(13) R. E. Goldsberry, D. E. Lewis, and K. Cohn, *J. Organomet. Chem.*, **15**, 491 (1968).
(14) Cleavage of ethers by alkali organophosphides have also been reported which do not yield hydroxyalkylphosphines owing to the nature of the initial ether: (a) H. Schindlbauer, L. Gloser, and V. Hilzensauer, *Chem. Ber.*, **97**, 1150 (1964); (b) H. Schindlbauer and V. Hilzensauer, *Monatsh. Chem.*, **96**, 961 (1965); (c) K. B. Mallion and F. G. Mann, *Chem. Ind. (London)*, 1558 (1963); (d) K. B. Mallion and F. G. Mann, *J. Chem. Soc.*, 4115 (1965).
(15) S. O. Grim and R. P. Molenda, *Phosphorus*, **4**, 189 (1974).
(16) H. Gilman, *J. Org. Chem.*, **22**, 1165 (1957).
(17) A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, **27**, 1001 (1962); S. O. Grim, R. P. Molenda, and R. L. Kelter, *Chem. Ind. (London)*, 1378 (1970).
(18) It was later determined that **8** may be treated directly with the aqueous $NaHCO_3$ and Na_2CO_3 without prior dissolution in $HCCl_3$ and that the reaction may also be facilitated by warming the aqueous layer to a gentle reflux under N_2.
(19) F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 1634 (1947).
(20) F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 4107 (1955).
(21) M. H. Beeby and F. G. Mann, *J. Chem. Soc.*, 411 (1951).
(22) G. Märkl, *Angew. Chem., Int. Ed. Engl.*, **2**, 153 (1963).
(23) G. Märkl, *Z. Naturforsch.*, **186**, 84 (1963).
(24) K. Isslieb and H. Völker, *Chem. Ber.*, **94**, 392 (1961).
(25) For a summary of the synthesis of phosphines including asymmetric phosphines, see L. Maier in "Organic Phosphorus Compounds", Vol. 1, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 1.
(26) These phospholanium salts are slightly hygroscopic and have a tendency to precipitate as an oil. In those cases, the precipitates were dissolved in $HCCl_3$ and the aqueous layer was also extracted (3 × 100 ml) with $HCCl_3$. The $HCCl_3$ extracts were combined, dried ($MgSO_4$), and evaporated in vacuo to afford the solid products.
(27) G. Märkl, *Angew. Chem., Int. Ed. Engl.*, **2**, 620 (1963); G. Märkl, *Angew. Chem.*, **75**, 859 (1963).
(28) Multiple extractions with $HCCl_3$ and concentration of the aqueous solution are absolutely necessary in this case, since the perchlorate salt **14** was found to be appreciably soluble in H_2O.
(29) A ^1H NMR analysis has been previously reported with J_{PH} = 205, J_{HPCH} = 6.7 Hz; see J. P. Albrand, D. Gagnaire, and J. B. Robert, *J. Mol. Spectrosc.*, **27**, 428 (1968).
(30) K. B. Mallion and F. G. Mann, *J. Chem. Soc.*, 5716 (1964).

Synthesis and Solvolysis of Tricyclo[4.3.2.0^{2,5}]undeca-3,8,10-trien-7-ol. An Unusual $[CH]_{11}^+$ Rearrangement[1]

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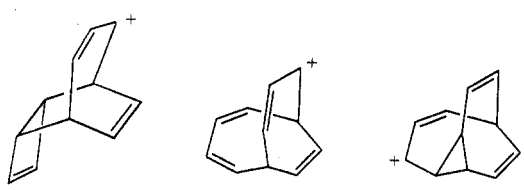
Synthesis of the title compound (**11**) has been achieved by two routes, the cycloaddition of cyclobutadiene to tropone and addition of tetrachlorocyclopropene to an appropriate bicyclo[4.2.0]diene (**6**) and subsequent transformations. Acetolysis of esters of **11** afforded a rearranged allylic acetate (**15**) and dihydroindenylenol acetate (**20**). Deuterium-labeling studies indicate that **20** derives from **15** via a bicyclo[2.1.0]pentane (**25**) and subsequent thermal fission. Activation parameters for this process ($\Delta H^\ddagger$ = 31.2 kcal/mol, $\Delta S^\ddagger$ = −6.2 eu) are in accord with the proposed mechanism.

Interest in the preparation and reorganization of $[CH]_n$ hydrocarbons and ions has been aroused by the surprising variety of rearrangements observed in these systems and by attempts to correlate experimental evidence regarding these energy surfaces to theoretical prediction. Particularly, the concepts of homoaromaticity,[2] bicycloaromaticity,[3] and spiroaromaticity[4] have served at least to focus attention on structures of importance. We were led to synthesize precursors of **1** in view of its relationship to the interesting ions **2** and **3**. Our expectations that **1** might lead to **2** or **3**



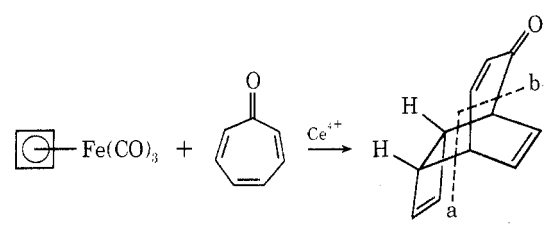
1 **2** **3**

were based upon the known σ participation of appropriately positioned cyclobutenes[5] and predictions regarding the stabilization of **2**.[3]

At the outset of this work no derivatives of the $[CH]_{11}$–X family of valence tautomers had been described. Since that time we[6] and others[7] have reported six other members of this series and a number of rearrangements relating them. We report here two independent synthetic approaches to the alcohol corresponding to **1** and evidence bearing on the mechanism of its unusual rearrangement to an enol acetate by thermal fission of a bicyclo[2.1.0]pent-2-yl intermediate.

Results and Discussion

Synthesis. Inspection of **4** suggested two attractive synthetic approaches, the annulation of a cyclobutene ring onto tropone (a) and the elaboration of an enone bridge onto an appropriate bicyclo[4.2.0]octane precursor (b). We have investigated both routes.



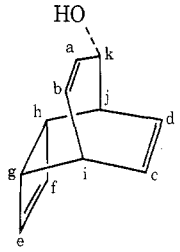
4

When cyclobutadiene was generated in situ[8] in the presence of freshly distilled tropone, only one volatile product was detected by analytical GLC. After column chromatography, a 14% yield of a 1:1 adduct was isolated. Of several possible isomers only **4** was consistent with the spectral data.

The presence of a single α,β-unsaturated carbonyl unit was indicated by the ^1H NMR spectrum (δ 7.0, 1 H, dd, J = 11, 8 Hz; δ 5.7, 1 H, dd, J = 11, 2 Hz) and an accordant ir spectrum (1680, 1640 cm^{-1}). A sharp singlet at δ 6.0 and an ir band at 1560 cm^{-1} were assigned to a cyclobutene. The spin-decoupled ^1H NMR spectrum revealed that the β carbon of the enone unit was adjacent to a bridgehead proton. Both the coupling constants and chemical shifts found in the ^1H NMR spectrum of enone **4** were in excellent agreement with those found in appropriate model compounds.[9]

While the direct, one-step approach to this ring system was successful, the yields of enone **4** remained uneconomical since excess cyclobutadieneiron tricarbonyl was used. In another approach (Scheme I) we have applied the known

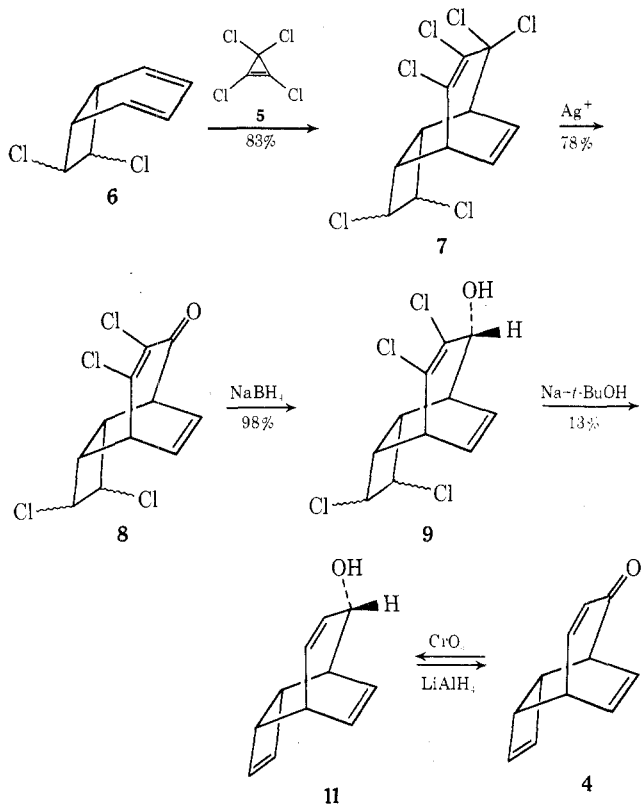
Table I
^{3}H NMR Spectrum of 11[a]



δ	a	b	c	d	e	f	g	h	i	j	k	Apparent multiplicity	ΔEu[b]
a	5.24	11 Hz							3 Hz		2.5 Hz	dt	5.4
	b	5.8							8 Hz				3.2
		c	6.10	8 Hz					8 Hz			t	1.2
			d	5.72						8 Hz		t	2.4
				e	5.96	2.7 Hz						d	1.1
					f	5.80						d	1.4
						g	3.16	3 Hz	3 Hz			t	2.4
							h	3.45		1–2 Hz		br s	5.6
								i	2.62			br t	2.0
									j	2.39	3 Hz	br d	5.1
										k	4.25	br s	2.2

[a] Diagonal elements are chemical shifts (δ) obtained in CCl_4; off-diagonal elements are coupling constants (hertz) assigned by decoupling. [b] Pseudocontact shifts for Eu(fod)$_3$.[16]

Scheme I



cycloaddition–ring opening reaction of tetrachlorocyclopropene[10] (**5**) with dienes to 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene (**6**). Thus, heating **6** in a large excess of **5** at 75° for 3 weeks[11] afforded hexachloride **7**, a mixture of stereoisomers, in 83% yield.

A more classical approach, Diels–Alder addition of acetoxyacrylonitrile, with the intent of subsequent ring expansion, produced no cycloadduct.[12]

When the hexachloride **7** was hydrolyzed with silver nitrate in aqueous dioxane, a 78% yield of a tetrachloro ketone **8** was isolated. Subsequent reduction with sodium borohydride without isolation of **8** led to the corresponding alcohol **9** in equally good yield from **7**.

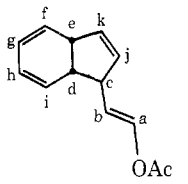
Reductive dehalogenation of **9** and several obvious derivatives under a variety of conditions was exceedingly complex. Under optimum conditions, treatment of **9** with sodium-*tert*-butyl alcohol[13] and oxidation of the crude product mixture with CrO_3–pyridine[14] afforded a 13% yield of **4** identical in every respect with the product. The remainder of the reaction product contained appreciable amounts of the corresponding hydrocarbon (**10**).[15]

The allylic alcohol **11** (ir 3540, 3400, 1025 cm^{-1}) was obtained in excellent yield from the reduction of enone **4** with lithium aluminum hydride in ether. The spectral data for **4** left the stereochemical relationship of the four-carbon and three-carbon bridges in doubt. By analysis of the europium-shifted and spin-decoupled ^{1}H NMR[16] spectrum of **11** (Table I), it was possible to definitively assign the stereochemistry.

The magnitudes of the pseudocontact shifts for the protons k (ΔEu 22 ppm), a (5.4 ppm), and j (5.1 ppm) are as expected for an allylic alcohol of this structure. However, the relatively large contact shift for proton h (5.6 ppm) indicates that one of the cyclobutene methine protons is spatially close to the hydroxyl group. This fact simultaneously fixes the stereochemistry of the alcohol and the cyclobutene bridge, and it becomes possible to identify **11** as (1α,2β,5β,6α,7β)tricyclo[4.3.2.0^{2,5}]undeca-3,8,10-trien-7-ol. From this stereochemical assignment, it is evident that the reduction of enone **4** has occurred with preferential approach of the hydride reagent from the α side, presumably reflecting the steric hindrance of the cyclobutene methine protons. In addition, the related stereochemistry of enone **4** indicates that cyclobutadiene has reacted as a reactive dienophile in accord with the endo rule.[17,18] The thermal reactivity of cyclobutadiene in this instance is in marked contrast with its photochemical reaction in the presence of tropone ketal, which leads to a [2 + 6] cycloadduct (eq 1).[19]

The 3,5-dinitrobenzoate (**12**) and the acetate **13** could be

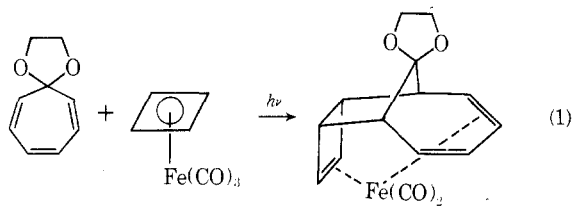
Table II
^{3}H NMR (CCl_4) Spectral Data of 20[a]



20

δ	a	b	c	d	e	f–k	Ac	Apparent multiplicity
a	7.05	12.8 Hz	1.0 Hz					d, d
	b	5.18	9.8 Hz					d, d
		c	3.48 Hz	8.2 Hz		$J_{c,j}$ = 1 Hz		t
			d	3.12	12.3 Hz	$J_{d,i}$ = 3.9 Hz		Heptet
				e	3.62			d
					f–k	5.70		m
						Ac	2.08	s

[a] Ir ($CDCl_3$) 3030, 2950, 2890, 1765, 1740, 1430, 1375, 1290, 1250, 1225, 400 cm^{-1}; uv (95% EtOH) λ_{max} 213, 255, 262, 272 nm (ϵ_{262} 3100); MS *m/e* (rel intensity) 202 (6.1), 160 (72), 142 (100, base), 104 (81), 95 (62), 91 (71); ^{13}C NMR ($CDCl_3$) from Me_4Si 167.8, 135.0, 133.2, 132.8, 126.1, 125.8, 123.0, 120.7, 116.2, 49.7, 43.6, 38.2, 14.7 ppm.

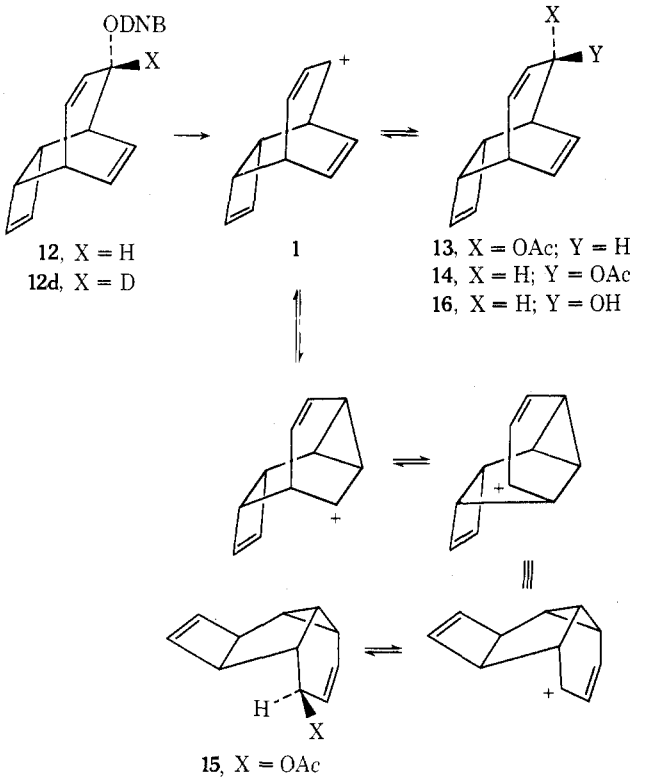


(1)

synthesized in excellent yield by the reaction of **11** with 3,5-dinitrobenzoyl chloride and acetic anhydride, respectively. Both **12** and **13** were shown to be unrearranged by their reduction with lithium aluminum hydride to afford only **11**.

Solvolysis. When **12** was solvolyzed in acetic acid at 118° for 4 hr, three isomeric acetates (**13, 14,** and **15**) were isolated in 100% yield (relative amounts 1.5:1.5:1). Compound **13** was identical with the product of acetylation of alcohol **11**. Compound **14** was epimeric with **13** as demonstrated by its reduction to alcohol **16** and oxidation to afford enone **4**.

Scheme II



12, X = H
12d, X = D

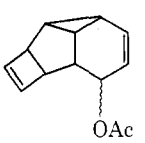
1

13, X = OAc; Y = H
14, X = H; Y = OAc
16, X = H; Y = OH

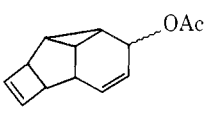
15, X = OAc
17, X = OH

The structure of the remaining acetate (**15**) was determined by analysis of its ^{1}H NMR spectrum. That a cyclobutene ring was present in the molecule was signaled by the two ^{1}H NMR doublets at δ 6.32 and 6.02 (J = 3 Hz[20a]). A three-hydrogen absorbance at δ 1.56 was assigned to a cyclopropyl ring, and the presence of an additional vinyl unit was evidenced by protons at δ 5.98 and 5.56. When **15** was reduced to the corresponding alcohol **17** with lithium aluminum hydride, a chemical shift of δ 4.48 was observed for the hydroxy methine proton and the resonance at δ 5.56 decreased from two protons to one proton. Accordingly, the acetoxy methine proton in **15** also comes at δ 5.56, a chemical shift too low for any acetate other than an allylic acetate.[20b]

On this basis the only reasonable structures for **15** are among the epimers of **18** and **19**. On mechanistic grounds



18



19

and the observation that **15** is in equilibrium with **13** and **14** in acetic acid at 118°, we tentatively assign the structure **15** (Scheme II).

When a solution of dinitrobenzoate **12** or acetate **13** was heated in acetic acid at 190°, the same mixture of three acetates (**13, 14,** and **15**) was initially formed. These products subsequently rearranged over 2 hr to afford a fourth isomer **20**. Analysis of spectral data for **20** indicated that it was a trans enol acetate ($\nu_{C=O}$ 1765 cm^{-1}, δ 7.05, d, 1 H, J = 12.8 Hz)[21] with no cyclobutene protons evident among the eight vinyl hydrogens (Table II).

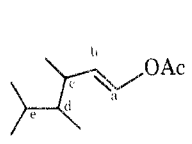
Spin decoupling of the ^{1}H NMR spectrum of **20** located the β carbon of the enol acetate adjacent to a bridgehead proton with J_{bc} = 9.8 Hz. The bridgehead proton, H_c, was shown to be adjacent to only one bridgehead proton, H_d, with $J_{c,d}$ = 8.2 Hz and H_d, in turn, was adjacent to the remaining bridgehead proton H_e with $J_{d,e}$ = 12.3 Hz, completing the structural unit **21**.

Table III
Vinyl Carbon Resonances for 20, 22, and 23

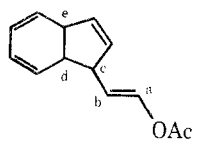
	Assignment					
	Cyclopentene		Cyclohexadiene			
20	133.2[a]	132.8	126.1	125.8	123.0	120.7
22	138.7	128.8	126.5	125.1	121.8	121.3
23	134.8	128.8	127.9	125.7	121.7	121.0

[a] Chemical shifts in parts per million downfield from Me_4Si.

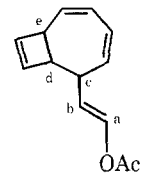
There are only two reasonable $[CH]_{11}$ structures (**20a** and **20b**) with three remaining double bonds which contain this connectivity.[22]



21



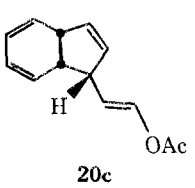
20a



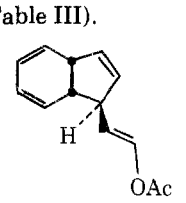
20b

The structure **20b** is eliminated on the basis of two pieces of information. The observed uv extinction coefficient (ϵ 3100) is too small for a homoannular diene in a seven-membered ring (ϵ 8000),[23] and is similar to those found in *cis*- and *trans*-3a,7a-dihydroindenes (ϵ_{cis} 4580, ϵ_{trans} 3700).[24] In addition the magnitude of the coupling constant, $J_{d,e}$ = 12.8 Hz, is too large for a cyclobutene ring and is only consistent with a cis-fused 3a,7a-dihydroindene.[25]

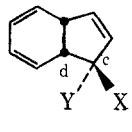
The stereochemical assignment for the attachment of the enol acetate group was more difficult and rests on an analysis of the ^{13}C NMR spectrum (Table III). The resonances at δ 135.0 and 116.2 were unambiguously assigned to the α and β carbons of the enol acetate group, respectively, by heteronuclear spin decoupling of the corresponding proton resonances. Calculation of the chemical shifts for these carbons is expected to be relatively accurate, since they are not part of the ring system. By applying the empirical parameters of Roberts[26] with vinyl acetate[27] as a model compound, calculated values of δ 134.6 and 116.8 are obtained for carbons a and b in **20**, in excellent agreement with the observed shifts. Particularly significant is the close agreement for carbon b. One consequent difference between epimers **20c** and **20d** is the very close approach of carbons b and i in **20c**. This spacial proximity would be expected to exert a strong shielding effect[28] (~4–5 ppm) on the interacting carbon atoms. Given the agreement of calculated and observed chemical shifts for carbon b, no such effect is evident and structure **20d** must be preferred. A similar argument can be constructed for carbon i, since there is close agreement in chemical shift for all the diene carbons in **20**, **22**, and **23** (Table III).



20c



20d



22, X = OAc; Y = H
23, X = COOEt; Y = H

Mechanism. To establish the mechanism for the formation of **15** and the unusual subsequent transformation to **20**, we have examined the acetolysis of deuterated benzoate **12-*d***. Integration of the ^1H NMR spectrum of **15-*d*** isolated from a solvolysis at 120° indicated the presence of 0.5 deuterium atom at the vinyl position adjacent to the acetoxymethine and 0.5 deuterium atom among the cyclopropyl protons consistent with Scheme II. Interestingly, the deuterium distribution in the recovered epimers **13-*d*** and **16-*d***, as determined by integration of the ^1H NMR spectra of the corresponding alcohols, revealed incomplete allylic scrambling presumably owing to some SN2 solvolysis.

Table IV
^{13}C NMR Spectrum of 20-*d*

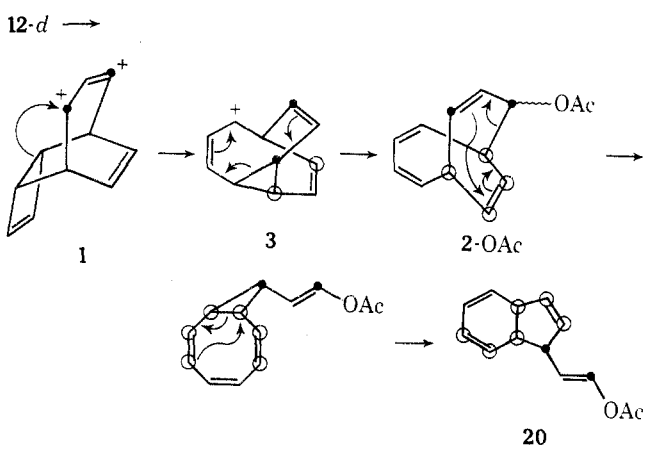
Carbon	δ Obsd	δ Calcd[26]	Rel D intensity	1st order multiplicity
a	135.0[a]	134.6		s
b	116.2[a]	117.8		s
c	49.7	49.3		Slight br
d	43.6	44.1		s and d
e	38.2	39.5		Slight splitting
f	120.7	125.0	0.1	t
g	126.1	126.4	0.4	t
h	125.8	127.9	0.1	1:1 d
i	123.0	123.5	0.4	t
j	133.2	132.8		s
k	133.3	130.3		s

[a] Assignment confirmed by heteronuclear spin decoupling.

At higher temperatures, under conditions leading to the formation of **20-*d***, the deuterium was found to be more widely distributed in all solvolysis products and, accordingly, ^1H NMR integration became less reliable. A definitive assignment of the deuterium distribution in **20-*d*** was made by analysis of its ^{13}C NMR spectrum, since individual carbon resonances could be assigned with some certainty. Virtually all the deuterium was found among the carbons of the conjugated diene unsymmetrically disposed (Table IV).

This distribution severely limits the range of mechanisms which might give rise to **20**. One mechanism to which we gave much initial attention because of the clear precedent for the thermal steps (Scheme III) is clearly inconsistent with the complete lack of deuterium content in the five atoms not part of the cyclohexadiene ring.

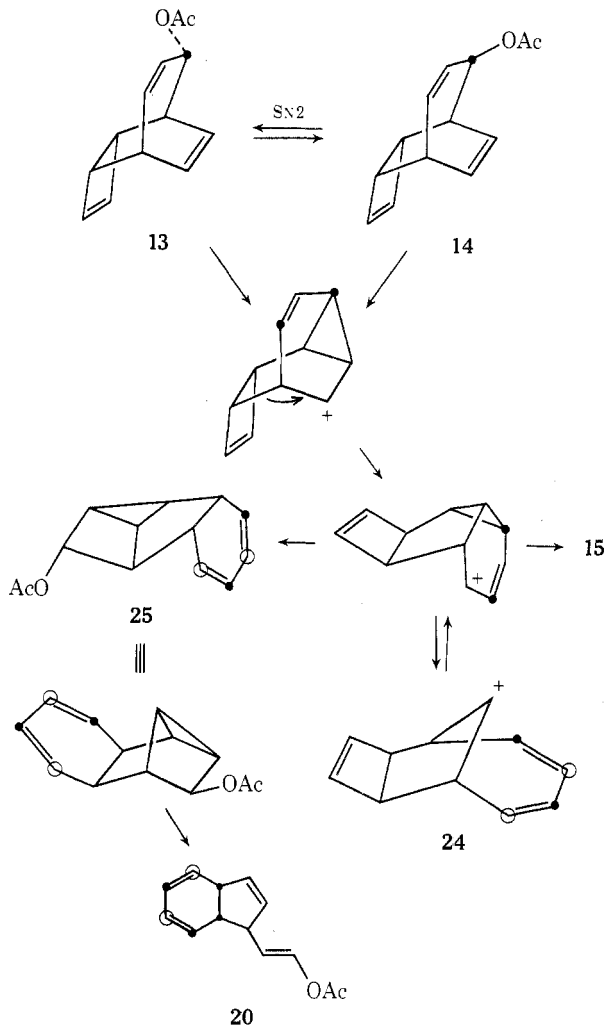
Scheme III



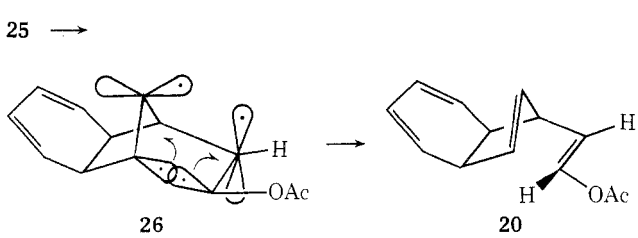
Scheme IV, involving an intermediate bicyclopentane (**25**), accounts for all the observations: incomplete allylic scrambling in the starting material, the intermediacy of **15**, the deuterium distribution in **20**, the formation of an enol acetate, and the exact stereochemistry of **20**.

The formation of an unseen intermediate (**25**) is supported by the thermal stability of **13**, **14**, and **15** at 200° in benzene. Additional evidence is derived from the kinetics for the formation of **20** (Table V) which gave good pseudo-first-order parameters, $\Delta H^{\ddagger}$ = 31.2 kcal/mol, $\Delta S^{\ddagger}$ = −6.2 eu.

Scheme IV



The solvolysis of *exo*-2-bicyclo[2.1.0]pentanes is known to be slow and proceeds via homolytic opening of the central bond.[28] Typical activation barriers for this process (32–38 kcal)[29] are in reasonable agreement with those measured for **20.** Further ring opening of the resultant 1,3-diradical is normally observed to have a substantially higher energy barrier[30] but this is almost quantitatively accounted for by the expected relief of a ca. 18 kcal of ring strain for the norbornyl system in **26.**[31] The more usually encountered hydrogen migration in 1,3-diradicals[32] would lead in this case to an untenably strained olefin.

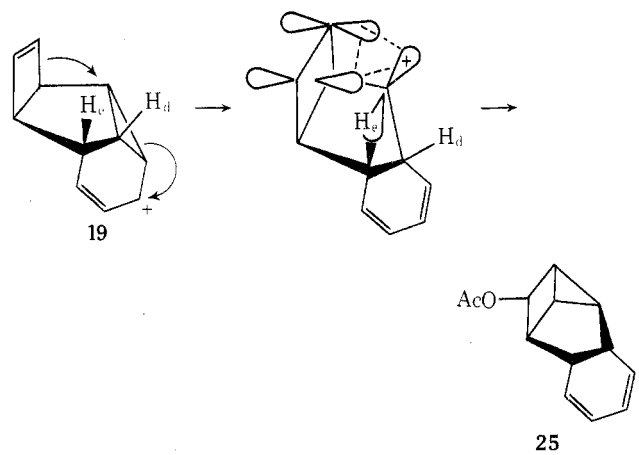


The formation of **25** is also of interest. Stereoelectronic control of the capture of the developing cyclobutyl carbonium ion would give rise to **25,** an *exo*-2-bicyclo[2.1.0]pentane. Least motion opening of the bicyclopentane would then lead to the observed trans enol acetate (**20**). More details regarding the mode of ring opening of constrained bicyclopentanes will have to await the isolation of compounds such as **25.**

Table V
First-Order Rate Constants for Rearrangement of 13, 14, and 15[a] in Acetic Acid

Temp, K[b]	Rate constant, sec^{-1}	Temp, K[b]	Rate constant, sec^{-1}
425.75	$3.7 \pm 0.7 \times 10^{-5}$	440.95	$1.5 \pm 0.2 \times 10^{-4}$
430.95	$5.4 \pm 0.6 \times 10^{-5}$	445.05	$2.2 \pm 0.3 \times 10^{-4}$
435.45	$1.4 \pm 0.2 \times 10^{-4}$	455.25	$4.2 \pm 0.4 \times 10^{-4}$

[a] Substrate concentration. [b] ±0.05°.



Recent developments in our laboratories[33] have succeeded in generating **3** under solvolytic conditions. This ion has been found to lead only to covalent derivatives of **2.** The failure to achieve the anticipated ring-opening reaction **1** ⟶ **3** thus leads to the conclusion that no great lowering of the barrier to cyclobutene ring opening is achieved by virtue of the adjacent allylic cation. More specifically, the transition state leading to **3** from **1** must be higher in energy than that reported here leading from **1** to **25** and, accordingly, any stabilization present in **3** is not manifested in the chemistry of **1** below 31 kcal/mol.

Experimental Section

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer grating spectrophotometers, Model 237B or Model 457. Ultraviolet spectra were obtained on a Cary 14 recording spectrophotometer. Varian T-60 and Jeol PS-100 nuclear magnetic resonance spectrometers were used to obtain ^1H NMR and ^{13}C NMR spectra. Mass spectra were obtained on an AEI MS-902 mass spectrometer.

Analytical GLC data were obtained with a Varian Aerograph gas chromatograph, Model 1200, equipped with a flame ionization detector. A Varian Aerograph 90-P gas chromatograph equipped with a thermal conductivity detector was used for preparative GLC. Brinkmann thin layer plates precoated with silica gel (0.25 and 2 mm) and fluorescent indicator were used for analytical and preparative thin layer chromatography, respectively. Woelm silica gel and basic alumina (0.05–0.2 mm) activity I was used for column chromatography, and dry column chromatography was done with Woelm silica gel with fluorescent indicator, "dry column chromatography grade".

Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Synthesis of Tricyclo[4.3.2.0^{2,5}]undeca-3,8,10-trien-7-one from Tropone. A solution of 2.86 g (0.015 mol of freshly distilled cyclobutadieneiron tricarbonyl and 0.86 g (0.008 mol) of freshly distilled tropone in 250 ml of reagent-grade acetone was cooled to −5° using an ice–salt bath. The system was maintained under argon. A flask containing 13.9 g (0.025 mol) of ceric ammonium nitrate was attached to the reaction system with a piece of Gooch tubing. The solution was stirred rapidly while the ceric ammonium nitrate was added in several small portions over a period of 30 min.

After stirring for an addition 2 hr, the dark brown reaction mixture was poured into 400 ml of 16% aqueous sodium chloride solu-

tion and washed with 3 × 200 ml of ether. The combined organic layers were washed with 250 ml of water and 200 ml of saturated sodium chloride. The ether layer was dried over anhydrous sodium sulfate and filtered, and the ether was removed under reduced pressure to yield 0.51 g of a dark brown oil.

The crude product was then chromatographed on 50 g of silica gel. Elution with 300 ml of benzene, followed by 2% ether–benzene, yielded 0.23 g (14.5%) of enone **4** as a pale yellow oil: ir (CCl_4) 3040, 2920, 1680, 1640, 1565, 1385, 1300, 1260, 1240, 1200, 1165 cm^{-1}; uv (ether) λ_{max} 229 nm (ϵ 4850), 256 (1950), 290 (266); MS *m/e* (rel intensity) (70 eV) 160 (0.5), 159 (7.5), 158 (55.9), 157 (32.0), 129 (83.2), 128 (41.2), 115 (44.4), 103 (34.5), 78 (100); ^{1}H NMR ($CDCl_3$) δ 7.0 (dd, 1 H, J = 11, 8 Hz), 6.2 (t, 1 H, J = 8 Hz), 6.0 (s, 2 H), 5.9 (t, 1 H, J , 8 Hz), 5.7 (dd, 1 H , J = 11, 2.2 Hz), 3.44 (d, 1 H, J = 8 Hz), 3.25 (t, 1 H, J = 8 Hz), 3.18 (br, s, 2 H); ^{13}C NMR ($CDCl_3$) δ 196.5, 152.0, 139.0, 136.0, 133.5, 130.0, 124.0, 55.9, 48.0, 42.4, 39.5.

Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.41; H, 6.36.

Tricyclo[4.3.2.0^{2,5}]undeca-3,4,7,7,8,9-hexachloro-8,10-diene (7). A stirred neat solution of 300 g (1.69 mol) of tetrachlorocyclopropene and 58 g (0.33 mol) of 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene was flushed with a fine stream of argon and the mixture was maintained at 75° with stirring for 3 weeks.

The reaction mixture was then allowed to cool to room temperature and the unreacted tetrachlorocyclopropene was removed by flash distillation (35–80°C, 0.1 mm), leaving 100 g of crude **7** as a pale tan, viscous oil, 83.5% yield.

Hexahalide **7** could be partially purified by trituration with pentane and recrystallization from petroleum ether, mp 120–136° (mixture of epimers at C-3 and C-4). Analytical GLC showed that crude **7** consisted of two major components with retention times of 11 and 12 min (SE-30, 100–200°).

Tricyclo[4.3.2.0^{2,5}]-3,4,8,9-tetrachloro-8,10-dien-7-one (8). A 2-l. three-neck round-bottom flask was equipped with a stirring rod and Teflon paddle, thermometer, and reflux condenser. Silver nitrate (100 g, 0.6 mol) was dissolved in 200 ml of distilled water and 700 ml of *p*-dioxane. This solution was then maintained at 55–65° while stirring and 100 g (0.28 mol) of hexahalide **7** dissolved in 100 ml of *p*-dioxane was added at once to the silver nitrate solution. The reaction mixture was then maintained at 55–65°, with stirring, for 20 hr.

The reaction mixture was then cooled and the silver chloride was removed by suction filtration. Saturated sodium chloride was added to the clear filtrate until the silver chloride precipitation ceased. The reaction mixture was filtered and used without purification for the sodium borohydride reduction. Dry silver chloride (62 g) was isolated (78%): ir (film) 3050, 2980, 2940, 1715, 1615, 1590, 1265, 860, 780, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.65 (t, 1 H, J = 8 Hz), 6.3 (t, 1 H, J = 8 Hz), 3.9 (m, 4 H), 3.2 (m, 2 H).

Tricycyo[4.3.2.0^{2,5}]undeca-3,4,8,9,-tetrachloro-8,10-dien-7-ol (9). The clear yellow dioxane–water solution of **8** (described above) was cooled to 0° in a 3-l. three-neck flask, equipped with an addition funnel, stirring rod with Teflon paddle, and a reflux condenser. A solution of 38 g (1.0 mol) of sodium borohydride in 1 l. of 95% ethanol was added dropwise over 1 hr while stirring. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was then heated at 80° for an additional 4 hr. Upon evaporation of solvent, the oily two-phase residue was washed with 3 × 300 ml of chloroform. The combined organic layers were dried over anhydrous sodium sulfate and filtered. Removal of the solvent under reduced pressure yielded 60 g (71.5%, calcd from **7**) of a viscous tan oil. Analysis of this oil by analytical GLC (SE-30, 100–200°) showed that it consisted of three major components (10.5, 11.0, 12.0 min), assumed to be epimers at C-3 and C-4.

Tricyclo[4.3.2.0^{2,5}]3,8,10-trien-7-one (4) from 9. A three-neck 1-l. round-bottom flask, equipped with a 250-ml addition funnel, Herchberg stirrer, reflux condenser, and gas bubbler, was flame dried under a nitrogen atmosphere. A suspension of 15 g (0.66 g-atom) of finely cut sodium in 400 ml of dry tetrahydrofuran was heated to reflux while stirring rapidly. Dry *tert*-butyl alcohol (5.0 g) was added to the refluxing suspension just prior to the addition of tetrachloro alcohol **9**. A solution of 5.0 g (0.017 mol) of crude **9**, 25 g of *tert*-butyl alcohol (total 30 g, 0.66 mol), and 100 ml of tetrahydrofuran was added dropwise over 1 hr. The vigorously stirred solution was maintained at reflux for an additional 8 hr, or until the sodium formed a large shiny lump. (Caution: the reaction cannot be left unattended after the first 2 hr of reaction time as the sodium ball can destroy the reaction vessel with rapid stirring).

The reaction was cooled in an ice bath and methanol was added slowly with gentle stirring, until the sodium was completely reacted.

The reaction mixture was poured into 400 ml of water and extracted with 3 × 100 ml of ether. The combined organic extracts were washed with 250 ml of 5% hydrochloric acid, 250 ml of water, and 2 × 250 ml of saturated sodium chloride. The ether layer was then dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure to yield 2.4 g of a dark brown oil.

A 500-ml three-neck round-bottom flask was equipped with a Herschberg stirrer and maintained under a nitrogen atmosphere. Chromium trioxide (1.5 g, 0.015 mol) was added to a stirred solution of 2.37 g (0.03 mol) of pyridine in 200 ml of methylene chloride. After stirring for 15 min, 2.4 g (0.015 mol) of the crude oil (**11**) in 50 ml of methylene chloride was added in one portion to the deep red, clear solution. Stirring was continued for an additional 15 min, followed by the addition of 2-propanol until the red color of the chromium oxide–pyridine complex was completely discharged.

The reaction mixture was decanted and the tarry residue was washed with 3 × 100 ml of ether. The combined organic layers were then washed with 3 × 200 ml of 5% sodium hydroxide, 100 ml of 5% hydrochloric acid, 100 ml of 5% sodium bicarbonate, and 200 ml of saturated sodium chloride. The organic layer was then dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to yield 2.3 g of a dark brown oil.

When this oil was chromatographed as described above, 0.34 g (13% from **9**) of enone **4** was isolated.

Tricyclo[4.3.2.0^{2,5}]-3,8,10-trien-7-ol (11) from 4. A clear lithium aluminum hydride ($LiAlH_4$) solution was prepared by refluxing 0.24 g (0.064 mol) of $LiAlH_4$ in 50 ml of dry ether under nitrogen for 30 min. The cooled solution was filtered under nitrogen with a Schlenk tube into a dry 100-ml three-neck round-bottom flask and cooled to −78°. A solution of 1 g (0.064 mol) of enone **4** in 10 ml of dry ether was added to the stirred $LiAlH_4$ solution dropwise over 15 min. After the reaction mixture had been maintained at −78° for an additional 1 hr, 5 ml of water was added dropwise over 5 min. The Dry Ice–acetone bath was then removed and the stirred reaction mixture was allowed to warm to room temperature. The mixture was then filtered and the aluminum oxide salts were washed with several portions of hot methanol.

The filtrate was washed with 3 × 50 ml of water, 50 ml of 5% hydrochloric acid, 50 ml of 5% sodium bicarbonate, and 50 ml of saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure to yield 1.0 g (99%) of the allylic alcohol **11**: ir (CCl_4) 3580, 3400, 3030, 2900, 1640, 1390, 1305, 1190, 1025 cm^{-1}; MS *m/e* (rel intensity) 162 (2.32), 161 (0.41), 60 (15.7), 142 (33.5), 141 (27.6), 131 (47), 117 (43.5), 104 (90.5), 91 (95), 82 (100).

Reduction of 4 with Lithium Aluminum Deuteride. When the procedure above was repeated using lithium aluminum deuteride, a 95% yield of **11-*d*** was obtained: ^{1}H NMR identical with that of **11** except absorption at δ 4.25 absent; MS (70 eV) *m/e* 161.

Tricyclo[4.3.2.0^{2,5}]undeca-3,8,10-trienyl 7-Acetate (13). A solution of 0.5 g (0.0032 mol) of allylic alcohol **11** and 5 ml of acetic anhydride in 25 ml of dry pyridine was heated at reflux for 1 hr. The reaction mixture was cooled and the pyridine was removed by flash distillation. The brown oil was dissolved in 50 ml of ether and washed with 3 × 100 ml of water, 100 ml of 5% hydrochloric acid, 100 ml of 5% sodium bicarbonate, and 2 × 100 ml of saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure to yield 0.6 g (93%) of **13** as an amber oil: ir (CCl_4) 3020, 2900, 1720, 1370, 1225, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.0 (m, 5 H), 5.4 (m, 2 H), 3.4 (d, 1 H, J = 3 Hz), 3.2 (t, 1 H, J = 3 Hz), 2.6 (m, 2 H), 2.05 (s, 3 H); MS (70 eV) *m/e* (rel intensity) 202 (2.7), 160 (35), 142 (100), 115 (58.5), 104 (57), 91 (89.2).

7-Deuterioallylic Acetate (13-*d*). When deuterated alcohol **11-*d*** was acetylated as above, **13-*d*** was isolated in a 90% yield: ^{1}H NMR (CCl_4) adsorption at δ 5.4 integrated for 1 H; MS (70 eV) *m/e* 203.

Tricyclo[4.3.2.0^{2,5}]undeca-3,8,10-trienyl *syn*-7-(3,5-Dinitrobenzoate) (12). A solution of 1.43 g (0.0064 mol) of 3,5-dinitrobenzoyl chloride and 1.0 g (0.0064 mol) of allylic alcohol **11** in 50 ml of dry pyridine was heated at 60° for 1 hr. The reaction mixture was cooled and the pyridine was removed by flash distillation. The yellow oil was dissolved in 100 ml of ether and washed successively with 10% HCl, water, and saturated salt solution. Concentration of the organic layer afforded 2.05 g (93%) of the allylic benzoate **12**: mp (acetone–water) 142–143°, iridescent plates; ir (CCl_4) 3080,

3030, 2900, 1730, 1640, 1550, 1350, 1270, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05 (s, 3 H), 6.2 (m, 2 H), 6.0 (m, 4 H), 5.5 (m, 1 H), 3.4 (m, 2 H), 2.8 (m, 2 H).

Anal. Calcd: C, 61.10; H, 3.96; N, 7.92. Found: C, 61.10; H, 4.06; N, 7.91.

7-Deuterioallylic Benzoate 12-*d*. When the benzoate of deuterated alcohol **11**-*d* was prepared as described above, a 90% yield of deuterated benzoate **12**-*d* was isolated; ^1H NMR (CCl_4) adsorption at δ 6.2 integrated for 1 H.

Solvolysis of Benzoate 12 at Reflux. A solution of 0.5 g of **12** in 50 ml of glacial acetic acid was heated at reflux for 2 hr under an argon atmosphere. The reaction mixture was cooled to room temperature and dissolved in 100 ml of ether. The organic layer was washed with 4 × 100 ml of water, 100 ml of 5% sodium bicarbonate, and 100 ml of saturated sodium chloride. The ether layer was dried over anhydrous sodium sulfate and filtered and the solvent was removed under reduced pressure.

The epimeric allylic acetates, **13** and **14**, were separated from the cyclopropyl allylic acetate **15** by preparative GLC (SE-30, 130°).

15: ^1H NMR ($CDCl_3$) δ 1.56 (3 H, br s), 1.9 (3 H, s), 2.80 (1 H, br s), 3.00 (2 H, m), 5.56 (2 H, m), 5.98 (1 H, d, J = 8 Hz), 6.04 (1 H, d, J = 3 Hz), 6.32 (1 H, d, J = 3 Hz).

The epimeric acetates were then reduced to their corresponding alcohols (**11** and **16**) with lithium aluminum hydride and separated by preparative GLC (20% Carbowax 60–80, 125°).

Solvolysis of 12 at 190°. A solution of 0.5 g of the benzoate **12** in 50 ml of glacial acetic acid in a combustion tube was degassed by bubbling a fine stream of argon through the solution for 1 hr. The tube was cooled to −78° and sealed under vacuum. The reaction mixture was then warmed to room temperature and maintained at 190° for 2 hr.

The reaction mixture was then cooled to 0° and then to −78°. After the combustion tube was opened, the reaction mixture was dissolved in 100 ml of ether. The ether layer was washed and the organic layer was evaporated.

The epimeric allylic acetates, **13** and **14**, were separated from the enol acetate **20** by preparative GLC (3% SE-52, 120°).

Thermal Stability of Solvolysis Products. One milligram of **13**, a mixture of the epimeric allylic acetates **13** and **14**, and a mixture of **13**, **14**, and **15** were each dissolved in 30 μl of benzene and sealed under vacuum in a capillary tube. The tubes were maintained at 180° for 2 hr, cooled, and analyzed by analytical GLC. All samples were unchanged.

Kinetics. A. Solvolysis at 118°. A solution of 0.77 g of dinitrobenzoate **12** in 50.0 ml of glacial acetic acid was immersed in a bath at 130°. Aliquots, taken at various intervals, were quenched by plunging into a Dry Ice–acetone bath. The rate of product formation was analyzed by analytical GLC (SE-52, 125°).

B. Solvolysis at Elevated Temperatures. A solution of the allylic acetate **13** and biphenyl (internal standard) in glacial acetic acid was sealed under vacuum in a series of capillary tubes. Eight tubes were immersed in an oil bath at temperatures ranging from 165 to 190°. Samples were quenched at various times by rapid cooling to −78°. The rate of disappearance of the acetates **13**, **14**, and **15** was then analyzed by analytical GLC (3%, SE-52, 125°).

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