starting material; the filtrate was evaporated to dryness under reduced pressure. The residue was treated with water and collected to give 0.015 g (61%) of **2d.**

3-Ethoxy-6*H*-indolo[2,3-*b*][1,8]naphthyridine (2e). To a solution containing 0.04 g (1.73 mmol) of sodium metal in 50 mL of absolute ethanol was added 0.075 g (0.29 mmol) of **2c;** the mixture was refluxed for 24 h. The obtained solution was evaporated to dryness, and the residue was treated with water, collected, and dried to give 0.05 g (64.3%) of **2e.**

11*H*-Tetrazolo[1,5-*a*]indolo[3,2-*g*][1,8]naphthyridine (13). A suspension of 0.15 g (0.59 mmol) of **2c** in 16 mL of DMF and 0.1 g (1.53 mmol) of NaN_3 was refluxed for 30 min. After cooling, the mixture was poured into water, and the precipitate was collected, washed with water, and dried to give 0.135 g (87.7%) of **13.** An analytical sample was prepared by crystallization from DMF: mp >320 °C; IR (Nujol) 3340, 1600, 1260, 1090, 790, 755 cm^{-1}.

Anal. Calcd for $C_{14}H_8N_6$: C, 64.61; H, 3.07; N, 32.31. Found: C, 64.90; H, 3.35; N, 32.21.

3-Amino-6*H*-indolo[2,3-*b*][1,8]naphthyridine (2a). A solution of 0.1 g of **13** in 120 mL of acetic acid was hydrogenated in the presence of 0.05 g of 10% Pd/C catalyst at 3 atm for 46 h at room temperature. After separation of the catalyst, the acetic solution was evaporated to dryness, and the obtained residue was treated with 10% NaOH solution, washed with water, and dried to give 0.04 g (44.4%) of **2a.**

3-Mercapto-6*H*-indolo[2,3-*b*][1,8]naphthyridine (2f). A. By Hydroxy Derivative 2b. A mixture of 0.3 g (1.27 mmol) of **2b** and 0.3 g (1.35 mmol) of P_2S_5 in 30 mL of anhydrous pyridine was refluxed for 2 h. The resulting warm solution was filtered and diluted with 300 mL of water. The obtained crude product was collected and purified by extraction with boiling CS_2 to remove a small quantity of sulfur and crystallized from DMF to give 0.25 g (78%) of **2f.**

B. By Chloro Derivative 2c. A sodium hydrosulfide–ethanol solution was prepared by passing H_2S for 30 min through 260 mL of absolute ethanol in which 0.16 g (6.95 mmol) of sodium metal had previously been dissolved. To this solution was added 0.260 g (1.02 mmol) of **2c** and the suspension was refluxed for 48 h. The resulting solution was reduced to half volume and, after cooling, filtered; addition of 10 mL of water and a few drops of concentrated HCl resulted in the precipitation of yellow solid, which was washed with water and collected to give 0.2 g (77.7%) of **2f.**

6*H*-Indolo[2,3-*b*][1,8]naphthyridine (2g). A suspension of 0.36 g of **2f** and 3 g of Raney nickel catalyst was refluxed and stirred for 8 h. The catalyst was separated by filtration and extracted several times with boiling ethanol. The combined extracts and solution were evaporated to small volume to give 0.15 g (47.7%) of **2g.** An analytical sample was obtained by crystallization from DMF, mp >320 °C.

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Registry No.—**11a,** 30167-89-6; **11b,** 30167-59-0; **11c,** 30167-85-2; **11d,** 61634-80-8; **11e,** 30167-60-3; **12,** 30167-81-8; **13,** 61634-81-9.

References and Notes

(1) (a) M. Hayat, G. Mathé, M. M. Janot, P. Potier, N. Dat-Xuong, A. Cavé, T. Sévenet, C. Kan-Fan, J. Poisson, J. Miet, J. Le Men, F. Le Goffic, A. Couyette, A. Ahond, L. K. Dalton, and T. A. Connors, *Biomedicine,* **21,** 101 (1974), and references cited therein; (b) G. H. Svoboda, G. A. Poore, and M. L. Montfort, *J. Pharm. Sci.,* **57,** 1720 (1968).

(2) (a) G. Büchi, D. W. Mayo, and F. A. Hochstein, *Tetrahedron,* **15,** 167 (1961); (b) K. N. Kilminster, M. Sainsbury, and B. Webb, *Phytochemistry,* **11,** 389 (1972), and references cited therein; (c) R. B. Woodward, G. A. Iacobucci, and F. A. Hochstein, *J. Am. Chem. Soc.,* **81,** 4434 (1959); (d) P. A. Cranwell and J. E. Saxton, *J. Chem. Soc.,* 3482 (1962); (e) K. N. Kilminster and M. Sainsbury, *J. Chem. Soc., Perkin Trans. 1,* 2264 (1972); (f) C. W. Mosher, O. P. Crews, E. M. Acton, and L. Goodman, *J. Med. Chem.,* **9,** 237 (1966); (g) E. Wenkert and K. G. Dave, *J. Am. Chem. Soc.,* **84,** 94 (1962); (h) T. Kametani, T. Suzuki, Y. Ichikawa, and K. Fukumoto, *J. Chem. Soc., Perkin Trans. 1,* 2102 (1975); (i) M. Sainsbury and R. F. Schinazi, *ibid.,* 1155 (1976); (j) M. Sainsbury, B. Webb, and R. F. Schinazi, *ibid.,* 289 (1975); (k) L. K. Dalton, S. Demerac, B. C. Elmes, J. W. Loder, J. M. Swan, and T. Teitei, *Aust. J. Chem.,* **20,** 2715 (1967); (l) T. Kametani, Y. Ichikawa, T. Suzuki, and K. Fukumoto, *Tetrahedron,* **30,** 3713 (1974); (m) R. Bessielevre, C. Thol, H. P. Hussan, and P. Potier, *J. Chem. Soc., Chem. Commun.,* 90 (1975); (n) R. W. Guthrie, A. Brassi, F. A. Mennana, J. G. Mullin, and R. W. Kierstead, *J. Med. Chem.,* **18,** 755 (1975); (o) Y. Langlois, N. Langlois, and P. Potier, *Tetrahedron Lett.,* 995 (1975); (p) F. Le Goffic, A. Gouyette, and A. Ahond, *Tetrahedron,* **29,** 3357(1973); (q) A. N. Fujiwara, E. M. Acton, and L. Goodman, *J. Heterocycl. Chem.* **5,** 853 (1968); (r) A. N. Fujiwara, E. M. Acton, and L. Goodman, *J. Med. Chem.,* **10,** 126 (1967).

(3) S. Carboni, A. Da Settimo, P. L. Ferrarini, and P. L. Ciantelli, *J. Heterocycl. Chem.,* **7,** 1037 (1970), and references cited therein.

(4) J. A. Hyatt and J. S. Swenton. *J. Org. Chem.,* **37,** 3216 (1969).

(5) J. B. Peterson and K. H. Lakowitz, *Acta Chem. Scand.,* **23,** 971 (1969).

(6) R. Y. Ning, P. B. Madan, and L. H. Sternbach, *J. Org. Chem.,* **38,** 3995 (1973).

(7) G. B. Marini-Bettolo and J. Schmutz, *Helv. Chim. Acta,* **42,** 2146 (1959).

(8) See, e.g., (a) C. Temple, Jr., and J. A. Montgomery, *J. Org. Chem.,* **30,** 826 (1965); (b) C. Temple, Jr., C. L. Kussner, and J. A. Montgomery, *ibid.,* **31,** 2210 (1966); (c) B. Stanovnik and M. Tišler, *Tetrahedron,* **23,** 387 (1967); (d) B. Stanovnik, M. Tišler, and P. Skufea, *J. Org. Chem.,* **33,** 2910 (1968).

(9) See, e.g., (a) R. N. Castle and K. Kaji, *Tetrahedron Lett.,* 393 (1962); (b) T. Kinoshita and R. N. Castle, *J. Heterocycl. Chem.,* **5,** 845 (1968); (c) S. F. Martin and R. N. Castle, *ibid.,* **6,** 93 (1969); (d) T. Nakashima and R. N. Castle, *ibid.,* **7,** 209 (1970); (e) S. Carboni, A. Da Settimo, D. Bertini, C. Mori, and I. Tonetti, *ibid.,* **8,** 637 (1971).

(10) (a) H. Auptmann and W. F. Walter, *Chem. Rev.,* **62,** 347 (1962); (b) M. Israel, L. C. Jones, and E. J. Modest, *J. Heterocycl. Chem.,* **9,** 255 (1972).

Synthesis and Reactivity of *anti,exo,exo*- and *anti,exo,endo*-Tetracyclo[5.4.0.$0^{2,5}$.$0^{8,11}$]undeca-3,9-dien-6-yl Tosylates. A Conformationally Restricted Bicyclo[3.2.0]hept-6-en-2-yl System

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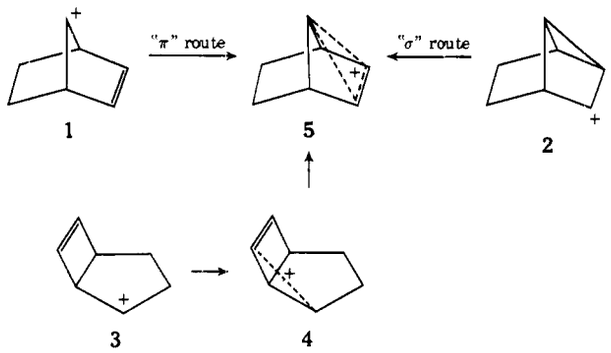
Synthesis of *anti,exo,exo*- and *anti,exo,endo*-tetracyclo[5.4.0.$0^{2,5}$.$0^{8,11}$]undeca-3,9-dien-6-yl tosylates (**11**-OTs and **10**-OTs, respectively) was carried out to investigate conformational effects on the reactivity and products of the bicyclo[3.2.0]heptenyl derivatives. The acetolysis rate of **11**-OTs indicates a rate enhancement of 65 (25 °C) when compared to that of *exo*-bicyclo[3.2.0]hept-6-en-2-yl tosylate (**12**-OTs) in spite of the fact that a similar transition state should be expected in their reactions. An exo/endo rate ratio of this rigid tetracyclic system (**11**-OTs/**10**-OTs = 12) is lower than that of the conformationally changed bicyclic system (**12**-OTs/**13**-OTs = 3500) by a factor of 290. Both **10**-OTs and **11**-OTs undergo acetolysis with stereospecific rearrangement to *exo,exo,syn*-tetracyclo[4.4.$1^{2,5}$.0.$0^{7,10}$]undeca-3,8-dien-11-yl acetate (**15**-OAc). Further, the *p*-nitrobenzoate (**15**-OPNB), obtained from **15**-OAc, possesses a solvolytic reactivity ca. 100 times as great as that of the *anti*-7-norbornenyl derivative (**19**). From the above results, the importance of conformational factors associated with Pitzer and *F* strains and of homoallylic and cyclobutyl participations is discussed in detail.

Interrelation of 7-norbornenyl **1** and tricyclo[2.2.1.-$0^{2,7}$]hept-3-yl **2** cations has provided many interesting aspects regarding the study of carbonium ion structure and reactivity.[1] Most recently, bicyclo[3.2.0]hept-6-en-2-yl carbonium ion **3**[2-7] has received a considerable amount of attention for an alternate route to the nonclassical carbonium ion (**5**) by way of

homoallylic interaction 4 between the cationic center and the double bond.

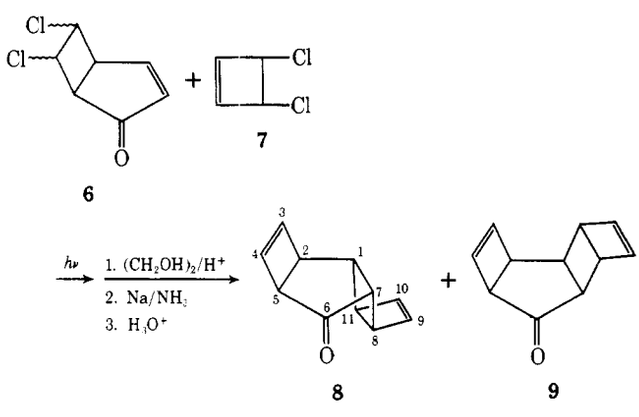


The exo:endo rate ratio (ca. 3500) of acetolysis of the bicyclo[3.2.0]heptenyl tosylates (**12**-OTs and **13**-OTs) and the difference of reactivity (ca. 21) between *anti*-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-yl tosylate **14**-OTs and **12**-OTs[6] have suggested the importance of homoallylic participation, conformational differences, and ground state–transition state energy differences to evaluate the solvolytic reactivity and products of the bicyclo[3.2.0]heptenyl derivatives.

In order to gain further information about these factors, it seems to be necessary to investigate a more rigid system containing the bicyclo[3.2.0]heptenyl ring in which the conformational factors are considered to be identical. Thus, *anti,exo,endo-* and *anti,exo,exo*-tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl tosylates (**10**-OTs and **11**-OTs, respectively) and, in addition, *exo,exo,syn*-tetracyclo[4.4.1^{2,5}.0.0^{7,10}]undeca-3,8-dien-11-yl *p*-nitrobenzoate (**15**-OPNB) have been synthesized and their solvolytic reactivity has been investigated. The present paper is concerned with presentation and comparison of these data with the previous results.[3,6]

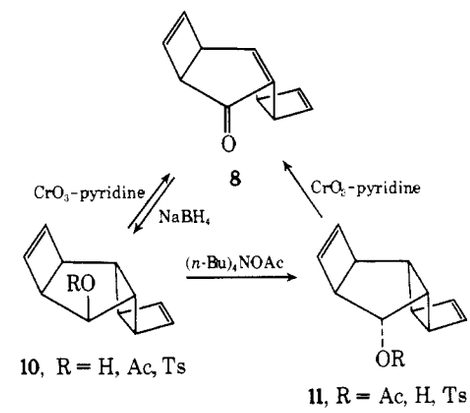
Results and Discussion

Photocycloaddition of 6,7-dichlorobicylo[3.2.0]hept-3-en-2-one (**6**)[8] and *cis*-3,4-dichlorocyclobutene (**7**) in methylene chloride, followed by ketalization, dehalogenation, and hydrolysis, gave a ca. 3:2 mixture of *anti,exo-* and *syn,exo*-tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-ones (**8** and **9**, respectively) in 17.6% overall yield. Their geometrical assignments were based upon the most plausible mechanism for the photocycloaddition of cyclopentenone with olefins[8,9] and upon the NMR spectral data of the vinyl protons of the ketones and the methine protons of the corresponding epimeric alcohols. The NMR spectra of both ketones show the presence of four vinyl protons at δ 6.30 (s, br, 3 H) and 6.04 (d, 1 H) for one and those at δ 6.60 (d, 1 H), 6.42 (m, 2 H), and 6.17 (d, 1 H) for the other. Since the NMR spectrum of a model compound, bicyclo[3.2.0]hept-6-en-2-one,[10] exhibits absorption of the vinyl protons at δ 6.27 (d, 1 H) and 6.07 (d, 1 H), the protons (H_9 and H_{10}) on the former ketone should correspond to the resonance band at δ 6.30 (2 H), and those on the latter to the resonance band at δ 6.42 (2 H). Further, the methine protons (H_6) of the epimeric alcohols (which will be discussed later) obtained from the former ketone show two doublets (coupled with H_5 and H_7) indicating the anti structure. On the other hand, the methine protons of the epimeric alcohols[11] from the latter ketone show a singlet for one and a triplet for the other indicating the syn structure.[12] On these bases, the former ketone was assigned to **8** and the latter to **9**.



This assignment is in good agreement with the solvolytic results which will be discussed later.

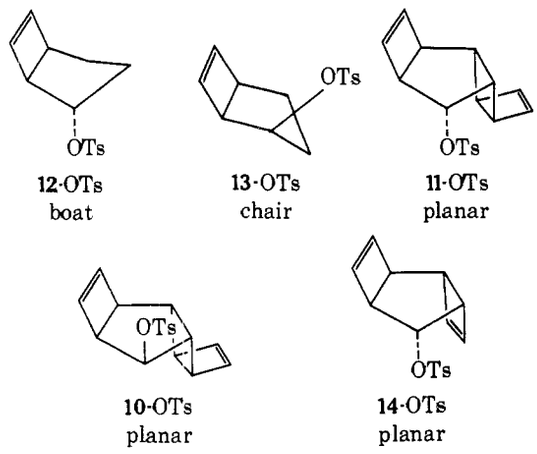
Reduction of **8** with sodium borohydride in methanol produced only one isomeric alcohol **10**-OH, which was converted to **10**-OTs (mp 73.0–74.0 °C) in the usual fashion. The exo alcohol (**11**-OH) was obtained by inversion of **10**-OTs with tetra-*n*-butylammonium acetate in dry acetone,[13] followed by lithium aluminum hydride reduction, and this alcohol was converted to **11**-OTs (mp 81.0–83.0 °C dec). The same skeleton of the epimeric alcohols was confirmed by formation of the starting ketone (**8**) from the oxidation reactions of **10**-OH and **11**-OH with chromium trioxide–pyridine.[14]



The relative stereochemistry of **10**-OH and **11**-OH was assigned on the basis of the induced changes in the chemical shifts of the vinyl protons (H_3 and H_4) comparing to those of H_9 and H_{10} in the presence of tris(dipivalomethanato)europium(III).[15] The alcohol with a larger magnitude of the changes of the chemical shifts of H_3 and H_4 was assigned to the endo epimer (**10**-OH), and the other to the exo epimer (**11**-OH). This assignment was supported by examination of the infrared spectra of these alcohols for intramolecular –OH···π absorption; **10**-OH showed a doublet absorption at 3636 (free OH) and 3616 cm^{-1} (–OH···π), whereas **11**-OH showed a singlet absorption at 3636 cm^{-1} (free OH).[16]

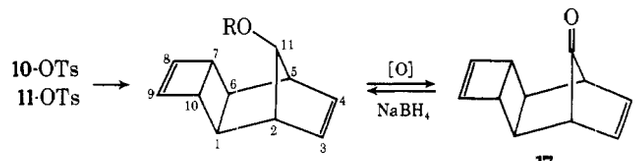
It has been suggested that the exo tosylate (**12**-OTs) is in a "boat" conformation and that the endo tosylate (**13**-OTs) is in a "chair" conformation on the basis of their NMR data.[2,6,7] In examining the NMR spectra of **10**-OTs, **11**-OTs, and **14**-OTs, it was found that the methine proton (CHOTs) of each tosylate has two doublets with coupling constants J = 2.3 and 7.7 Hz for **10**-OTs, J = 2.3 and 8.0 Hz for **11**-OTs, and J = 1.5 and 7.7 Hz for **14**-OTs. Using the Karplus equation[17] these values correspond to the dihedral angles of 121 and 14°, 121 and 9°, and 116 and 14°, respectively. The molecular models with the above dihedral angles indicate that these tosylates are nearly in the same conformation with a planar cyclopentane ring.

Acetolysis of **10**-OTs and **11**-OTs gave rise to *exo,exo,syn*-tetracyclo[4.4.1^{2,5}.0.0^{7,10}]undeca-3,8-dien-11-yl acetate (**15**-OAc, >95%) of which structure was assigned by its NMR spectral data compared to those of *exo,syn*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl acetate (**16**-OAc).[3] A charac-



teristic triplet peak of the vinyl protons H_3 and H_4 indicates an *anti*-7-norbornenyl acetate structure.[18] Further, the lack of significant coupling between H_1 and H_2[19] and the high-field chemical shift of H_1 and H_6 (δ 2.14, compared to δ 2.61 of 16-OAc) suggested the exo,exo orientation of the bicyclo[2.2.0]hexene ring.

In order to confirm this assignment, ketone **17** was prepared by oxidation of 15-OH obtained by lithium aluminum hydride



R = Ac, H, PNB

reduction of 15-OAc. The NMR spectrum of **17** indicates two different kinds of the vinyl protons at δ 6.45 (t, H_3 and H_4) and 6.24 (m, H_8 and H_9) supporting the structure of **17**. Furthermore, the selective hydride reduction of **17** to 15-OH supports the syn isomeric structure.

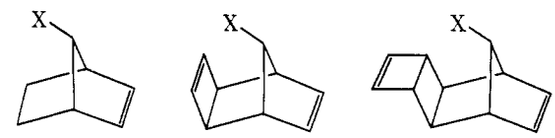
Attempts to convert 15-OH to its corresponding tosylate were unsuccessful, presumably because the tosylate is too reactive. Thus, *p*-nitrobenzoate 15-OPNB (mp 134.0–136.0 °C) was prepared in the usual fashion.

The solvolytic reactivity of 10-OTs and 11-OTs was measured in buffered acetic acid by the UV absorbance method,[3] and the rate of 15-OPNB was measured in 50% aqueous acetone by titrating the liberated *p*-nitrobenzoic acid. The reactions displayed nice first-order behavior. The kinetic data are summarized in Table I, where literature values for related compounds are included for comparison.

The exo tosylate (11-OTs) undergoes acetolysis at a rate 65 times faster than does the model compound (12-OTs), and is about 3 times more reactive than 14-OTs in spite of the fact that an analogous mechanism should be expected in their acetolysis reactions. Thus, the rate enhancement of 11-OTs, when compared to 12-OTs, is presumably associated to a large degree with a combination of relief of Pitzer strain[20] of the planar cyclopentane ring and relief of the ground state interaction of the leaving group with the cyclobutane ring (*F* strain)[21] in achieving the transition state. On the other hand, the slight rate acceleration (ca. 3) of 11-OTs compared to 14-OTs is probably due to a decreased reactivity of 14-OTs by an inductive effect of the additional double bond.[22]

It is of interest to compare an exo/endo rate ratio of this rigid tetracyclic system (11-OTs/10-OTs = 12)[23] with that of the conformationally changed bicyclic system (12-OTs/13-OTs = 3500).[6] The former rate ratio is lower than the latter by a factor of ca. 290, which mainly arises from a large increase in rate of 10-OTs compared to that of 13-OTs. Since the acetolysis rate of 13-OTs (2.70×10^{-9} at 25 °C) is comparable to that of 2-adamantyl tosylate (5.94×10^{-9} at 25 °C) which is reported to be an unassisted secondary tosylate (k_c-type behavior) by Schleyer,[24] the remarkable variation in relative rates between 10-OTs and 13-OTs must be attributed to their conformational differences (by a factor of ca. 10^2),[25] and anchimeric assistance by the cyclobutane[26] (by a factor of ca. 10^2)[25] in 10-OTs.

The *p*-nitrobenzoate (15-OPNB) is 5 times more reactive than 16-OPNB and ca. 6 times less reactive than 7-norbornadienyl *p*-nitrobenzoate (18-OPNB) at 125 °C. Thus, 15-OPNB is considered to possess a solvolytic reactivity approximately 10^2 times as great as that of *anti*-7-norbornenyl *p*-nitrobenzoate **19** assuming that 18-OPNB is ca. 10^3 more reactive than **19**.[27] These relative rates show that the increase

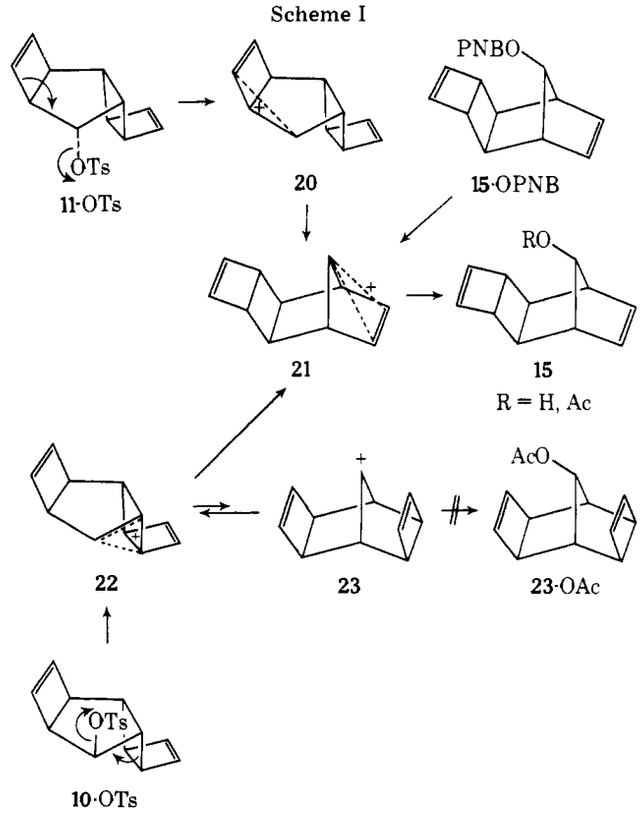


[a] K_{rel} in parentheses.

in reactivity in the series **19** → 15-OPNB is in line with an increase in ground state interaction (*F* strain) suggesting that the relief of *F* strain plays an important role in the different reactivity of these compounds.

The possible mechanisms for the reactions of 15-OPNB, 11-OTs, and 10-OTs are summarized in Scheme I. The hydrolysis of 15-OPNB quantitatively gives the unrearranged alcohol (15-OH) through a highly stabilized 7-norbornenyl carbonium ion (**21**) as expected from the results of solvolysis of **19** and 16-OPNB.[3]

Scheme I



The formation of 15-OAc from acetolysis of 11-OTs is in accord with a pathway of the initial stabilized carbonium ion (**20**) followed by a rapid rearrangement leading to **21** which gives 15-OAc by solvent attack as observed in the bicyclic system.[2-7] On the other hand, 10-OTs would produce **22**[28] by

Table I. Kinetic Data for Acetolysis of *anti,exo,endo*- and *anti,exo,exo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl Tosylates (10-OTs and 11-OTs, Respectively), and Hydrolysis of *exo,exo,syn*-Tetracyclo[4.4.1^{2,5}.0.0^{7,11}]undeca-3,8-dien-11-yl *p*-Nitrobenzoate (15-OPNB) and Related Compounds

Registry no.	Substrate	Temp, °C	k, s^{-1}	$H^{\ddagger}$, kcal/mol	$S^{\ddagger}$, eu	k_{rel}
61650-13-3	10-OTs[a]	25.0[e]	(5.05 ± 0.01) × 10^{-5} [f]	21.7 ± 0.1	−5.6 ± 0.1	
		50.0[e]	(9.27 ± 0.07) × 10^{-4} [f]			
61688-37-7	11-OTs[a]	16.9[e]	(1.88 ± 0.05) × 10^{-4} [f]			
		25.0[e]	(6.19 ± 0.06) × 10^{-4} [f]	24.6 ± 0.3	+9.4 ± 1.0	65
41326-96-9	14-OTs[c]	25	1.97 × 10^{-4}	25.2 ± 1.4	+9.0 ± 4.8	21
53585-69-6	12-OTs[d]	25	9.59 × 10^{-6}	23.9 ± 0.2	−1.5 ± 0.7	1.0
41326-98-1	13-OTs[d]	25	2.70 × 10^{-9}	28.1 ± 0.6	−3.6 ± 1.5	
61650-14-4	15-OPNB[b]	125.0[e]	(5.56 ± 0.06) × 10^{-4} [f]			5
61650-15-5	16-OPNB[c]	125	1.14 × 10^{-4}			1.0
33686-56-5	18-OPNB[c]	125	3.30 × 10^{-3}			29

[a] Ca. 0.02 M in acetic acid buffered with 0.045 M sodium acetate. [b] Ca. 0.006 M in 50% acetone–50% water (v/v). [c] Reference 3. [d] Reference 6. [e] ± 0.1 °C. [f] The errors are deviation from the average of two runs.

the anchimeric assistance of the cyclobutane. This ion may rapidly rearrange to the highly stabilized carbonium ion (**21**) rather than **23** by way of either a Wagner–Meerwein rearrangement or a new, different type carbonium ion. This should be expected from a striking difference in stability between **21** and **23** as a result of *exo,syn*- and *exo,anti*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl derivatives.[3]

The possibility for the rearrangement of 11-OAc, which is formed from 10-OTs through a solvent-assisted path, to 15-OAc under the acetolysis condition (50 °C, 26 h) is eliminated by examination of the stability of 11-OAc under the above condition.

Experimental Section

Melting points were taken on a Yamato MP-21 melting point apparatus and uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer and ultraviolet spectra were determined with a Shimadzu UV-200 spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Hitachi R-24 instrument with the chemical shift (δ) given in parts per million down from Me_4Si. Gas–liquid chromatography was performed on a Shimadzu GC-4B instrument. Mass spectra were determined with a JEOL-Q10 mass spectrometer. Microanalyses were determined in the microanalytical laboratory of the Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan.

***anti,exo*- and *syn,exo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-ones (8 and 9).** A mixture of 6,7-dichlorobicyclo[3.2.0]hept-3-en-2-one (**6**, 5 g) and *cis*-3,4-dichlorocyclobutene (**7**, 20 g) in 10 mL of methylene chloride was irradiated with a 100-W Hg lamp through a Pyrex probe for 24 h under nitrogen atmosphere. The unreacted cyclobutene **7** (16 g) was recovered by distillation to give a brown, oily residue. This residue was dissolved in a mixture of 100 mL of benzene and 60 mL of ethylene glycol with a few drops of sulfuric acid and the resulting mixture was refluxed until no water came out (usually 2 days). After neutralizing the mixture with dilute sodium bicarbonate solution the ketal was extracted with ether several times. The ethereal solution was washed with water once, dried ($MgSO_4$), and evaporated under vacuum to give a dark brown oil. This oil, dissolved in 50 mL of dry ether, was added to 500 mL of liquid ammonia. To the stirred solution was added sodium metal until the blue color persisted for 30 min. Excess ammonium chloride was added, and the ammonia was allowed to evaporate. After addition of water, the solution (200 mL) was added to 100 mL of 1.5 M hydrochloric acid, and the resulting mixture was allowed to stir at room temperature overnight. The organic layer was separated, and aqueous layer was extracted with ether three times. The combined ethereal solution was washed with 5% sodium bicarbonate solution once and water twice, dried ($MgSO_4$), and condensed to give a brown oil. This oil was purified twice by chromatography on a silica gel column eluting with 15% ether in pentane to give a ca. 3:2 mixture (17.6% overall yield) of **8** and **9**. *syn,exo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-one (**9**): IR (film) 3120, 3050, 2950, 1722 (>C=O), 1295, 1225, 1160, 1150, 900, 779, 740, and 680 cm^{-1}; NMR ($CDCl_3$ + CCl_4) δ 6.60 (d, 1, H, vinyl, J = 2.5 Hz), 6.42 (m, 2 H, vinyl), 6.17 (d, 1 H, vinyl, J = 2.5 Hz), 3.65 (s, br, 2 H), 3.46 (m, 1 H), 3.30 (m, 1 H), 2.90 (m, 1 H), and 2.59 (m, 1 H); mass spectrum *m/e* 158 (M$^+$). Although **9** appeared to be pure according to spectral data and GLC analysis, a satisfactory combustion analysis was not obtained. *anti,exo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]-undeca-3,9-dien-6-one (**8**): IR (film) 3120, 3050, 2950, 1722 (>C=O), 1290, 1220, 1160, 915, 820, 775, 730, and 665 cm^{-1}; NMR ($CDCl_3$ + CCl_4) δ 6.30 (s, br, 3 H, vinyl), 6.04 (d, 1 H, vinyl, J = 2.0 Hz), 3.60 (s, br, 1 H), 3.30–2.95 (4 H), and 2.53 (m, 1 H); mass spectrum *m/e* 158 (M$^+$).

Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.48; H, 6.38.

***anti,exo,endo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl Acetate (10-OAc).** To a solution of ketone **8** (300 mg, 1.90 mmol) in 30 mL of methanol was added sodium borohydride (35.9 mg, 0.96 mmol) at room temperature. The resulting solution was allowed to stir at room temperature overnight. After removal of the solvent, 10 mL of water was added, and the product was extracted with ether three times. The ethereal solution was washed with water, dried ($MgSO_4$), and concentrated under vacuum to give 300 mg of the endo alcohol (**10-OH**) as a clear liquid: NMR (CCl_4) δ 6.30 (m, 2 H, vinyl), 6.15 (s, 2 H, vinyl), 4.10 and 3.96 (2 d, 1 H, J = 2.3, 8.0 Hz), 3.73 and 3.59 (2 d, 1 H, J = 3.3, 8.0 Hz), 2.99 (2 H), 2.85 (1 H), and 2.63–2.22 (3 H).

A mixture of **10-OH** (51 mg, 0.32 mmol), sodium acetate (11.40 mg, 0.14 mmol), and acetic anhydride (33.49 mg, 0.33 mmol) in 5 mL of benzene was allowed to reflux at 95 °C for 24 h. After neutralization with 5% sodium bicarbonate solution, the resulting solution was extracted with ether three times. The ethereal solution was washed with water once, dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column eluting with 7.5% ether in pentane to give 34.06 mg of **10-OAc** (53%): IR (film) 3100, 3040, 2945, 1719 (>C=O), 1370, 1290, 1240, 1025, 910, 785, and 750 cm^{-1}; NMR (CCl_4) δ 6.30 (s, br, 2 H, vinyl), 6.07 and 5.95 (2 d, 2 H, vinyl, J = 2.7, 7.0 Hz), 4.81 and 4.70 (2 d, 1 H, J = 2.2, 7.0 Hz), 3.82 and 3.71 (2 d, 1 H, J = 3.6, 7.0 Hz), 3.28–2.80 (3 H), 2.79–2.27 (2 H), and 1.93 (s, 3 H, CH_3–).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.95; H, 7.04.

***anti,exo,endo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl Tosylate (10-OTs).** To a solution of **10-OH** (300 mg, 1.88 mmol) in 30 mL of pyridine was added *p*-toluenesulfonyl chloride (718 mg, 3.76 mmol) at −10 °C. The resulting solution was allowed to stand in a refrigerator for 5 days. The mixture was poured onto 100 g of ice with 3 mL of concentrated hydrochloric acid, and extracted with ether three times. The ethereal solution was washed with 5% sodium carbonate once and water twice, dried ($MgSO_4$), and evaporated under reduced pressure to give crystalline **10-OTs** (359 mg, 60%): mp 73.0–74.0 °C; IR (CCl_4) 3120, 3050, 2960, 1600, 1370 (–SO_2–), 1190 and 1180 (–SO_2–), 1095, 980, 920, 890, 865, 825, and 660 cm^{-1}; NMR (CCl_4) δ 7.78 and 7.30 (2 d, A_2B_2, 4 H, aromatic, J = 8.2 Hz), 6.22 (m, 2 H, vinyl), 6.03 (s, 2 H, vinyl), 4.71 and 4.59 (2 d, 1 H, J = 2.3, 7.7 Hz), 3.72 and 3.60 (2 d, 1 H, J = 3.0, 7.7 Hz), 3.10–2.82 (m, 3 H), 2.82–2.53 (m, 1 H), 2.47 (s, 3 H, CH_3–) and 2.52–2.27 (m, 1 H).

Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found: C, 68.68; H, 5.84.

***anti,exo,exo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl Acetate (11-OAc).** A solution of **10-OTs** (242 mg, 0.77 mmol) in 25 mL of tetra-*n*-butylammonium acetate–acetone solution (0.09 g/1 mL of acetone) was allowed to stir at 55 °C for 24 h.[13] After removal of the solvent water was added to the oily solution, and extracted with ether

three times. The ethereal solution was washed with dilute sodium bicarbonate solution once and water twice, dried ($MgSO_4$), and concentrated to give a crude acetate (151 mg). This acetate was purified by chromatography on a silica gel column eluting with 7.5% ether in pentane to give 67 mg of pure **11**-OAc (70%): IR (film) 3100, 3040, 2950, 1719 (>C=O), 1299, 1240, 1025, 910, 760, and 735 cm^{-1}; NMR (CCl_4) δ 6.29 (m, 2 H, vinyl), 6.05 (m, 2 H, vinyl), 5.03 and 4.90 (2 d, 1 H, J = 2.0, 9.6 Hz), 3.41 (s, br, 1 H), 3.31–2.70 (4 H), 2.40 (m, 1 H), and 1.96 (s, 3 H, CH_3–).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.08; H, 7.01.

***anti,exo,exo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl Tosylate (11-OTs).** Acetate **11**-OAc (67 mg, 0.33 mmol) was reduced with lithium aluminum hydride (12.6 mg, 0.33 mmol) in 5 mL of ether by stirring at room temperature for 2 days. After workup in the usual way, the exo alcohol, **11**-OH (51 mg), was obtained as a clear liquid: NMR (CCl_4) δ 6.31 (m, 2 H, vinyl), 6.07 (s, 2 H, vinyl), 4.32 and 4.21 (2 d, 1 H, J = 1.5, 7.0 Hz), 3.50–3.30 (2 H), 3.30–2.88 (3 H), and 2.60–2.10 (2 H).

This alcohol (50 mg) was converted to **10**-OTs (56.4 mg, 55%) by previously described procedure: mp 81.0–83.0 °C dec; IR (CCl_4) 3120, 3050, 2960, 1600, 1370 (–SO_2–), 1185 and 1175 (–SO_2–), 1095, 980, 955, 915, 880, 835, and 660 cm^{-1}; NMR (CCl_4) δ 7.78 and 7.32 (2 d, A_2B_2, 4 H, aromatic, J = 8.1 Hz), 6.26 (m, 1 H, vinyl), 6.15 (m, 1 H, vinyl), 6.03 (s, 2 H, vinyl), 4.95 and 4.79 (2 d, 1 H, J = 2.3, 8.0 Hz), 3.62–3.30 (m, 2 H), 3.20–2.96 (m, 2 H), 2.90 (m, 1 H), 2.46 (s, 3 H, CH_3–), and 2.46–2.29 (m, 1 H).

Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found: C, 68.33; H, 5.86.

***exo,exo,syn*-Tetracyclo[4.4.1^{2,5}.0.0^{7,10}]undeca-3,8-dien-11-ol (15-OH).** A solution of **10**-OTs (100 mg, 0.32 mmol) in 10 mL of anhydrous acetic acid buffered with 41 mg of sodium acetate was allowed to stand for 21 h at 50 °C. The resulting solution was neutralized with sodium bicarbonate and extracted with ether three times. The ethereal solution was washed with water twice, dried ($MgSO_4$), and evaporated under reduced pressure to give 70.1 mg of crude acetate **15**-OAc: NMR (CCl_4) δ 6.21 (s, br, 2 H, vinyl), 5.94 (t, 2 H, vinyl, J = 2.0 Hz), 4.40 (m, 1 H), 3.00 (2 H), 2.77 (2 d, 2 H, J = 1.5, 4.0 Hz), 2.14 (s, 2 H), and 1.90 (s, 3 H, CH_3–).

This acetate (70.1 mg, 0.35 mmol) in 2 mL of ether was added to a suspension of lithium aluminum hydride (13.2 mg, 0.35 mmol) in 10 mL of ether at room temperature. The resulting mixture was allowed to stir for 2 days. The product was isolated by ether extraction and recrystallized from hexane yielding 49.5 mg of **15**-OH (97%): mp 76.0–77.0 °C; IR (Nujol) 3300 (–OH), 1300, 1230, 1215, 1180, 1140, 1080, 820, 800, 730, and 680 cm^{-1}; NMR (CCl_4) δ 6.33 (s, br, vinyl), 5.95 (t, 2 H, vinyl, J = 1.8 Hz), 3.77 (s, br, 1 H), 3.25 (m, 2 H), 2.60 (2 d, 2 H, J = 2.0, 5.0 Hz), 2.16 (s, br, 2 H), and 1.98 (s, 1 H, –OH).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.54; H, 7.50.

***exo,exo,syn*-Tetracyclo[4.4.1^{2,5}.0.0^{7,10}]undeca-3,9-dien-11-yl p-Nitrobenzoate (15-OPNB).** To a solution of **15**-OH (100 mg, 0.63 mmol) in 15 mL of pyridine was added *p*-nitrobenzoyl chloride (232 mg, 1.25 mmol) at room temperature. The resulting mixture was allowed to stir at room temperature until the chloride dissolved completely, and then to stand in a refrigerator for 2 days. The mixture was poured onto ice and extracted with chloroform three times. The extract was washed with water, dried ($MgSO_4$), treated with charcoal, and concentrated under reduced pressure to give crystalline **15**-OPNB (168 mg, 87%): mp 134–136 °C; IR (Nujol) 1715 cm^{-1} (>C=O); NMR (CCl_4 + $CDCl_3$) δ 8.25 (A_2B_2, 4 H, aromatic, J = 8.0 Hz), 6.41 (s, br, 2 H, vinyl), 6.16 (t, 2 H, vinyl, J = 2.0 Hz), 4.89 (m, 1 H), 3.18 (s, br, 2 H), 3.00 (2 d, 2 H, J = 1.5, 4.0 Hz), and 2.30 (s, 2 H).

Anal. Calcd for $C_{18}H_{15}O_4N$: C, 69.89; H, 4.89. Found: C, 69.47; H, 4.99.

NMR Measurements in Presence of Eu(dpm)$_3$. Alcohol **10**-OH or **11**-OH (15–17 mg) were dissolved in 0.4 mL of carbon tetrachloride in a NMR tube. Eu(dpm)$_3$ (ca. 10 mg) was added to the solution and the resulting mixture was allowed to stand at 30 °C until the solution became clear. Then, it was used for the NMR measurement of the vinyl protons of the alcohol. The chemical shift differences are $\Delta\delta$ 1.95 (H_4), 1.03 (H_3), and 0.40 (H_9 and H_{10}) for **10**-OH and $\Delta\delta$ 0.40 (H_3, H_4, H_9, and H_{10}) for **11**-OH.

Oxidations of 10-OH and 11-OH. To a mixture of chromium trioxide (56.4 mg, 0.564 mmol) and pyridine (89.2 mg, 1.128 mmol) in 1.4 mL of methylene chloride was introduced a solution of **10**-OH or **11**-OH (15 mg, 0.094 mmol) in 0.4 mL of methylene chloride at room temperature.[14] After workup, the product (70–73%) was identified by NMR comparison of the ketone (**8**).

Reduction of *exo,exo*-Tetracyclo[4.4.1^{2,5}.0.0^{7,10}]undeca-3,9-dien-11-one (17). The procedure for the conversion of **15**-OH to **17** was used essentially as described above, 240.6 mg (1.50 mmol) of **15**-OH affording 189 mg (80%) of **17**: IR (film) 3045, 2960, 1780 (>C=O), 1320, 1290, 1240, 1175, 1095, 750, and 680 cm^{-1}; NMR (CCl_4) δ 6.45 (t, 2 H, vinyl, J = 2.1 Hz), 6.24 (m, 2 H, vinyl), 2.89 (m, 2 H), 2.65 (m, 2 H), and 2.16 (s, 2 H).

The alcohol (18 mg, 85%) from reduction of **17** (21 mg) with sodium borohydride (5.05 mg) was identified by NMR comparison of the starting alcohol (**15**-OH).

Kinetic Measurements. The acetic acid solvent was heated at reflux with acetic anhydride and sodium acetate overnight and distilled. Tosylate **10**-OTs or **11**-OTs (ca. 30 mg) was solvolyzed in 5 mL of the acetic acid containing sodium acetate (18.4 mg) at indicated temperature (Table I), and **15**-OPNB was solvolyzed in 50% aqueous acetone. The rates were measured as previously described.[3] The kinetic data are shown in Table I.

Stability of 10-OAc and 11-OAc under Acetolysis Conditions. Each acetate (10 mg) in 1 mL of the acetic acid buffer was sealed in a test tube under nitrogen. The tube for **10**-OAc was heated at 50 °C for 26 h, and the tube for **11**-OAc was heated at 25 °C for 12 h and at 50 °C for 26 h. Each cooled solution was neutralized, and each acetate extracted with ether was identified by NMR comparison of its starting acetate.

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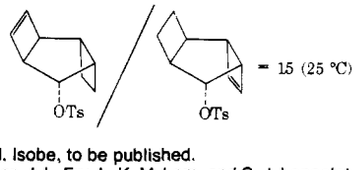
Registry No.—**6**, 25995-00-0; **7**, 2957-95-1; **8**, 61650-16-6; **9**, 61688-38-8; **10**-OH, 61650-17-7; **10**-OAc, 61650-18-8; **11**-OH, 61688-39-9; **11**-OAc, 61688-40-2; **15**-OH, 61650-19-9; **15**-OAc, 61650-20-2; **17**, 61650-21-3; ethylene glycol, 107-21-1; *p*-toluenesulfonyl chloride, 98-59-9; *p*-nitrobenzoyl chloride, 122-04-3.

References and Notes

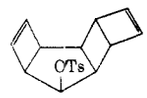
(1) (a) For a recent review, see P. R. Story and B. C. Clark, Jr., in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, pp 1019–1024; (b) J. J. Tufariello and R. J. Lorence, *J. Am. Chem. Soc.*, **91**, 1546 (1969); (c) J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969).
(2) S. C. Lewis and G. H. Whitham, *J. Chem. Soc. C*, 274 (1967).
(3) R. M. Coates and K. Yano, *J. Am. Chem. Soc.*, **95**, 2203 (1973).
(4) B. J. A. Cook and P. R. Story, *Tetrahedron Lett.*, 1705 (1974).
(5) T. Svensson, *Chem. Scr.*, **6**, 82 (1974).
(6) K. Yano, *J. Org. Chem.*, **40**, 414 (1975).
(7) B. J. A. Cook and P. R. Story, *J. Org. Chem.*, **40**, 2656 (1975).
(8) R. L. Cargill, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Org. Chem.*, **36**, 1423 (1971).
(9) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962).
(10) C. G. Scouten, F. E. Barton, J. R. Burgess, P. R. Story, and J. F. Garst, *Chem. Commun.*, 78 (1969).
(11) K. Yano and K. Yoshida, unpublished results.
(12) L. A. Paquette, O. Cox, M. Oku, and R. P. Henzel, *J. Am. Chem. Soc.*, **96**, 4892 (1974).
(13) S. Winstein, E. C. Friedrich, R. Baker, and Y. I. Lin, *Tetrahedron, Suppl.*, **8**, 621 (1966).
(14) R. Patcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).
(15) See Experimental Section.
(16) The author wishes to thank Mr. Y. Kuroishi at Saitama University for measurements of the IR spectra of these alcohols.
(17) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(18) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).
(19) D. H. Barton and N. H. Werstiuk, *J. Chem. Soc. C*, 148 (1968).
(20) (a) J. E. Kilpatric, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947); (b) K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959).
(21) (a) H. M. Hoffmann, *J. Chem. Soc. B*, 6753 (1965); (b) D. Cocker and M. L. Sinnott, *J. Chem. Soc., Chem. Commun.*, 414 (1972); (c) J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickason, and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 1969 (1974), and references cited therein.
(22) H. J. Reich and J. M. Renga, *Tetrahedron Lett.*, 2747 (1974), and references cited therein.
(23) Recently we observed a similar acetolysis rate ratio of the following compounds.



= 15 (25 °C)

K. Yano and M. Isobe, to be published.
(24) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Am. Chem.*

Soc., 92, 2542 (1970).
(25) These factors are roughly estimated from the rate ratios of I/13-OTs and 10-OTs/I.



I

$k = 3.54 \times 10^{-7}$ (25 °C)

K. Yano and K. Yoshida, unpublished result.
(26) S. Winstein, F. Gadient, E. J. Stafford, and P. E. Klinedinst, J. Am. Chem. Soc., 80, 5895 (1958).
(27) S. Winstein and C. Ordronneau, J. Am. Chem. Soc., 82, 2084 (1960).
(28) A rather small heat of activation and a negative entropy of activation for 10-OTs, when compared to those for 11-OTs, may also suggest a possible existence of the stabilized carbonium ion (22). However, owing to inaccuracy of these values of 11-OTs because of the narrow temperature range, it does not seem to be reasonable to discuss the possibility by comparison of those data.

Studies on $(CH)_{2n}$ Hydrocarbons. Alternative Syntheses of [3]Peristylane (Triaxane)

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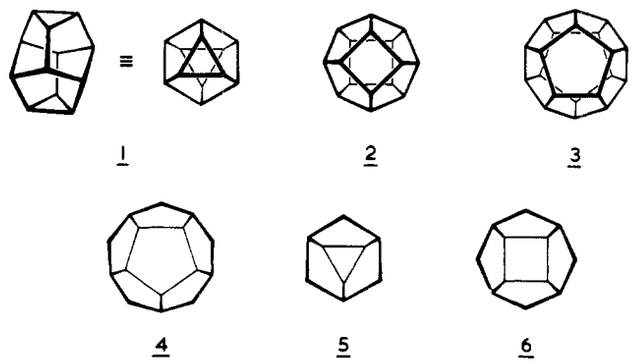
Two routes to [3]peristylane (**5**) are described, both starting from norbornadiene. Conversion of norbornadiene to *endo*- and *exo*-3-carboxybicyclo[3.2.1]octan-6-ene (**7**) was carried out by known procedures and the acid separated into the exo and endo isomers. Reduction of the endo isomer **7a** with lithium aluminum hydride gave the corresponding alcohol, which was reoxidized with *N*-chlorosuccinimide and dimethyl sulfide to the endo aldehyde **10**. The sodium salt of the corresponding tosylhydrazone **11** was pyrolyzed to 4,5-diazatetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene (**12**), which itself on pyrolysis gave [3]peristylane (**5**). Treatment of the endo acid **7a** with thionyl chloride led to the formation of *exo*-4-chloronoradamantan-2-one (**14**), which was reduced with sodium borohydride to the corresponding alcohol **15**. Reaction of **15** with thionyl chloride gave 2,4-dichloronoradamantane (**16**) which, on treatment with disodium naphthalenide, gave **5**. Reduction of **5** with hydrogen over PtO_2 gave noradamantane.

The $(CH)_{2n}$ hydrocarbons, for reasons of symmetry, have different properties when n is an odd to those when n is an even integer. This difference has been most clearly demonstrated in the case of the annulenes, those compounds in which n is odd being aromatic whereas those in which n is even are antiaromatic.[1,2] Similarly the topology of polycyclic saturated $(CH)_{2n}$ systems will also depend on the nature of n. We have been interested in the series of molecules composed of a central n-membered ring connected by alternate carbon atoms to two $n/2$-membered rings. Such systems are only possible when n is an even integer, and this type of system can be illustrated by the first three members of the series **1**, **2**, and **3**, in which n is respectively 6, 8, and 10.[3]



1 2 3

4 5 6

The only compound of this series which has received any extensive synthetic attention up to the present time has been dodecahedrane (**3**),[4,5] which has attracted interest as it represents one of the five Platonic solids, being composed entirely of planar five-membered rings.[6] Compounds **1** and **2** do not represent regular solids since the faces of the five-membered rings are not planar (see **1**). For the purpose of synthesis these systems can be dissected in a number of ways. Eaton and Mueller[4] have approached the synthesis of dodecahedrane by a route in which one of the five-membered rings is to be added in the final step, and they have prepared a derivative of the compound **4**, in which a five-membered ring is joined by alternate carbon atoms to a ten-membered ring. They have called this compound peristylane, but as it is a member of a second series of compounds in which an n-membered ring is joined by alternate carbon atoms to a $2n$-membered ring we would like to generalize their nomenclature and call this compound [5]peristylane. The related systems to **1** and **2** would then be [3]peristylane (**5**) and [4]peristylane (**6**),[6] which require the addition of a three- and a four-membered ring, respectively, to complete the $(CH)_{2n}$ system. [3]Peristylane has previously been prepared by Nickon and Pandit,[7] who called it triaxane, but we would prefer to use the peristylane nomenclature in the interest of economy of trivial nomenclature.[8] We now describe two alternative routes to **5** which we hope will be susceptible to extension to the synthesis of **1**.[9]

As **1** was our eventual synthetic goal, we wished to explore a route to **5** in which the intermediate would be capable of being modified so that substituents could be introduced at the appropriate positions. To this end, *endo*-bicyclo[3.2.1]oct-6-ene-3-carboxaldehyde (**10**) appeared to be a suitable precursor, since the preparation of compounds in which functional groups had been introduced at the 2, 4, and 6 positions, those necessary for construction of the final three-membered ring, seemed eminently feasible.

A mixture of *endo*- and *exo*-3-carboxybicyclo[3.2.1]oct-6-ene (**7**) was prepared in 14% yield from norbornadiene by the previously described route.[10,11] The exo and endo acids could be separated as previously described;[11] treatment with iodine in potassium iodide converted the endo acid into the iodolactone **8**, which could be separated and reconverted to the endo acid **7a** (ca. 70%) by treatment with zinc in ethanol. Lithium aluminum hydride reduction of **7a** gave the corresponding endo alcohol **9**, 89%, mp 30–32 °C. Oxidation of **9** by the method of Corey and Kim,[12] *N*-chlorosuccinimide and dimethyl sulfide, gave the colorless endo aldehyde **10**, mp