1,2-dichloroethane was carried out, giving colorless crystals of **5f**: ν_{max} (KBr) 2990, 2910, 2330, 1478, 1332, 1298, 1091, 830, 740, 696, and 680 cm^{-1}.

Chemical Conversion of the Cycloaddicts. 5a to 5c. A mixture of 100 mg of the cis-endo dicarboxylic anhydride (**5a**), 5 ml of methanol, and a catalytic amount of concentrated sulfuric acid was refluxed at 90° for 6 hr. After the solution was neutralized with an aqueous solution of sodium bicarbonate, the product was extracted with chloroform. Evaporation of chloroform gave a white solid and this product was identified as the dimethyl cis-endo dicarboxylate (**5c**) by means of the vapor phase chromatographic analysis and the infrared spectrum.

5d to 5c. A mixture of 100 mg of the trans dicarboxylate (**5d**) and 10 ml of the solution of sodium methoxide in methanol from 0.15 g of sodium and 30 ml of wet methanol was refluxed at 90° for 20 hr. The white precipitate of monosodium salt of tricyclo-[4.2.1.0^{2,5}]-7-nonene-3,4-*cis-endo*-dicarboxylic acid was filtered and was dissolved in a small amount of water. The solution was acidified with hydrochloric acid and the water was evaporated *in vacuo*. The residual solid was dissolved in 5 ml of methanol and a catalytic amount of concentrated sulfuric acid was added. This solution was refluxed for 3 hr and neutralized with an aqueous solution of sodium bicarbonate. Extraction with chloroform gave a white solid. The product was identified to be the cis-endo dicarboxylate (**5c**) by means of glpc analysis and the infrared spectrum.

A mixture of 50 mg of the trans dicarboxylate **5d** and 10 ml of the solution of sodium methoxide in methanol, freshly prepared from 0.15 g of sodium and 30 ml of dry methanol, in a 20-ml microflask equipped with a stopper was heated to 80° for 20 hr. Precipitation was not observed in this case. The solution was extracted with 20 ml of ether twice and the combined ether solution was condensed with a rotary evaporator. Glpc analysis revealed that 83% of the trans dicarboxylate **5d** and 17% of the cis dicarboxylate **5c** were involved.

5f to 5c. A mixture of 100 mg of the cis-endo dinitrile (**5f**) in 10 ml of the freshly prepared solution of sodium methoxide in slightly *wet* methanol was refluxed at 90° for 20 hr. The white precipitate of the sodium salt of the dicarboxylic acid (**13**) was treated as described. The solid thus obtained was identified to be the cis-endo dicarboxylate (**5c**) from the glpc analysis and the infrared spectrum.

5e to 5c. Treatment of 100 mg of the trans dinitrile (**5e**) with sodium methoxide in methanol was the same as described, and the cis-endo dicarboxylate (**5c**) was obtained.

5e to 5d. A solution of 100 mg of the trans dinitrile (**5e**) and 2 ml of concentrated hydrochloric acid in 5 ml of methanol was refluxed at 90° for 5 hr. After methanol and water were evaporated, methanol and a catalytic amount of concentrated sulfuric acid were added to the residue. The solution was refluxed for 3 hr and neutralized with an aqueous solution of sodium bicarbonate. Extraction of the solution with chloroform gave a white solid, the trans dicarboxylate **5d**.

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