terated compound) 134°) $\alpha^{20}D$ −0.385 ± 0.004° (*l* 1, neat), $[\alpha]^{20}D$ −0.282 ± 0.003° (neat, corrected,[47] based on d^{20} = 1.494 for the nondeuterated compound[49]); uv max (cyclohexane) 254 nm (ε 600); nmr ($CDCl_3$) δ 1.08 (s, 9 H, *t*-Bu) and 3.16 ppm (m, *ca.* 1 H, -C*H*D-), corresponding to previous reported values for the racemic compound.[16,17]

Acknowledgment. We are grateful to Mrs. Ruth Records and Dr. Günter Barth for the ORD measurements, Dr. Alan Duffield for the mass spectral determinations, and Mr. Eric Meier for the microanalysis. We are especially indebted to Dr. A. Moscowitz for stimulating discussions concerning the interpretation of the ORD–CD spectra.

Solvolytic Studies of Unsaturated 11-Hydroxymethylbicyclo[4.4.1]undecane 3,5-Dinitrobenzoates. Valence Isomerization Leading to Conformationally Distinguishable Annulated Norcaradienylcarbinyl Cations and the Question of Remote pπ Stabilization of Such σ-Delocalized Systems

Gerald L. Thompson,[1] William E. Heyd, and Leo A. Paquette*

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received December 21, 1973*

Abstract: Evidence is presented that *syn*- and *anti*-11-hydroxymethylbicyclo[4.4.1]undeca-1,3,5-triene 3,5-dinitrobenzoates undergo solvolysis *via* initial valence isomerization to the epimeric tricyclic norcaradienyl forms. The rates of solvolysis have been compared with those of 11-hydroxymethyl[4.4.1]propella-3,8-diene and 11-hydroxymethyl[4.4.1]propellane 3,5-dinitrobenzoates which contain preformed cyclopropylcarbinyl systems. The "aromatic" 1,6-methanocyclodecapentaene analog was also examined. The products of ionization have been isolated and compared throughout the series. In all cases but the cyclodecapentaene derivative, the formation of bicyclic vinyl alcohols and hydrocarbons is most prevalent signifying that these intermediate cyclopropylcarbinyl cations suffer largely ring opening. The spread of solvolytic rate constants throughout the series is quite small and attempts to dissect these rate constants into their preequilibrium and ionization components are described. Deuterium labeling studies have established that no isotopic scrambling accompanies departure of the 3,5-dinitrobenzoate group.

Sargent's study of the solvolytic behavior of 7-cyclohepta-1,3,5-trienylcarbinyl 3,5-dinitrobenzoate (**1**) was the first which demonstrated that in certain judiciously chosen molecules ionization can be preceded and perhaps even initiated by valence isomerization.[2] Discovery of its clean, unimolecular hydrolysis to unrearranged alcohol (73%, stable to the reaction conditions) and styrene led to the postulate that **1** solvolyzes with extensive cyclopropyl participation from its norcaradiene valence tautomer.[3-5] Evidence for the intervention of such an intermediate was further deduced from the rate constant which, when appropriately corrected for the preequilibrium, was found to be 100-fold greater than any other reported value for a similarly substituted cyclopropylcarbinyl system. This highly enhanced reactivity was accounted for in terms of a σ-delocalized ion in which partial double bond character had developed between the carbon atoms β to the site of C–O bond heterolysis resulting in an aromatic-like transition state.

Conformational analysis studies of cycloheptatriene have provided evidence that rapid interconversion between a pair of boat conformations separated by an inversion barrier of *ca.* 6 kcal/mol does operate.[6,7] For 7-substituted cycloheptatrienes, this conformational ring flipping comprises a nondegenerate process, *e.g.*, **1a** ⇄ **1b**, which for most,[8] but not all,[9] derivatives lies in favor of equatorial positioning of the attached group as in **1a**.[10] Since each of these conformers is in turn

(1) Phillips Petrolcum Fellow, 1970–1971; University Dissertation Fellow, 1971–1972.

(2) G. D. Sargent, N. Lowry, and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 5985 (1967).

(3) The intermediacy of cycloheptatrienylcarbinyl cations had been invoked in a number of earlier reactions.[4] The first suggestion of possible valence isomerization to a norcaradienylcarbinyl cation seems to have been advanced by Bonner.[4d]

(4) (a) A. C. Cope, N. A. Nelson, and D. S. Smith, *J. Amer. Chem. Soc.*, **76**, 1100 (1954); (b) C. R. Ganellin and R. Pettit, *J. Chem. Soc.*, 576 (1958), and relevant references cited therein; (c) W. von E. Doering, private communication reported in ref 4b; (d) W. A. Bonner, E. K. Raunio, and D. M. Bowen, *J. Org. Chem.*, **31**, 912 (1966).

(5) More recent studies of 7-cyclohepta-1,3,5-trienylcarbinyl cations include: (a) J. Daub and W. Betz, *Tetrahedron Lett.*, 3451 (1972); (b) S. Kohen and S. J. Weininger, *ibid.*, 4403 (1972).

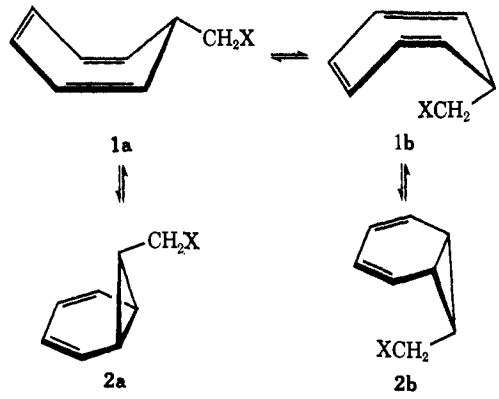
(6) (a) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964); (b) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(7) This subject and the cycloheptatriene–norcaradiene equilibrium problem have recently been reviewed: G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1966); W. Tochtermann, *Fortschr. Chem. Forsch.*, **15**, 378 (1970).

(8) (a) H. Günther, M. Gorlitz, and H. H. Hinrichs, *Tetrahedron*, **24**, 5665 (1968); (b) H. Kessler and E. Muller, *Z. Naturforsch. B*, **22**, 283 (1967); (c) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 3527 (1966); (d) A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 741 (1963).

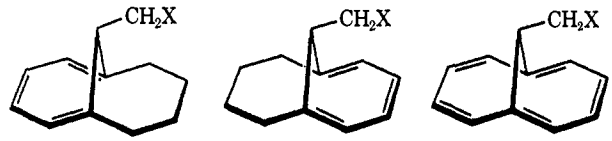
(9) W. E. Heyd and C. A. Cupas, *J. Amer. Chem. Soc.*, **91**, 1559 (1969); **93**, 6086 (1971).

(10) A number of 7,7-disubstituted cycloheptatrienes have also been examined. See, for example (a) H. J. Reich, E. Ciganek, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 5166 (1970); (b) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *ibid.*, **87**, 3896 (1965); (c) K. Conrow, M. E. Howden, and D. Davis, *ibid.*, **85**, 1929 (1963).



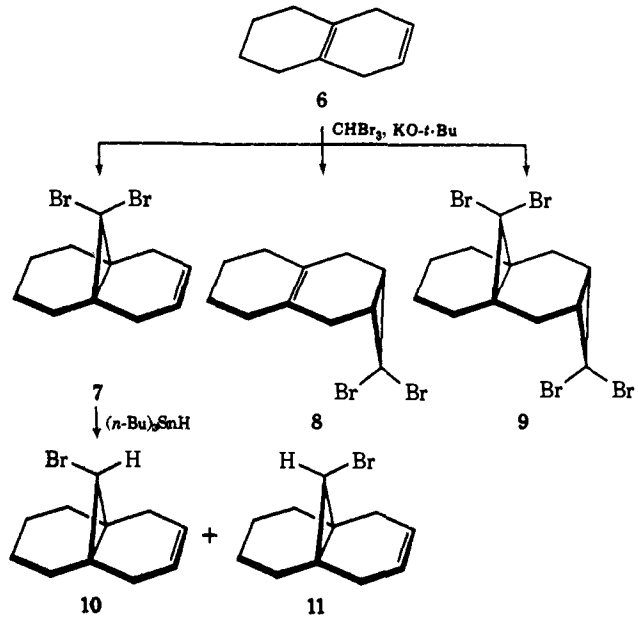
in potential equilibrium with the corresponding bicyclic form (**2a**, **2b**), the question as to whether or not ionization occurs preferentially from the more thermodynamically stable **2a** (fewer nonbonded interactions) or that isomer (**2b**) in which the electron deficient center could profit from remote $p\pi$ stabilization (if indeed available) stands as the central problem in norcaradienylcarbinyl cation chemistry.

Because bridging of C_1 and C_6 in **1** with a tetramethylene chain is capable of effectively isolating the two conformers, we were of the opinion that some light could be shed on this question by an investigation of the solvolytic rate and product profiles of annulated 7-cycloheptatrienylcarbinyl derivatives such as **3**–**5**.[11]

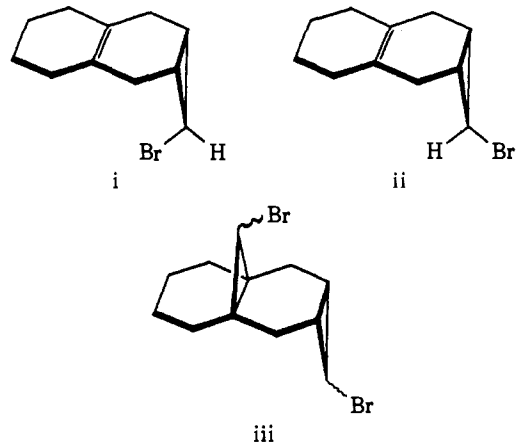


The tetramethylene bridged systems were selected for study over their trimethylene counterparts[12] because of the earlier demonstration by Vogel and his coworkers[13] with the parent hydrocarbons that the former would not be sufficiently constrained so as to provide detectable (pmr) amounts of the norcaradiene valence tautomers at equilibrium. In contrast, the bracketing effect in the next lower homologs is adequate to force the equilibrium completely in the tricyclic direction. Consequently, the chemical reactivity of **3** and **4** could be compared directly with that of **1** and **5** where the aromatic character of the 1,6-methano[10]annulene nucleus would likewise deter valence isomerization to the "double norcaradiene" tautomer.[14]

Synthesis. At the outset of this study, 11-substituted derivatives of bicyclo[4.4.1]undeca-2,4-diene were unknown and accordingly a modifiable synthetic entry to this class of compounds was unavailable. Our first objective was therefore to develop a scheme which would specifically allow isolation of both possible epimers in a pure state on a reasonably large scale. When dihydrotetralin (**6**) was exposed to the combined action of bromoform (1 equiv) and potassium *tert*-butoxide in pentane at $-50°$,[15] there was produced a mixture consisting of unreacted **6**, dibromides **7** and **8**,



and tetrabromide **9**. Column chromatography on silica gel could be used to separate **9**, but this technique was not of preparative value for the isolation of **7**. Fractional distillation was likewise impractical due to the instability of both **7** and **8** under these conditions, and so the unpurified reaction mixture was utilized directly after removal of **6** at low temperature under vacuum. Tri-*n*-butyltin hydride[16] reduction of the black oil and distillation afforded a mixture of **10** and **11** in 28% over-all yield.[17] The epimeric bromides could be readily separated by careful annular spinning band (Teflon) distillation and were distinguished on the basis of the cyclopropyl proton pmr shifts. In agreement with a phenomenon characteristic of all the [4.4.1]propell-3-ene derivatives examined herein (*vide*



basis of their pmr spectra.

(11) For a preliminary account of a portion of this work, see L. A. Paquette and G. L. Thompson, *J. Amer. Chem. Soc.*, **95**, 2364 (1973).

(12) Subsequent to the completion of this study, the work of P. Warner and S.-L. Lu, *J. Amer. Chem. Soc.*, **95**, 5099 (1973), on such derivatives made its appearance.

(13) E. Vogel, W. Weidemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963); E. Vogel, W. Weidemann, H. D. Roth, J. Eimer, and H. Günther, *Justus Liebigs Ann. Chem.*, **759**, 1 (1972).

(14) The 1,6-methano[10]annulene–tricyclo[4.4.1.$0^{1,6}$]undeca-2,4,7,9-tetraene energy gap is not as large as might be expected on the basis of a delocalized π-electron decet in one tautomer. Appropriate substitution at C-11 is now recognized to be capable of reducing the energy barrier for interconversion to less than 6.6 kcal/mol: H. Günther, H. Schmickler, W. Bremser, F. A. Straube, and E. Vogel, *Angew. Chem.*, **85**, 585 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 570 (1973).

(15) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).

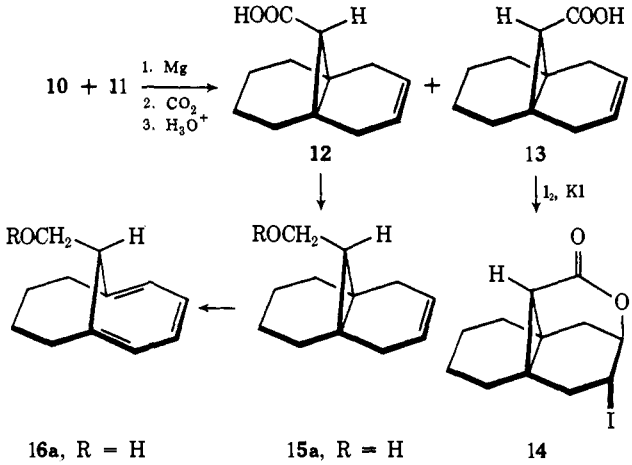
(16) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(17) Two additional monobromides and a dibromide were also isolated by preparative vpc techniques and assigned structures i–iii on the

post), anti isomer **10** displays a singlet which is shifted 0.26 ppm downfield from that of **11**.

The selectivity of attack by reagents at the di- and tetrasubstituted double bonds of dihydrotetralin and isotetralin has been discussed by several investigators. In general, selective electrophilic reactions such as bromination[18] and epoxidation[19] take place primarily at the more highly substituted and electron rich olefinic center. The halo carbenes display the expected[20] trend of selectivities (CCl_2 > CBr_2 > CHCl), but the added steric congestion about the tetrasubstituted double bond in **6** relative to isotetralin decreases the level of attack at that site.[21] In this work the ratio of **7** to **8** was found to be approximately 2:1. Sim's value of 4:1 for the reaction[21] is not reconcilable with our observations and is somewhat surprising considering that this same ratio is also claimed for the more selective dichlorocarbene reagent. Relevant also is the finding that the copper-catalyzed addition of ethyl diazoacetate to isotetralin results in attack only at the disubstituted π bond.[22]

The Grignard reagents from **10** and **11** were readily prepared in tetrahydrofuran[23] but were found to be relatively unreactive, no reaction being observed with ethyl chloroformate at reflux or with carbon dioxide bubbled through the solution. Moderate yields (35–40%) of **12** and **13** could be obtained only by pouring



16a, R = H
b, R = Ac
c, R = DNB

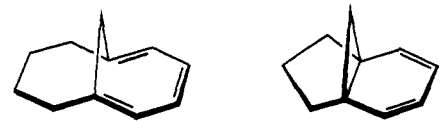
15a, R = H
b, R = Ac

14

the Grignard solution over a large excess of powdered Dry Ice.[23] This diminished nucleophilicity was attributed to the steric bulk of the bisneopentyl system. Because separation of these epimeric carboxylic acids could be accomplished conveniently by iodolactonization,[24] the homologation reaction was routinely performed upon a mixture of **10** and **11**. Treatment of a sodium bicarbonate solution containing the resulting **12** and **13** with iodine and potassium iodide for 24 hr provided a 29% yield of iodolactone **14** and returned 71% of **12** (crude yields).[25]

Lithium aluminum hydride reduction of **12** in tetrahydrofuran gave *anti*-alcohol **15a** (75%) which was protected for further transformations as the acetate (83%). Unlike the air-sensitive alcohol, the stable **15b** provided an opportunity for purification by distillation and for analysis. Bisdehydrobromination of the trans dibromide derived from **15b** was accomplished by reaction with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in refluxing tetrahydrofuran[26] for 21 hr. After distillation and chromatography, there was obtained 45% of **16b**. These results are in contrast to those of Warner[27] who found that treatment of the dibromide of a [4.3.1]propell-3-ene derivative with DBU in warm benzene gave only the vinyl bromide.

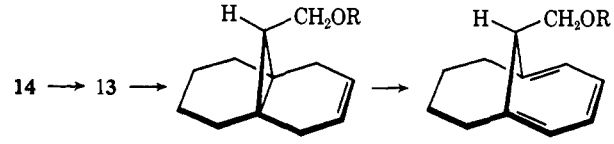
Evidence supporting the cycloheptatriene formulation for **16b** was gained from the pmr spectrum: an AA'BB' pattern in the vinyl region at δ 5.90–6.05 (H_2, H_5) and 6.62–6.75 (H_3, H_4), a doublet (J = 7.8 Hz) at 4.69 for $-CH_2O-$, and a triplet (J = 7.8 Hz) at 1.10 for the bridge proton. The high upfield position of this methine hydrogen, situated as it is β to an electron withdrawing group, reflects the great shielding effect of the cycloheptatriene ring ($\Delta_{\text{chem shift}}$ between pseudoequatorial and pseudoaxial H_7 in cycloheptatriene $\approx$75 Hz at $-150°$[6a]). For comparative purposes, the characteristic olefinic hydrogens of **17** appear as multi-



17 **18**

plets centered at δ 5.82 and 6.55,[13,28] while those of **18** are seen as a narrow multiplet centered at 5.91.[13] Acetate **16b** underwent facile reduction with lithium aluminum hydride in ether, and the alcohol so produced (**16a**) was converted to the bright yellow 3,5-dinitrobenzoate **16c** according to standard procedures.

Reduction of **14** with zinc dust in cold acetic acid



19a, R = H
b, R = Ac

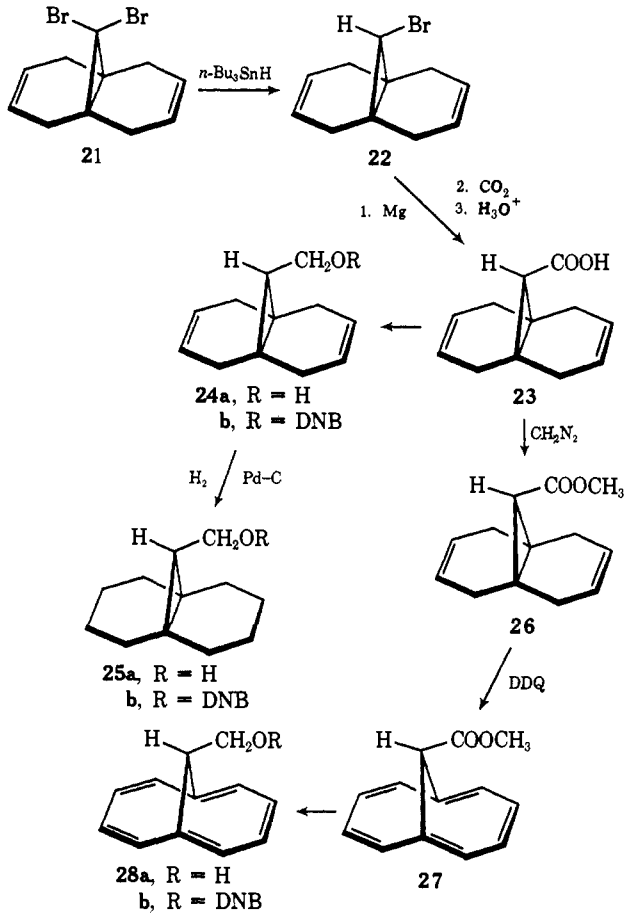
20a, R = H
b, R = Ac
c, R = DNB

quantitatively regenerated *syn*-carboxylic acid **13**. Application of the same sequence of reactions as above proceeded in somewhat higher yield to provide ester **20c**. The pmr spectra of all intermediates were quite distinct from those of the anti series and were particularly characteristic in the chemical shift differences of the $-CH_2O-$ and >CH resonances (see Experimental

(18) A. Shani and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 6310 (1967).
(19) W. Hückel and H. Schlee, *Chem. Ber.*, **88**, 346 (1955).
(20) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 190.
(21) J. J. Sims and V. K. Honwad, *J. Org. Chem.*, **34**, 496 (1969).
(22) G. L. Thompson, unpublished observations. For reports on similar systems, see ref 21; R. D. Stipanovic and R. B. Turner, *J. Org. Chem.*, **33**, 3261 (1968); H. O. House and C. J. Blankley, *ibid.*, **33**, 47 (1968).
(23) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964).
(24) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303 (1968), and pertinent references contained therein.
(25) (a) H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, 30, 2519 (1965); (b) J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, **85**, 582 (1963); (c) E. E. van Tamelen and M. Shamma, *ibid.*, **76**, 2315 (1954).
(26) E. Vogel, R. Schubart, and W. A. Böll, *Angew. Chem., Int. Ed. Engl.*, **3**, 510 (1964). For an analogous result at room temperature, see L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Amer. Chem. Soc.*, **94**, 4739 (1972).
(27) P. M. Warner, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1972.
(28) H. D. Roth, Ph.D. Dissertation, Köln, 1965.

Section). The AA'BB' vinyl pattern of **20c** was slightly narrower (δ 5.87–6.45) than in **16c** and the $-CH_2O-$ doublet was upfield shifted by 1.32 ppm. Although the methine proton is not distinguishable in the acetate (**20b**), the signal in **20a** appears 1.90 ppm downfield from that of **16a**.

The preparation of **28b** brought with it access to two



other reference molecules (**24b** and **25b**) required for a meaningful analysis of the solvolysis data. All three substances were available from the common intermediate **23** whose synthesis was mirrored upon the previous results. In this instance, the sequence was facilitated by the obtention of crystalline intermediates. Cyclopropyl bromide **22** was conveniently purified on a large scale by column chromatography. Lithium aluminum hydride reduction of **23** gave the crystalline (but unstable) alcohol **24a** which was converted to its 3,5-dinitrobenzoate (**24b**). Saturated alcohol **25a** was prepared by catalytic hydrogenation of **24a**.

Oxidation of methyl ester **26** was achieved in 64% yield by heating for 48 hr with DDQ in dioxane solution.[29] The pmr spectrum of the pale yellow aromatic ester (**27**) exhibited signals characteristic of 1,6-bridged cyclodecapentaenes[30] (see Experimental Section). Treatment of **27** with lithium aluminum hydride resulted in attack at the aromatic ring to produce a mixture of nonaromatic alcohols (ir and pmr analyses) which were not further characterized. Comparable hydride reductions of nonconjugated olefins have been previously observed in rigid systems containing an oxygen atom proximate to the site of unsaturation.[31] This propensity for destruction of the desired electron decet was avoided by saponification, preparation of the acid chloride with oxalyl chloride, and reduction with sodium borohydride.[32] Using this route, aromatic alcohol **28a** was obtained in 92% over-all yield from **27**.

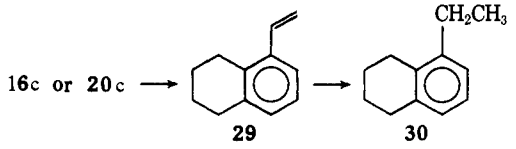
Kinetics. Solvolysis rates of four of the 3,5-dinitrobenzoates were determined in 80% aqueous acetone by titration of liberated acid. The 0.02 *M* concentrations of esters used represent nearly saturated solutions at room temperature for several of the compounds. Due to the insolubility of **28b** in this solvent system, the aromatic ester was solvolyzed in 75:25 tetrahydrofuran–methanol as was **20c** for comparison purposes (Table I).

Table I. Solvolysis of **20c** and **28b** in 75:25 Tetrahydrofuran–Methanol at 129.6°

Compd	k, sec^{-1}	k_{rel}
20c	8.48×10^{-5}	1.0
28b	3.38×10^{-5}	0.4

The rate constants, derived thermodynamic parameters, and calculated relative rate constants at 70 and 100° are given in Table II for duplicate kinetic runs made at each temperature. The infinity titer values were calculated since experimentally derived values were consistently in excess of 100% at 10 half-lives and increased further with added time. Measurements were made over approximately 0.6 $t_{1/2}$ to minimize the error evident at 10 $t_{1/2}$.

Preparative Scale Solvolysis in Aqueous Acetone. The product studies were carried out in 80% acetone buffered with 2,6-lutidine. After work-up, the products were analyzed using vpc and pmr spectroscopy. It was found that both the *anti*- (**16c**) and *syn*-triene dinitro-



benzoates (**20c**) undergo virtually exclusive conversion to 5-vinyltetralin (**29**), structural assignment to which was confirmed by hydrogenation to the known 5-ethyltetralin (**30**). The formation of **29** has a direct parallel in the conversion of **1** (X = ODNB) to styrene (23% yield)[2] but differs meaningfully from the behavior of this prototypical ester in that it is now the exclusive pathway of product formation.

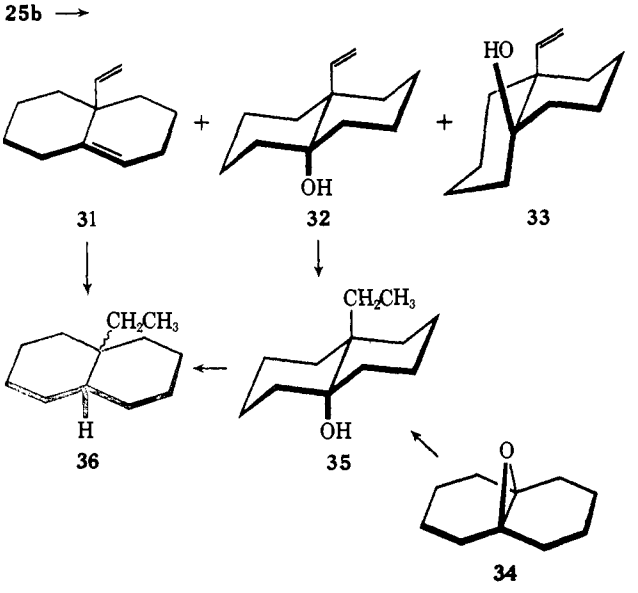
Interestingly, solvolysis of **25b** produced as the major product (65%) a diene hydrocarbon (**31**) corresponding in structure to **29** but without a migrated vinyl group. The isomeric 9-vinyldecalols **32** (15%) and **33** (19%) were also isolated, together with a third minor alcohol (1.5%) which was not identified because of inadequate quantities. In contrast to the stability of these alcohols to the reaction conditions, **31** underwent slight (*ca.* 10%) decomposition to unidentifiable substances.

(29) P. H. Nelson and K. G. Untch, *Tetrahedron Lett.*, 4475 (1969).
(30) E. Vogel, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, 12, 215 (1968).
(31) (a) B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, 87, 3423 (1965); (b) M. Sakai, R. F. Childs, and S. Winstein, *J. Org. Chem.*, 37, 2517 (1972).
(32) (a) H. C. Brown, E. J. Mead, and B. C. S. Rao, *J. Amer. Chem. Soc.*, 77, 6209 (1955); (b) L. A. Paquette and N. A. Nelson, *J. Org. Chem.*, 27, 2272 (1962).

Table II. Solvolysis Data for 3,5-Dinitrobenzoates in 80:20 Acetone–Water

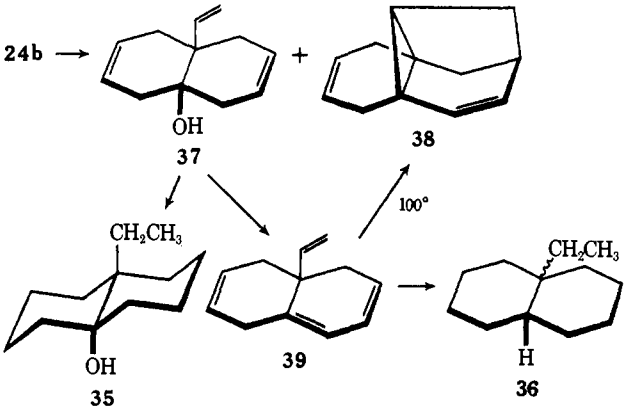
Compd	T, °C[a]	k, sec^{-1}	k_{rel} (100°)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
16c	69.6	$(5.11 \pm 0.01) \times 10^{-6}$	4.1	27.5 ± 1.2	-2.9 ± 3.4
	70.0[b]	5.47×10^{-6}			
	84.4	$(3.01 \pm 0.01) \times 10^{-5}$			
	99.5	$(1.41 \pm 0.01) \times 10^{-4}$			
	100.0[b]	1.52×10^{-4}			
20c	70.0[b]	1.71×10^{-6}	1.2	27.0 ± 0.6	-6.6 ± 1.5
	84.3	$(8.72 \pm 0.04) \times 10^{-6}$			
	99.4	$(4.12 \pm 0.03) \times 10^{-5}$			
	100.0[b]	4.44×10^{-5}			
	114.9	$(1.89 \pm 0.02) \times 10^{-4}$			
25b	69.6	$(1.63 \pm 0.00) \times 10^{-5}$	10	25.5 ± 0.2	-6.2 ± 0.5
	70.0[b]	1.71×10^{-5}			
	84.3	$(8.02 \pm 0.13) \times 10^{-5}$			
	99.5	$(3.59 \pm 0.19) \times 10^{-4}$			
	100.0[b]	3.77×10^{-4}			
24b	70.0[b]	1.27×10^{-6}	1.0	28.1 ± 0.6	-4.0×1.6
	84.3	$(6.78 \pm 0.09) \times 10^{-6}$			
	99.5	$(3.64 \pm 0.03) \times 10^{-5}$			
	100.0[b]	3.75×10^{-5}			
	114.8	$(1.64 \pm 0.01) \times 10^{-4}$			

[a] ±0.1°. [b] Extrapolated or interpolated values based upon thermodynamic parameters.

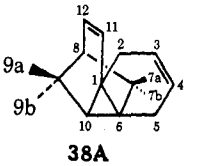


To establish that all three products were of the same structural class, **32** and **33** were converted directly to **31** by dehydration with ethyl(carboxysulfamoyl)triethylammonium hydroxide inner salt.[33] Catalytic reduction of **32** to *trans*-9-ethyldecal-10-ol (**35**), available in unequivocal fashion from the ring opening of epoxide **34** with ethylmagnesium bromide,[34] provided confirmation of the ring fusion stereochemistry which was first suggested by the pmr spectrum. Comparison of the spectra of **32** and **33** reveals the pattern expected for a trans/cis decalin pair;[35] that of **32** exhibits a complex multiplet from δ 1.2 to 1.8, a consequence of its rigid conformational features and the resultant noninterconvertibility of anisochronous axial and equatorial protons; in contrast, the more conformationally mobile **33** exhibits a broad singlet ($W_{1/2}$ = 0.15 ppm) centered at 1.53 (the approximate mid point of the signal for **32**). Further identification of **31** was achieved by hydrogenation to the same 9-ethyldecalin mixture (**36**) obtained by additional chemical modification of **35** (see Experimental Section).

When heated under analogous conditions, **24b**



afforded two products whose relative ratios were noted to vary somewhat from run to run (differing in the time factor). Gleaned from control experiments were the observations that bicyclic alcohol **37** (77–91%) does not undergo dehydration or further rearrangement during solvolysis but that hydrocarbon **38** (23–9%) does suffer gradual decomposition (56% complete in 58 hr or 11 solvolytic half-lives). The decreasing relative proportion of **38** with time is consequently comprehensible. Conclusions regarding the trans stereochemistry of **37** were confirmed by its catalytic hydrogenation to **35**. The novel structural elements in **38** were initially suggested by the pmr spectrum (in $CDCl_3$) which consists of an AB quartet for H_{11} and H_{12} (J_{AB} = 8.5 Hz, ν_{11} δ 5.71, ν_{12} = 5.94), which due to additional coupling of H_{12} with H_8 ($J_{8,12} \approx$ 8.5 Hz, see **38A** for numbering scheme) gives H_{12} the appearance



38A

(33) E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *J. Org. Chem.*, **38**, 26 (1973); *J. Amer. Chem. Soc.*, **92**, 5224 (1970).

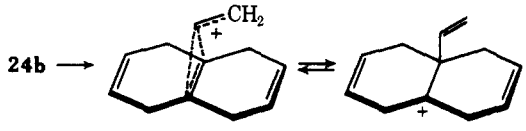
(34) For an analogy, consult J. C. Gasc and L. Nedelec, *Tetrahedron Lett.*, 2005 (1971).

(35) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1965, pp 580 and 709.

of a triplet. There is also seen a broad upfield singlet at 1.21 attributable to H_{10}. The appearance of H_{11} as a simple doublet denotes that the adjacent bridgehead carbon (C_1) bears no proton. Double irradiation studies confirmed that H_{9a} and H_{9b} form a basic AB quartet (J_{AB} = 10.7 Hz, ν_{9a} = 0.81, ν_{9b} = 1.63) which possesses additional multiplicity because of spin interactions of H_{9b} with H_8 (J = 4 Hz) and H_{10} (J = 2 Hz); likewise, H_{7a} and H_{7b} comprise an AB quartet (J_{AB} = 11.1 Hz, ν_{7a} = 0.80, ν_{7b} = 1.42) in which the H_{7b} signal is further split by coupling to H_8 (J = 4.8 Hz). It follows that the molecule is tetracyclic but not the result of intramolecular ($_\pi4 + {}_\pi2$) cycloaddition from a [1,5]-hydrogen shift isomer of **39**.

To determine the plausibility of intramolecular Diels–Adler cyclization in **39**, alcohol **37** was dehydrated with the Burgess reagent.[33] Attempted vpc purification (100°) of the resulting oil, the pmr spectrum of which was entirely consistent with the tetraene formulation (see Experimental Section), afforded a nonseparated mixture of **38** and **39** which upon reinjection resulted in the isolation of pure **38**. Of greater relevance, **39** is converted to **38** under the solvolysis conditions and thus is capable of ready closure to **38**. Related thermal processes have recently been the subject of considerable mechanistic scrutiny.[36] We cannot of course rule out the possibility that **38** may result directly from π-bond alkylation of the cyclopropylcarbinyl cation.

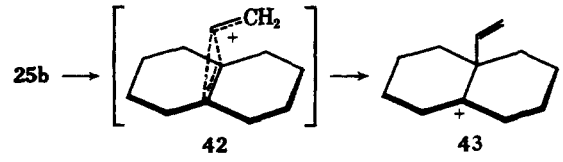
Drawing on analogy,[37] the simplest reaction path for ionization of **24b** would appear to be departure



40 **41**

of the leaving group with generation of delocalized cationic intermediate **40**. Ring opening to give homoallylic cation **41** and subsequent deprotonation would lead *via* **39** to **38**, while solvent capture from the anti surface would afford alcohol **37**. The partition between ion capture and olefin formation is most certainly dependent upon structure and the solvolysis medium. The exclusive formation of *trans*-alcohol **37** can be rationalized in terms of solvent assistance to ionization, a conformational effect of the two cyclohexene double bonds, and/or involvement in the product-forming step of a delocalized cationic species such as **40**.

That the stereochemistry of solvent capture is controlled to a meaningful extent by the conformational energetics of these cyclopropylcarbinyl derivatives is suggested by the behavior of the fully saturated system **25b**. In this example, the cis and trans alcohols are produced in approximately a 1:1 ratio. This fact rules out the possibility that both **32** and **33** arise from symmetrical ion **42**. Quite possibly, however, the greater conformational driving force of the cyclohexyl rings to adopt chair-like arrangements may be sufficient to render bridged species **42** less energetically favorable than open ion **43**[38] and cause the former species to be

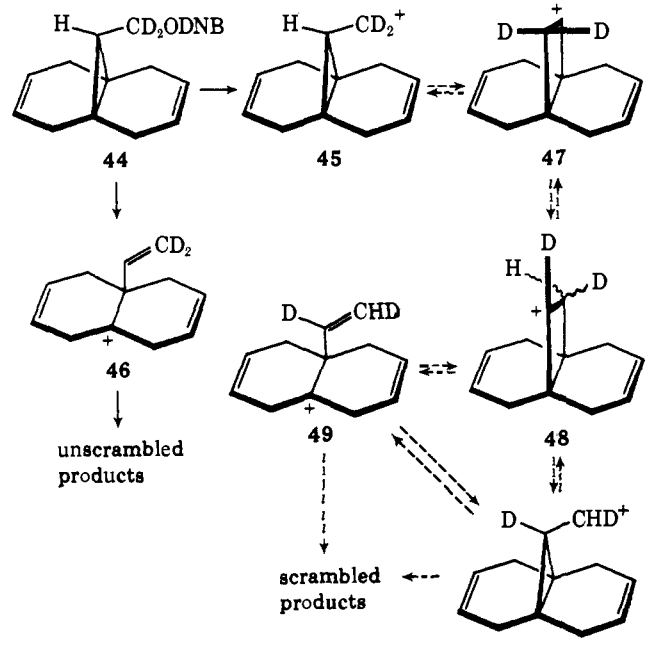


42 **43**

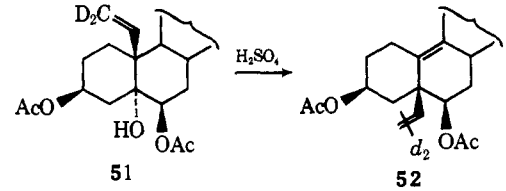
but a transition state on the reaction profile leading to **43**.[39,40] We are inclined at present to believe that the differing stereoselectivity of solvent capture arises from a reversal of stability orders for the **40**:**41** and **42**:**43** pairs.

Deuterium Labeling Experiments. Although product formation from **24b** and **25b** is satisfactorily accommodated by the above scheme, the alternative pathway outlined in Chart I deserves serious consideration be-

Chart I



cause of its possible importance in the recently reported work of Guest, Jones, and Marples[41] and the commonly observed ring expansion of cyclopropylcarbinyl cations to cyclobutyl products.[42] The Loughborough group noted that sulfuric acid catalyzed rearrangement of the 10β-ethenyl steroidal alcohol **51** gave **52** in which



51 **52**

(36) A. C. Krantz and C. Y. Lin, *J. Amer. Chem. Soc.*, **95**, 5662 (1973), and relevant references compiled therein.

(37) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966), and references cited therein.

(38) Whereas bridging as in **42** requires a coplanar alignment of C_9 and C_{10} with accompanying fixation of the six-membered rings in boat or twist-boat conformations, the C_9 and C_{10} centers in **43** are considered to be mutually independent and amenable to conformational perturbation. A similar driving force does not exist in **40** since the boat conformations in the more unsaturated rings are of greater stability.

(39) A solvolysis study of the epimeric *cis*- and *trans*-9-decalyl and *cis*- and *trans*-8-hydrindanyl *p*-nitrobenzoates has been reported by R. C. Fort, Jr., R. E. Hornish, and G. A. Liang, *J. Amer. Chem. Soc.*, **92**, 7558 (1970).

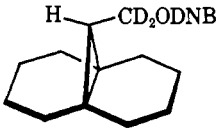
(40) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960; A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, Wiley, New York, N. Y., 1961.

(41) I. G. Guest, J. G. Ll. Jones, and B. A. Marples, *Tetrahedron Lett.*, 1979 (1971).

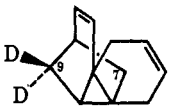
(42) For leading references, consult I. Lilien and L. Handloser, *J. Amer. Chem. Soc.*, **93**, 1682 (1971); Z. Majerski and P. v. R. Schleyer, *ibid.*, **93**, 665 (1971).

the isotopic label was scrambled among the three vinyl positions, presumably as a result of 1,2-D shifts in cyclobutyl cations analogous to **47** and **48**.

To achieve a resolution of this issue, the deuterium labeled 3,5-dinitrobenzoates **44** and **53** were prepared



53

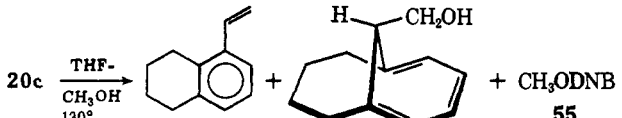


54

and solvolyzed as before. No detectable scrambling of the isotope from the terminal methylene position was observed in any of the products (pmr analysis, see Experimental Section). Of particular fascination were the spin decoupling experiments with **54** in C_6D_6 solution which convincingly established C_9 as the exclusive (>95%) site of deuterium substitution.

These data do not rule out possible rapid equilibration of **45** (and its tetrahydro derivative) with cyclobutyl cations such as **47** but do eliminate from further consideration the incursion of 1,2-deuteride (hydride) shifts in these intermediates. Before **47** and structurally related ions can be completely dismissed, solvolyses of derivatives of such systems require investigation. Such studies have yet to be performed.

Product Studies in Tetrahydrofuran–Methanol (3:1). The earlier necessity of conducting the solvolysis of **28b** and, for reference purposes, **20c** in tetrahydrofuran–

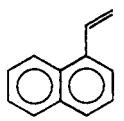


29 **20a** **55**

methanol (3:1) provided an opportunity for a comparative product study in the case of **20c**. Preparative scale solvolysis of this ester at 130° carried to 10 half-lives gave evidence that not only solvolysis but also (to a lesser extent) ester interchange had occurred. There was isolated in addition to the expected 5-vinyltetralin (**29**, 88.3%) lesser quantities of unrearranged alcohol **20a** (8%) and methyl 3,5-dinitrobenzoate (**55**, 11.7%).

Comparable treatment of **28b** at both 100 and 103° gave results which have been compiled in Table III.

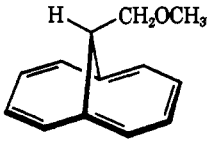
Table III. Solvolysis Products of **28b** in THF–CH_3OH (3:1)



56

	At 100°		At 130°	
Compd	Yield, %	Yield excluding **28b**, %	Yield, %	Yield excluding **28b**, %
28b	53.5		11.3	
28a	46.5	100	56.5	63.8
55	37.1	80	44.5	50.2
56	0	0	32.1	36.2

The appreciable quantities of methyl 3,5-dinitrobenzoate produced in these runs point to a notably higher level of ester interchange compared to **20c**. Repetitive 100° solvolysis experiments and accompanying pmr product analyses consistently gave the result that, on a molar basis, more of alcohol **28a** was formed than **55**. No evidence for the formation of 1-vinylnaphthalene was obtained at 100°. Yet this hydrocarbon was produced in greater than 30% yield at 130°. Control experiments showed that alcohol **28a** and methyl ether **57** were



57

stable to the reaction and work-up conditions; however, heating **28b** at 130° in tetrahydrofuran alone, with or without 2,6-lutidine, led only to ether-insoluble polymeric products. In contrast, conversion of **28b** uniquely to 1-vinylnaphthalene (**56**) was evidenced upon injection of solutions of the ester into a gas chromatograph (injector temperature, 250°; column temperature, 150°).

These data suggest, but do not require, that the principal solvolysis product of **28b** is retained alcohol **28a** and that the formation of **56** is chiefly the result of a purely thermal process. In particular, it is deemed unlikely that the *solvolytic* formation of 1-vinylnaphthalene would be reduced from 36% at 103° to 0% at 100°.[43] The rate of acid production (3.38×10^{-5} sec^{-1}) could then be a composite of solvolysis and decomposition reactions, since decomposition would likely produce acid as well. Were this so, the actual solvolysis rate would be more accurately represented by 9.23×10^{-6} sec^{-1} and would point to a kinetic rate ratio possibly as large as 9 (rather than 2.5) for **20c**/**28b** (see Table I).

The Question of Cycloheptatriene–Norcaradiene Preequilibration. The spread of relative rate constants at 100° for **16c**, **20c**, **24b**, and **25b** is seen to consist of merely a tenfold difference between the extremes. Clearly, these data support the Sargent proposal[2] that ionization reactions of 7-cycloheptatrienylmethyl derivatives proceed through the norcaradienylcarbinyl valence isomers and are cyclopropyl assisted. The tenfold rate decrease observed for **24b** relative to **25b** agrees with the factor estimated for the inductive contribution of two β-oriented double bonds.[2,44]

When the product-forming steps accompanying solvolysis of **16c** and **20c** are compared, it becomes evident that the cyclopropylcarbinyl structures are of major importance in both instances. Three plausible mechanisms may be advanced to account for the observed vinyl migration (Chart II). Because intermediate **61** offers the greatest degree of $p\pi$ delocalization (compare **62** and **63**) and many closely related spirocyclic processes are known,[45,46] we infer that the **60** →

(43) Despite this, the possibility does remain open that the more elevated temperature promotes a higher degree of valence isomerization to the cyclopropylcarbinyl tautomer which, in turn, affords **56**. However, see ref 14.

(44) (a) E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, **94**, 5899 (1972); (b) C. F. Wilcox, Jr., and H. D. Banks, *ibid.*, **94**, 8231 (1972); (c) H. Tanida and T. Irie, *J. Org. Chem.*, **36**, 2777 (1971).

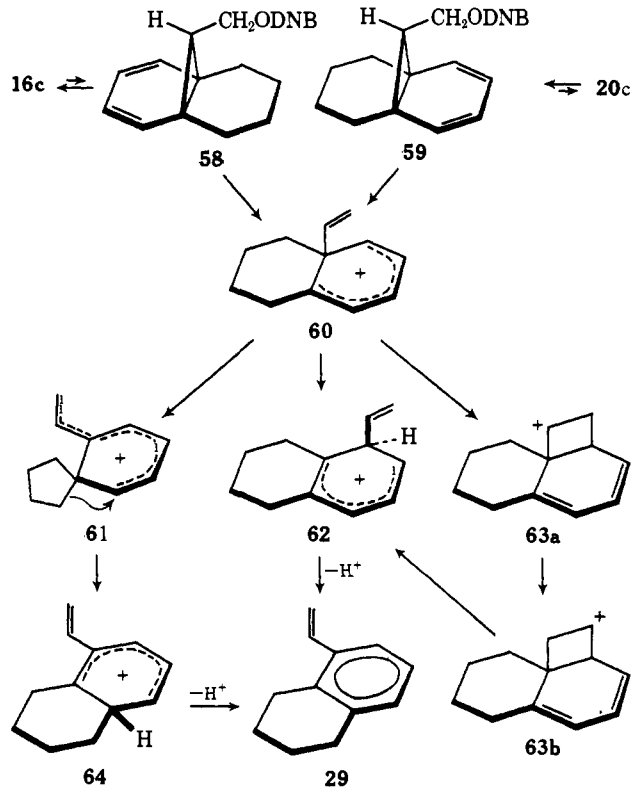
(45) For a recent example, see A. R. Hochstetler, 166th National Meeting of the American Chemical Society, Chicago, Ill., August 1973, Abstract ORGN 128.

(46) For a recent brief review, consult M. S. Newman, *Accounts Chem. Res.*, **5**, 354 (1972).

Table IV. Proton Chemical Shifts of Esters **16c** and **20c** at Various Temperatures (δ 100 MHz)

Compd	T, °C/Solvent	H_{11} triplet			OCH_2– doublet		
		$CDCl_3$	$(CD_3)_2CO$	$(CD_3)_2CO/CCl_2F_2$	$CDCl_3$	$(CD_3)_2CO$	$(CD_3)_2CO/CCl_2F_2$
16c	94	1.32			5.07		
	67	1.32			5.08		
	32	1.31	1.29		5.08	5.12	
	−86		1.25	1.25		5.09	5.07
	−107			1.23			5.04
	−112			1.22			5.03
20c	94	2.74			3.73		
	67	2.76			3.72		
	32	2.80	2.97		3.71	3.68	
	−30	3.11				3.64	
	−74		3.27			3.60	
	−86		3.33			3.59	
	−90			3.17			3.58
	−102			3.28			3.55

Chart II



61 → **64** → **29** pathway is most likely but do not dismiss the other options.

From a consideration of these data, it may be surmised that the solvolyses of **16c** and **20c** (and perhaps also **28b**) are dependent upon the operation of pre-equilibria involving **58** and **59**, respectively. The observed rate constants consequently are comprised of pseudo-first-order rate and equilibrium constants as shown in eq 1–3. Comparison of the kinetic behavior

$$\mathbf{16c} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{58} \xrightarrow{k_2} \text{products} \qquad K_{eq} = k_1/k_{-1} \tag{1}$$

$$\mathbf{20c} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \mathbf{59} \xrightarrow{k_2'} \text{products} \qquad K_{eq}' = k_1'/k_{-1}' \tag{2}$$

$$k_{solv}(\mathbf{16c}) = K_{eq}k_2 \qquad k_{solv}(\mathbf{20c}) = K_{eq}'k_2' \tag{3}$$

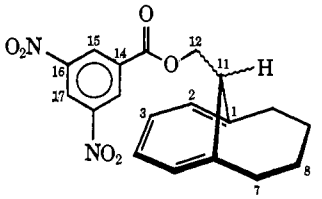
of **16c** and **20c** (Table II) reveals merely a 3.4-fold rate enhancement favoring the anti isomer (**16c**). In these isomeric systems, therefore, rigid orientation of the developing positive charge directly above the center of the 1,3-diene moiety in **20c** promotes little or no *overt* rate effect not available also to anti isomer **16c**.

As originally pointed out by us,[11] this absence of a measurable reactivity difference may arise either from a sizable imbalance in K_{eq} and K_{eq}' or from a combination of steric and adverse through-space effects in the two systems. In an effort to evaluate the first of these parameters, variable temperature pmr and cmr studies of **16c** and **20c** were carried out. H_{11} chemical shift data for the *syn*- and *anti*-3,5-dinitrobenzoates in the temperature range +94 to −120° (Table IV) indicate that the methine resonance of **20c** experiences a proportionately larger chemical shift change (0.57 ppm) than does the same proton in **16c** (0.09 ppm) and in an opposite direction. Unfortunately, neither valence tautomerism could be slowed to the intermediate or slow range on the pmr time scale before crystallization of the solute occurred. Consequently, no definitive answers were realized by this technique. The downfield position of H_{11} in **20c** and the upfield location of H_{11} in **16c** point to differing proportions of the triene forms, but without knowledge of the precise chemical shifts of the methine signals in the four individual tautomers, meaningful conclusions cannot be drawn. In particular, the chemical shift difference of H_{11} in the pair **16c** and **58** (under conditions of no exchange) could be considerably smaller than that of the pair **20c** and **59**.

Cmr spectroscopy is potentially more useful in such circumstances since carbon chemical shift differences under conditions of no exchange are frequently greater than those of the respective protons.[47] The possibility arises that the slow exchange limit would occur at a faster rate of tautomerism and thus at a more elevated temperature. At 25°, the cmr spectra of **16c** and **20c** reveal sizable differences in the chemical shifts of the respective C_1, C_6, and C_{11} carbon atoms, with those of the anti isomer appearing at lower field (Table V). As the temperature was lowered, small additional changes were encountered down to −70° in both systems, and for **20c** this temperature dependence was

(47) For some earlier applications of cmr spectroscopy to problems of valence isomerization, see H. Günther and T. Keller, *Chem. Ber.*, 103, 3231 (1970); H. Günther, B. D. Tunggal, M. Regitz, H. Scherer, and T. Keller, *Angew. Chem.*, **83**, 585 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 563 (1971); E. Wenkert, E. W. Hagaman, L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *Chem. Commun.*, 135 (1973); H. Günther, H. Schmickler, W. Bremser, F. A. Straube, and E. Vogel, *Angew. Chem.*, **85**, 585 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 570 (1973); H. Günther and G. Jikeli, *Chem. Ber.*, **106**, 1863 (1973).

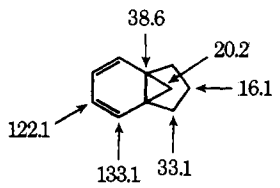
Table V. Cmr Shifts of Esters **16c** and **20c** at Various Temperatures (ppm from Capillary TMS, Acetone)



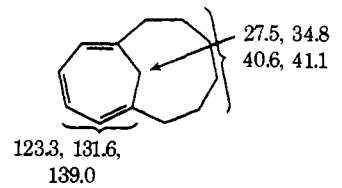
Ester	Temp, °C	1,6	2,5	3,4	7,10	8,9	11	12	13	14	15,19	16,18	17
16c	+25	123.5	121.4	129.3	31.1	25.9	47.1	63.5		129.7	128.7		122.8
	−70	123.8	120.7	128.4	30.8	25.3	46.3	64.8	162.5	132.7	128.8	148.6	122.4
20c	+25	79.3	122.7	124.7	34.3	23.4	*a*	61.3			129.3		122.7
	−30	82.1	123.4	124.8	33.9	23.1	30.8[b]	60.8	162.7	133.3	129.0	148.8	122.6
	−70	84.8	123.4	124.8	33.7	22.9	30.8[b]	60.4	162.7	132.7	128.8	148.6	122.4
CH_3ODNB							(as CH_3)	53.1	163.0	132.7	128.8	148.6	122.4

[a] Masked beneath acetone signal centered at 30.1 ppm. [b] Shoulder downfield of acetone peak. Because of the broadness of the solvent signal, these values are necessarily approximate.

reasonably linear. On this basis, it seems certain that C_{11} stereochemistry exerts a very marked effect on the direction of valence tautomerization, with **16c** existing chiefly as a cycloheptatriene derivative and **20c** partaking of substantial norcaradiene character. That the geometric differences in these molecules are of significant proportions is further revealed by a direct comparison of the data in Table V with the reported[47] cmr spectra of **18** and **65** (CCl_4, TMS as internal



18



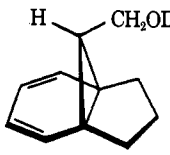
65

standard). From a consideration of these data, the important conclusion can be drawn that **16c** (chiefly bicyclic) and **20c** (predominantly tricyclic) do differ meaningfully in their ground state structural features. Since it has not yet been possible to slow down the rate of either valence tautomerization sufficiently to permit direct observation of the individual cmr spectra of the two isomers of each pair, it is assumed that the energy barriers of the processes are quite low and probably in the range of 2.6–6 kcal/mol.[48]

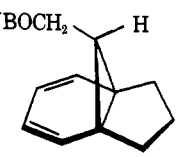
Conclusion

In light of these cmr data, it is clear that differences in K_{eq} profoundly affect the relative solvolytic reactivities of **16c** and **20c**. Perhaps because *anti*-norcaradienyl dinitrobenzoate **58** (as well as the derived carbocation[11]) is predisposed to experience steric compressions with the axially oriented hydrogens of the tetramethylene "bracket," the formation of this tricyclic valence tautomer is relatively unfavorable. Molecular models indicate that similar nonbonded repulsions are of little consequence in **59** and its carbonium ion counterpart. Given this set of circumstances, the observed solvolysis rate for **16c** actually underestimates the true solvolytic reactivity of its cyclopropylcarbinyl tautomer **58**. With the assumption that the free energy difference between **16c** and **58** is *ca.* 4 kcal/mol, subtraction of this value from the observed free energy of activation of solvolysis of **16c** leads to an approximate solvolytic rate constant for **58** at 100° of 2.4×10^{-2} sec^{-1}.[49] This value is approximately 200-fold greater than the *unfactored* rate constant for **20c** $\rightleftarrows$ **59**.

The magnitude of this reactivity difference compares favorably with that recently observed by Warner and Lu for **66** and **67** (80:1).[12] The origin of this kinetic



66



67

k_{rel} (70°)	80	1

imbalance cannot reside in a positive through-space effect; rather, proximity of the developing cationic center to the conjugated diene unit is unmistakingly nonaccelerating. Consequently, the possibility remains that subtle, yet important, electronic factors may be at play and further investigations are necessary to clarify this issue.[49a] We do not wish to dismiss completely the possibility, as does Warner,[12] that steric crowding in anti isomer **58** contributes to the rate acceleration. Since nonbonded interactions may be partly at the root of the differences in K_{eq}, these steric compressions might contribute to steric acceleration and more rapid ionization in the anti series.

In summary, we feel that the evidence is very strong that 7-cycloheptatrienylcarbinyl derivatives (**1**) undergo solvolysis through the intermediacy of norcaradienylcarbinyl cations (k_{rel} for **2** at 100° in 60% aqueous acetone = 2.6×10^{-1} sec^{-1} [2]). Given that ionization appears to be significantly accelerated from the more stable form **2a**, kinetic and thermodynamic considera-

(48) We assume that the two tautomers are still interconverting rapidly on the nmr time scale. Recently, a number of norcaradiene–cycloheptatriene equilibria have been studied and energy gaps of 4–9 kcal/mol have been reported: (a) see ref 12; (b) see ref 14; (c) T. Tsuji, S. Turatake, and H. Tanida, *Bull. Chem. Soc. Jap.*, 42, 2033 (1969); (d) A. Cairncross, private communication.

(49) Determined on the basis of the Eyring relationship $-\log (k_1/k_2) = (\Delta H^{\ddagger}_1 - \Delta H^{\ddagger}_2)/2.3RT$. Assuming $\Delta F = 6$ kcal/mol, $k_2 = 8.3 \times 10^{-2}$ sec; when $\Delta F = 2.5$ kcal/mol, $k_2 = 2.5 \times 10^{-3}$ sec^{-1}.

(49a) NOTE ADDED IN PROOF. Recent EH calculations by W.-D. Stohrer and J. Daub [*Angew. Chem., Int. Ed. Engl.*, 13, 86 (1974)] confirm the difference in stability of 7-norcaradienylcarbinyl cations. They find the additional through-space interaction between the diene and acceptor orbitals to be antibonding in nature and thus destabilizing.

tions point to reaction of an unconstrained derivative chiefly through valence isomer **2a** rather than **2b**. Notwithstanding, a number of important questions still remain to be answered, not the least of which is the true origin of the anchimeric assistance available to the *anti*-norcaradienyl derivatives.

Experimental Section

All melting points were taken in open capillaries and are corrected; boiling points are uncorrected. Infrared spectra were obtained on Perkin–Elmer Model 137 and 467 spectrophotometers and proton magnetic resonance spectra were recorded with Varian A-60A and HA-100 spectrometers as well as a Joelco MH-100 instrument. Apparent splittings are given in all cases. Mass spectra were obtained with a CEC-MS9 instrument at an ionization potential of 70 eV, and ultraviolet spectra were determined with a Cary 14 spectrometer. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***anti*- and *syn*-11-Bromo[4.4.1]propell-3-ene (10 and 11).** A solution of 397 g (1.57 mol) of bromoform in 1.25 l. of petroleum ether (bp 38–57°) was added dropwise over 3.0 hr to a stirred slurry of 258 g (82% pure, 1.57 mol) of dihydrotetralin[13] and 350 g (3.13 mol) of potassium *tert*-butoxide in 1.25 l. of petroleum ether held at $-50 \pm 5°$ under nitrogen. The mixture was allowed to warm slowly to room temperature with stirring overnight. The reaction mixture was worked up as described for **21** (see below), but due to the thermal instability of the liquid octalin dibromide, purification by distillation was precluded, and the black oil was employed without purification. In another experiment on a smaller scale, the tetrabromide **9** was isolated by column chromatography (silica gel), mp 158–158.5° (hexane).

Anal. Calcd for $C_{12}H_{14}Br_4$: C, 30.16; H, 2.95. Found: C, 30.29; H, 2.94.

Tri-*n*-butylin hydride (260 g, 0.85 mol) was added dropwise to the stirred residue cooled with an ice bath under nitrogen, and the mixture was stirred at room temperature for 12 hr. The resulting two bromides (**10** and **11**, 100 g, 28% from **6**) were isolated by distillation through a 6-in. Vigreux column followed by fractionation through a 19-in. Teflon annular spinning band column, bp 60° (0.02 mm). The isomers could be separated as colorless oils by vpc (0.25 in. × 6 ft 5% Carbowax 20M-1% KOH, 145°, t_{ret} = 10 and 15 min). The more rapidly eluted *anti*-bromide (**10**) was the major product (60%); $\delta_{TMS}^{CDCl_3}$ 5.4–5.6 (m, 2, vinyl), 3.34 (s, 1, >C*H*Br), 2.1–2.4 (m, 4, allylic), and 1.1–2.0 (m, 8).

Anal. Calcd for $C_{11}H_{15}Br$: C, 58.16; H, 6.66. Found: C, 58.13; H, 6.65.

The minor product (40%) was the *syn*-bromide (**11**): $\delta_{TMS}^{CDCl_3}$ 5.5–5.6 (m, 2, vinyl), 3.08 (s, 1, >C*H*Br), 2.25 (br s, 4, allylic), and 1.1–2.0 (m, 8).

Anal. Calcd for $C_{11}H_{15}Br$: C, 58.16: H, 6.66. Found: C, 57.94; H, 6.74.

Samples of monobromides i and ii (see ref 17) were also isolated by vpc (longer retention times). The third isomer to be eluted was tentatively assigned structure i; $\delta_{TMS}^{CDCl_3}$ 2.65 (t, $|J|$ = 3.0 Hz, 1, cyclopropyl) and 1.4–2.8 (m, 14, $-CH_2-$). The last isomer to elute was assumed to be ii: $\delta_{TMS}^{CDCl_3}$ 3.25 (t, $|J|$ = 7.8 Hz, 1, cyclopropyl) and 1.2–2.7 (m, 14, $-CH_2-$).

[4.4.1]Propell-3-enyl-*anti*-11-carboxylic Acid (12) and *exo*-3-Hydroxy-*endo*-4-iodo[4.4.1]propellanyl-*syn*-11-carboxylic Acid Lactone (14). The isomeric Grignard reagents of **10** and **11** (31 g, 0.14 mol) were prepared and carbonated as described below for **22** to provide a mixture of octalin acids **12** and **13** (9.5 g, 37%). This material together with that from a smaller reaction (total of 10.3 g, 53.7 mmol) was dissolved in 0.5 l. of 0.5 *M* sodium bicarbonate solution by warming on a steam bath. The solution was cooled to room temperature, a solution of 45 g (0.27 mol) of potassium iodide and 21 g (0.081 mol) of iodine in 0.2 l. of water was added, and the black mixture was allowed to stand in the dark for 1 day. Sodium thiosulfate was added to discharge the color, and the aqueous mixture was extracted with methylene chloride (3 × 150 ml). The organic solution was washed with 10% sodium hydroxide (200 ml) and saturated sodium chloride solutions, dried, and concentrated. The residue was chromatographed on silica gel (elution with 1:1 ether–petroleum ether, bp 38–57°) to provide 4.87 g (15.3 mmol, 29%) of iodolactone **14**, mp 140–140.5° dec (from ether): $\delta_{TMS}^{CDCl_3}$ 4.5–4.7 (m, 2, >C*H*I and >C*H*O–) and 1.3–3.5 (m, 13).

Anal. Calcd for $C_{12}H_{15}IO_2$: C, 45.30; H, 4.75; I, 39.59. Found: C, 45.34; H, 4.73; I, 39.74.

The alkaline solutions were combined, acidified with hydrochloric acid, and extracted with methylene chloride (3 × 150 ml). The organic solution was washed with saturated sodium chloride solution, dried, and concentrated to yield 7.3 g (38 mmol, 71%) of **12**, mp 199–202° (ether): $\delta_{TMS}^{CDCl_3}$ 9.2 (br s, 1, CO_2H, shifts position on dilution), 5.42–5.58 (m, 2, vinyl), 1.0–2.7 (m including s at 1.81 for cyclopropyl, 13).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.64; H, 8.41.

***anti*-11-Hydroxymethyl[4.4.1]propell-3-ene (15a).** A solution of 7.3 g (38 mol) of unpurified **12** in 225 ml of anhydrous tetrahydrofuran was added dropwise to a stirred slurry of 2.9 g (76 mmol) of lithium aluminum hydride in 25 ml of the same solvent, and the mixture was stirred at reflux for 4.0 hr. An alkaline work-up was employed to give 5.1 g (75%) of **15a** as a viscous oil; $\delta_{TMS}^{CDCl_3}$ 5.37–5.53 (m, 2, vinyl), 3.72 (d, $|J|$ = 7.4 Hz, 2, $-CH_2O-$), 2.85 (br s, 1, hydroxyl, shifts on dilution), and 0.9–2.7 (m, including t at 1.12 for cyclopropyl, $|J|$ = 7.4 Hz, 13).

***anti*-11-Acetoxymethyl[4.4.1]propell-3-ene (15b).** Acetyl chloride (12 g, 0.15 mol) was added dropwise to a stirred solution of 5.1 g (29 mmol) of **15a** and 20 ml of pyridine in 200 ml of dry ether cooled in an ice bath, and the mixture was stirred at room temperature for 2.0 hr. The contents were poured onto 200 ml of ice and water, and the organic layer was washed with cold 200-ml portions of water, 3% hydrochloric acid (twice), and saturated sodium bicarbonate solution. The solution was dried and concentrated. The residue was distilled through a short path distillation head to provide 5.23 g (83%) of **15b** as a colorless oil, bp 85° (0.10 mm). An analytical sample was obtained by preparative vpc purification (0.25 in. × 6 ft 5% XF-1150, 145°); $\delta_{TMS}^{CDCl_3}$ 5.37–5.53 (m, 2, vinyl), 4.22 (d, $|J|$ = 7.6 Hz, 2, $-CH_2O-$), and 0.9–2.7 (m, including s at 2.01 for CH_3CO_2 and t, $|J|$ = 7.6 Hz, at 1.18 for cyclopropyl, 16).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.58; H, 9.25.

***anti*-11-Acetoxymethylbicyclo[4.4.1]undeca-1,3,5-triene (16b).** A solution of 4.2 g (26 mmol) of bromine in 10 ml of methylene chloride was added to a stirred solution of 5.23 g (23.8 mmol) of **15b** in 90 ml of methylene chloride at room temperature, and the solution was stirred for 5 min. The solvent was evaporated leaving an orange viscous oil which was treated with 11 g (72 mmol) of DBU in 100 ml of anhydrous tetrahydrofuran at reflux under dry oxygen-free argon with stirring for 21 hr. The black mixture was cooled, poured onto 0.3 l. of ice–water, and extracted with ether (3 × 150 ml). The ethereal solution was washed with cold portions of water (2 × 0.5 l.), 3% hydrochloric acid (3 × 0.2 l.), and saturated sodium bicarbonate solution. The organic phase was dried and concentrated, and the dark residual oil was distilled, bp 80–105° (0.02 mm). This distillate was chromatographed on silica gel to give 2.34 g (45%) of a colorless oil. An analytical sample was obtained by preparative vpc (0.25 in. × 3 ft 5% SF-96, 142°): $\lambda_{max}^{isooctane}$ 253 nm (ϵ 4830); $\delta_{TMS}^{CDCl_3}$ 6.62–6.75 and 5.90–6.05 (AA′BB′, 4, H_3 and H_2, respectively), 4.69 (d, $|J|$ = 7.8 Hz, 2, $-CH_2O-$), and 0.7–2.8 (m, including s at 2.01 for CH_3CO_2 and t, $|J|$ = 7.8 Hz, at 1.10 for >C*H*–, 12).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.68; H, 8.35.

***anti*-11-Hydroxymethylbicyclo[4.4.1]undeca-1,3,5-triene (16a).** A solution of 2.34 g (10.7 mmol) of **16b** in 40 ml of dry ether was added to a stirred slurry of 0.50 g (13 mmol) of lithium aluminum hydride in 10 ml of ether, and the mixture was stirred at reflux for 1.0 hr. An alkaline work-up gave 1.90 g (100%) of viscous colorless oil: $\delta_{TMS}^{CDCl_3}$ 5.95–6.02 and 6.56–6.71 (AA′BB′, 4, vinyl), 4.14 (d, $|J|$ = 7.7 Hz, 2, $-CH_2O-$), 3.3 (br s, 1, hydroxyl), and 0.8–2.8 (m including t, $|J|$ = 7.7 Hz, at 0.93 for >C*H*–, 9).

The corresponding 3,5-dinitrobenzoate (**16c**) was prepared by the general procedure. Samples for analysis and solvolysis were obtained by recrystallization from methylene chloride–ether, mp 132–133°.

Anal. Calcd for $C_{18}H_{18}N_2O_6$: C, 61.61; H, 4.90; N, 7.56. Found: C, 61.47; H, 5.10; N, 7.64.

[4.4.1]Propell-3-enyl-*syn*-11-carboxylic Acid (13). A solution of 3.68 g (11.6 mmol) of **14** in 200 ml of glacial acetic acid was cooled to the freezing point, 13 g of zinc dust was added, and the mixture was vigorously shaken with intermittent cooling for 15 min. The zinc was removed by filtration through Celite, and the solvent was evaporated. A solution of the residue in 100 ml of 10% sodium hydroxide solution was washed with methylene chloride (100 ml) and acidified with hydrochloric acid. The aqueous mixture was extracted with ether (3 × 100 ml), and the organic solution was

washed with water (2 × 100 ml) and saturated sodium chloride solution, dried, and concentrated to yield 2.24 g (100%) of white crystals, mp 121–122° (from ether): $\delta_{TMS}^{CDCl_3}$ 11.5 (s, 1, CO_2H), 5.4–5.6 (m, 2, vinyl), and 1.2–2.4 (m, 13).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.84; H, 8.15.

***syn*-11-Hydroxymethyl[4.4.1]propell-3-ene (19a).** Treatment of 2.18 g (11.4 mmol) of **13** with lithium aluminum hydride in ether as described for **15a** provided 1.99 g (98%) of **19a** as a colorless oil which crystallized upon standing overnight: $\delta_{TMS}^{CDCl_3}$ 5.5–5.6 (m, 2, vinyl), 3.68 (d, $|J|$ = 7.5 Hz, 2, $-CH_2O-$), 3.05 (s, 1, hydroxyl, moves on dilution), 1.1–2.7 (m, 12, $-CH_2-$), and 0.87 (t, $|J|$ = 7.5 Hz, 1, cyclopropyl).

***syn*-11-Acetoxymethyl[4.4.1]propell-3-ene (19b).** Treatment of 1.99 g (11.2 mmol) of **19a** with acetyl chloride as described for **15b** provided 2.48 g (100%) of **19b**. The analytical sample was obtained by preparative vpc (0.25 in. × 2 ft 5% SF-96, 140°): $\delta_{TMS}^{CDCl_3}$ 5.5–5.7 (m, 2, vinyl), 4.20 (d, $|J|$ = 7.2 Hz, 2, $-CH_2O-$), 1.2–2.7 (m including s at 1.99 for CH_3CO_2, 15), and 0.93 (t, $|J|$ = 7.2 Hz, 1, cyclopropyl).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 75.97; H, 8.95.

***syn*-11-Acetoxymethylbicyclo[4.4.1]undeca-1,3,5-triene (20b).** A mixture of 4.00 g (18.2 mmol) of **19b** and 8.0 g (25 mmol) of pyridinium hydrobromide perbromide in 150 ml of 1:1 carbon tetrachloride–acetic acid was stirred at room temperature for 1.0 hr. The mixture was poured into 0.3 l. of ice and water, and the aqueous layer was extracted with ether (2 × 100 ml). The combined organic layers were washed with 0.5 l. of cold water and saturated sodium bicarbonate solution, dried, and concentrated. A stirred solution of the viscous yellow residue in 100 ml of anhydrous tetrahydrofuran under dry oxygen-free argon was treated with 14 g (0.09 mol) of DBU at reflux for 40 hr. The dark mixture was cooled, poured into 0.3 l. of ice and water, saturated with sodium chloride, and extracted with ether (3 × 100 ml). The organic solution was washed with cold 3% hydrochloric acid (2 × 0.25 l.) and saturated sodium bicarbonate solutions, dried, and concentrated. The yellow residual oil (3.88 g) was carefully distilled through a 6-in. Vigreux column to yield 1.97 g (50%) of colorless oil, bp 76.5–77.5°, which was pure by vpc, tlc, and nmr analysis. A sample for elemental analysis was purified by preparative vpc (0.25 in. × 3 ft 5% SF-96, 142°): $\lambda_{max}^{isooctane}$ 258 nm (ε 3200); $\delta_{TMS}^{CDCl_3}$ 5.87–6.45 (AA'BB', 4, vinyl), 3.37 (d, $|J|$ = 7.0 Hz, 2, $-CH_2O-$), and 0.8–2.8 (m including s at 1.95 for CH_3CO_2, 12).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.60; H, 8.34.

***syn*-11-Hydroxymethylbicyclo[4.4.1]undeca-1,3,5-triene (20a).** Treatment of 1.97 g (9.04 mmol) of **20b** with lithium aluminum hydride in ether as described for **16a** provided 1.55 g (97%) of **20a** as white crystals, mp 73–75°; $\delta_{TMS}^{CDCl_3}$ 5.9–6.6 (m, 4, vinyl) and 0.8–3.2 (m, 12).

The corresponding 3,5-dinitrobenzoate (**20c**) was prepared by the general procedure. Samples for analysis and solvolysis were obtained by recrystallization from ether, mp 92–92.5°.

Anal. Calcd for $C_{19}H_{18}N_2O_6$: C, 61.61; H, 4.90; N, 7.56. Found: C, 61.37; H, 4.99; N, 7.62.

11,11-Dibromo[4.4.1]propella-3,8-diene (21). A solution of 307 g (1.21 mol) of bromoform in 1 l. of pentane was added dropwise over 1.7 hr to a mechanically stirred slurry of 160 g (1.21 mol) of isotetralin[50] and 204 g (1.82 mol) of potassium *tert*-butoxide in 2 l. of pentane cooled to −40° under nitrogen. After the addition was complete, the stirred mixture was allowed to slowly warm to room temperature over 4 hr. The supernatant solution was decanted, washed with cold water, and concentrated. The wash water was added to the reaction sludge with an additional 2 l. of water, the aqueous mixture was extracted with methylene chloride (4 × 750 ml), and the combined organic material was washed with saturated sodium chloride solution, dried, and concentrated. The semisolid residue (334 g) was heated until molten, diluted with 150 ml of hot ethyl acetate, and triturated with 150 ml of methanol. After cooling the product was filtered, washed with methanol, and dried to give 200 g (54%) of tan powder, mp 104–120° (lit.[16] mp 124–125°).

11-Bromo[4.4.1]propella-3,8-diene (22). To a stirred solution of 91.6 g (0.301 mol) of **21** in 0.25 l. of anhydrous benzene was added 104 g (0.357 mol) of tri-*n*-butyltin hydride over 10 min at 27–30° and the solution was stirred at 36–40° for 2.5 hr. The solvent was evaporated, the residue was distilled through a 6-in. Vigreux column (bp 57–77° (0.1 mm)), and the distillate was chromatographed on alumina (neutral activity I, 10:1) eluting with petroleum ether (bp 38–57°) to provide 37.5 g (55%) of white crystals, mp 48–51° (lit.[15] mp 51°): $\delta_{TMS}^{CDCl_3}$ 5.47–5.62 (m, 4, vinyl), 3.34 (s, 1, cyclopropyl), and 1.9–2.8 (m including br s at 2.22, 8, allylic).

[4.4.1]Propella-3,8-dienyl-11-carboxylic Acid (23). A stirred mixture of 20.4 g (90.7 mmol) of **22** and 8.8 g (0.36 g-atom) of magnesium turnings in 220 ml of anhydrous tetrahydrofuran under dry oxygen-free nitrogen was brought to reflux, 1.0 ml of ethylene bromide was added dropwise, and the mixture was stirred at reflux for 9.5 hr. After cooling to room temperature, the supernatant solution was decanted under nitrogen from excess magnesium onto a large excess of crushed Dry Ice, and the slurry was stirred under nitrogen until the temperature had risen to room temperature. The mixture was acidified with 10% hydrochloric acid (100 ml) and saturated with sodium chloride, and the aqueous layer was extracted with ether (2 × 100 ml). The combined organic layers were extracted with 10% sodium hydroxide solution (3 × 100 ml), and the alkaline phase was washed with ether (200 ml), acidified with concentrated hydrochloric acid, and treated as above. After drying and concentration there remained 7.2 g (42%) of **23**, mp 134.5–135.5° (white micro needles from ether): $\delta_{TMS}^{CDCl_3}$ 11.7 (s, 1, CO_2H, moves on dilution), 5.4–5.6 (m, 4, vinyl), and 1.8–2.9 (m including s at 1.85 for cyclopropyl, 9).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.79; H, 7.47.

11-Hydroxymethyl[4.4.1]propella-3,8-diene (24a). A solution of 3.24 g (16.8 mmol) of **23** in 40 ml of anhydrous ether was added dropwise to a stirred slurry of 1.14 g (30 mmol) of lithium aluminum hydride in 10 ml of ether at room temperature, and the mixture was stirred at reflux for 1.4 hr. After alkaline work-up there remained 2.92 g (97%) of white crystals, mp 66–67°, from hexane, which were too unstable to permit an accurate microanalysis: $\delta_{TMS}^{CDCl_3}$ 5.48–5.68 (m, 4, vinyl), 3.71 (d, $|J|$ = 7.1 Hz, 2, $-CH_2O-$), 1.8–2.8 (m, 9, allylic and hydroxyl), and 1.24 (t, $|J|$ = 7.1 Hz, 1, cyclopropyl).

The corresponding 3,5-dinitrobenzoate (**24b**) was prepared by the general procedure. Samples for analysis and solvolysis were obtained by recrystallization from ether, mp 100.5–101°.

Anal. Calcd for $C_{19}H_{18}N_2O_6$: C, 61.61; H, 4.90; N, 7.56. Found: C, 61.56; H, 4.94; N, 7.53.

11-Hydroxymethyl[4.4.1]propellane (25a). A mixture of 2.62 g (14.9 mmol) of **24a** and 0.50 g of 10% Pd–C in 20 ml of ethyl acetate and 50 ml of methanol was treated with hydrogen at 50 psi in a Parr apparatus. The catalyst was removed by washing through a short column of silica gel, and the solvent was evaporated to give 2.62 g (98%) of viscous colorless oil: $\delta_{TMS}^{CDCl_3}$ 3.80 (d, $|J|$ = 7.6 Hz, 2, $-CH_2O-$), 2.03 (s, 1, hydroxyl), 1.1–2.0 (m, 16, $-CH_2-$), and 0.81 (t, $|J|$ = 7.6 Hz, 1, cyclopropyl).

The corresponding 3,5-dinitrobenzoate (**25b**) was prepared by the general procedure. Samples for analysis and solvolysis were obtained by recrystallization from ethanol, mp 86.2–87.0°.

Anal. Calcd for $C_{19}H_{22}N_2O_6$: C, 60.95; H, 5.92; N, 7.48. Found: C, 60.79; H, 6.01; N, 7.44.

Methyl[4.4.1]propella-3,8-dienyl-11-carboxylate (26). A stirred solution of 5.00 g (26.3 mmol) of **23** in anhydrous ether (100 ml) was treated with an excess of an ethereal solution of diazomethane (from *N*-methyl-*N*-nitrosourea; dried over potassium hydroxide pellets but not distilled). The solution was warmed to remove excess diazomethane, dried, and concentrated to give 5.36 g (100%) of colorless oil. An analytical sample was purified by preparative gas chromatography (0.25 in. × 5 ft 5% SE-30, 140°): $\delta_{TMS}^{CDCl_3}$ 5.4–5.6 (m, 4, vinyl), 3.53 (s, 3, CO_2CH_3), 1.9–2.9 (m, 8, $-CH_2-$), and 1.79 (s, 1, cyclopropyl).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.43; H, 8.12.

11-Carbomethoxy-1,6-methanocyclodecapentaene (27). A mixture of 5.36 g (26.3 mmol) of **26** and 18 g (79 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 100 ml of anhydrous dioxane was stirred at reflux under dry oxygen-free nitrogen for 45 hr. The mixture was cooled to room temperature, diluted with 0.5 l. of ether, filtered, and concentrated. The residue was chromatographed on alumina (neutral activity I) eluting with ether to give 3.85 g (73%) of light yellow solid. Recrystallization from hexane yielded 3.36 g (64%) of light yellow needles, mp 125.5–126°; $\delta_{TMS}^{CDCl_3}$ 6.8–7.6 (m, 8, olefinic), 3.26 (s, 3, CO_2CH_3), and 0.49 (s, 1, $>CHCO_2-$).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.93; H, 6.12.

(50) W. Hückel and U. Worfell, *Chem. Ber.*, **89**, 2098 (1956).

11-Hydroxymethyl-1,6-methanocyclodecapentaene (28a). A mixture of 3.36 g (16.8 mmol) of **27** and 5 g of potassium hydroxide in 80% aqueous ethanol was stirred at reflux under nitrogen for 6 hr. The solution was cooled with an ice bath and acidified with hydrochloric acid. The precipitated acid was filtered, washed with water, and dried to give 3.08 g (99%) of light yellow powder, mp 241–242°. A mixture of the crude acid and 21 g (0.17 mol) of oxalyl chloride in anhydrous benzene (20 ml) was stirred at room temperature for 0.3 hr and at reflux for 1.6 hr. The solution was concentrated to give a brown solid which was immediately reduced with 6.3 g (0.17 mol) of sodium borohydride in 50 ml of anhydrous diglyme with stirring at 100° under nitrogen for 1.2 hr. The mixture was cooled to room temperature, poured into 250 ml of cold 2% hydrochloric acid, and extracted with ether (3 × 100 ml). The organic solution was washed with water (2 × 200 ml) and saturated sodium bicarbonate solution, dried, and concentrated to give 2.63 g (92%) of cream-colored crystals, mp 107.5–108.5° (ether–hexane): $\delta_{TMS}^{CDCl_3}$ 6.73–7.42 (m, 8, olefinic), 2.18 (d, $|J|$ = 7.5 Hz, 2, $-CH_2O-$), 1.27 (br s, 1, hydroxyl), and 0.15 (t, $|J|$ = 7.5 Hz, 1, $>CHCH_2-$).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.66; H, 7.02.

The corresponding 3,5-dinitrobenzoate (**28b**) was prepared by the general procedure. Samples for analysis and solvolysis were obtained by recrystallization from methylene chloride–ether, mp 150.5–151.5°.

Anal. Calcd for $C_{19}H_{14}N_2O_6$: C, 62.29; H, 3.85; N, 7.65. Found: C, 62.15; H, 3.98; N, 7.73.

Kinetic Method. (A) Reagents. Reagent grade acetone was purified by distillation first from phosphorous pentoxide and then potassium permanganate. Tetrahydrofuran was distilled from lithium aluminum hydride and reagent grade methanol was used from a freshly opened bottle. Pure 2,6-lutidine was obtained by fractional distillation from calcium oxide. Reagents were degassed by boiling for several minutes and were then equilibrated at 25° before mixing.

(B) Kinetic Measurements. An approximately 0.02 *M* solution of the 3,5-dinitrobenzoate was prepared by dissolving an accurately weighed sample in 80:20 acetone–water or 75:25 tetrahydrofuran–methanol (both v/v) in a 25-ml volumetric flask. Aliquots (1.2 ml) of this solution were sealed under a slight vacuum (*ca.* 0.5 atm) into ampoules which had been scrupulously cleaned and dried. A set of ampoules was simultaneously placed in a constant temperature bath. After 10 min the first tube was withdrawn and an accurate timer was started. The sample was cooled in ice, brought to room temperature, and opened. A 1.032-ml aliquot was withdrawn and titrated potentiometrically using a Fisher "Accumet" model 310 pH meter fitted with a Fisher microprobe combination electrode. Additional samples were removed at different time intervals, and by titration the amount of liberated 3,5-dinitrobenzoic acid was determined. The various values were subtracted from the original amount of dinitrobenzoate to give the concentration of dinitrobenzoate which values were plotted against time *t*. The slopes and activation parameters were evaluated by the method of least squares.

Preparative Scale Solvolyses. General Procedure. Preparative solvolyses were conducted in a reusable glass bomb equipped with an internal thermometer, and temperature control of the reactions was within ±3°. For the reactions conducted in 80:20 acetone–water, work-up consisted of organic solvent evaporation, saturation of the aqueous residue with sodium chloride, and threefold ether extraction. The combined ether layers were then shaken in sequence with 10% hydrochloric acid (three times), 10% sodium carbonate solution (three times), and brine, followed by drying and concentration on a rotary evaporator without external heating. The reactions conducted in 75:25 tetrahydrofuran–methanol were evaporated to dryness and the residue was dissolved in ether. Subsequent processing was identical with the above. Crude yields were approximately quantitative. In the vpc determinations of product ratios, no account was taken of possible differences in the thermal conductivities of the materials.

Solvolysis of 16c. A 350-mg (0.946 mmol) sample of **16c** and 203 mg (1.89 mmol) of 2,6-lutidine in 50 ml of 80:20 acetone–water were heated at 100° for 15.2 hr (12 half-lives). Work-up gave 148 mg of yellow oil. Vpc analysis (6 ft × 0.25 in. 5% SE-30 on 60–80 mesh Chromosorb G, 142°) showed one major component (99%), collection of which gave 80 mg of 5-vinyltetralin (**29**): $\delta_{TMS}^{CDCl_3}$ 6.8–7.4 (m, 4, aromatic and X portion of ABX system), 5.69, 5.51, 5.34, and 5.22 (9 lines, 2, AB part of ABX), 2.77 (br s, 4, allylic), and 1.80 (m, 4).

Anal. Calcd for $C_{12}H_{14}$: C, 91.09; H, 8.92; *m/e* 158.1095. Found: C, 91.15; H, 8.88; *m/e* 158.1097.

Hydrogenation of 29. Catalytic reduction of **29** (41 mg) over palladium on carbon (10 mg) in 25 ml of ethyl acetate at atmospheric pressure, followed by filtration, concentration, and preparative vpc isolation afforded 32 mg of 5-ethyltetralin (**30**): $\delta_{TMS}^{CDCl_3}$ 6.9–7.2 (m, 3, aromatic), 2.46–2.92 (m, 6, allylic, including q at 2.58 ($|J|$ = 7.4 Hz) for the $-CH_2-$ part of the ethyl group), 1.6–2.0 (m, 4, methylenes), and 1.19 (t, $|J|$ = 7.4 Hz, methyl).

Anal. Calcd for $C_{12}H_{16}$: *m/e* 160.1252. Found: *m/e* 160.1254.

The infrared spectrum was identical with that of an authentic sample.[51]

Solvolysis of 20c in Aqueous Acetone. Heating a solution containing 200 mg (0.54 mmol) of **20c** and 116 mg (1.08 mmol) of 2,6-lutidine in 30 ml of 80:20 acetone–water at 100° for 47 hr (11 half-lives) followed by the predescribed work-up gave 85 mg of yellow oil. Vpc isolation as above afforded 36 mg of **29** as the lone product.

Solvolysis of 25b. Reaction of **25b** (800 mg, 2.14 mmol) and 2,6-lutidine (463 mg, 4.32 mmol) dissolved in 120 ml of 80:20 acetone–water at 100° for 5.2 hr (10 half-lives) and customary work-up led to the isolation of 217 mg of light yellow oil. Vpc analysis (12 ft × 0.25 in. 5% Carbowax 20 M on 60–80 mesh Chromosorb G, 160°) showed the material to be composed of (order of elution) **31** (65%), an unidentified vinyl alcohol (1.5%), **32** (15%), and **33** (19%). The retention times were sufficiently separated to permit separation by this technique.

For **31**: $\delta_{TMS}^{CDCl_3}$ 5.56 (4 lines, 1, X part of ABX), 5.53 (br s, 1, olefinic ring proton), 5.18, 5.08, 4.93, 4.78 (8 lines, AB portion of ABX), and 1.1–2.4 (m, 14).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18; *m/e* 162.1408. Found: C, 88.67; H, 11.52; *m/e* 162.1411.

For **32**: $\delta_{TMS}^{CDCl_3}$ 6.11 (4 lines, 1, X part of ABX), 5.22, 5.12, 4.95 (6 lines, AB part of ABX), and 1.2–1.8 (m, 17); *m/e* 180 (base peak 162, $M^+ - H_2O$).

For **33**: $\delta_{TMS}^{CDCl_3}$ 6.42 (4 lines, 1, X part of ABX), 5.24, 5.19, 5.13, 5.01 (8 lines, 2, AB portion of ABX), and 1.53 (br s, 17); *m/e* 180 (base peak 162, $M^+ - H_2O$).

The minor component exhibited infrared bands at 3600 (free OH) and 3450 cm^{-1} (bonded OH): $\delta_{TMS}^{CDCl_3}$ 6.14 (4 lines, 1, X part of ABX), "doublets" at 5.36 and 5.05, and a "triplet" at 5.18 (7 lines, AB part of ABX) and 1.55 (br s),

Anal. Calcd for $C_{12}H_{20}O$: *m/e* 180.1514. Found: *m/e* 180.1517.

In a control experiment, the crude mixture of products was heated under the solvolysis conditions for 21 hr and no alteration in the distribution was noted except for **31** which decreased to 59% of its original amount. Thus, in the duration of the solvolysis, **31** would suffer approximately 10% decomposition.

Hydrogenation of 31. Catalytic reduction of 29 mg of **31** in 15 ml of ethyl acetate containing 50 mg of 5% palladium on carbon at atmospheric pressure followed by preparative vpc collection (12 ft × 0.25 in. 5% Carbowax 20 M on 60/80 mesh Chromosorb G, 145°) gave a mixture of ethyldecalins **36**. The nmr spectrum was essentially identical with that obtained for the authentic mixture (see below).

Anal. Calcd for $C_{12}H_{22}$: *m/e* 166.1721. Found: *m/e* 166.1724.

Hydrogenation of 32. Approximately 15 mg of **32** in 10 ml of ethyl acetate was hydrogenated over Adams' catalyst at atmospheric pressure. Work-up and vpc isolation gave a colorless oil with nmr and ir spectra identical with those of authentic **35** (see below).

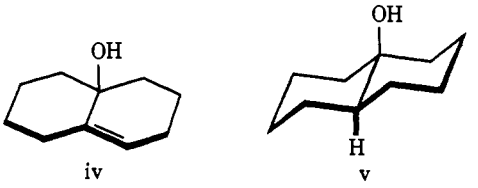
Anal. Calcd for $C_{12}H_{22}O$: *m/e* 182.1671. Found: *m/e* 182.1672.

Dehydration of 32/33. To a solution containing 41.4 mg (0.188 mmol) of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt[38] in 5 ml of dry tetrahydrofuran was added dropwise with stirring a solution of 17 mg (0.094 mmol) of **32/33** (*ca.* 1:1) in 5 ml of the same solvent. The mixture was heated at 56–60° for about 12 hr and 10 ml of water was added to the oil obtained upon solvent evaporation. The organic product was extracted with ether and the combined ether layers were washed with 10% hydrochloric acid and sodium carbonate solutions and brine. After drying and concentration, the resulting crude product was purified by preparative vpc (6 ft × 0.25 in. 12% Carbowax 20 M on 60–80 mesh Chromosorb W, 140°) to give **31**.

trans-**9-Ethyldecal-10-ol (35).** To ethylmagnesium bromide (from 4.8 g (198 mg-atom) of magnesium turnings and 10.8 g (99

(51) Sadtler spectrum no. 8216.

mmol) of ethyl bromide, 29-fold molar excess) in 75 ml of dry tetrahydrofuran was added dropwise a solution of 500 mg (3.29 mmol) of epoxide **34**[52] in 5 ml of the same solvent. After the mixture was refluxed for 44 hr, it was cooled to 45° and saturated ammonium chloride solution was cautiously introduced. Water (75 ml) and pentane (125 ml) were added, the pentane layer was washed further with water (3 × 75 ml), and the individual water layers were extracted with pentane (2 × 50 ml). The combined organic layers were dried and concentrated to give 550 mg of colorless oil. Vpc analysis (6 ft × 0.25 in. 12% carbowax 20 M on 60–80 mesh Chromosorb W, 160°) revealed the material to be composed of **35** (46%), iv (6%), and v (48%),[53] each of which was collected on a preparative scale. Another experiment using a ten-fold excess of ethylmagnesium bromide furnished a mixture composed of 41% **35**, 16% iv, and 42% v.



iv v

Alcohol v, mp 54.5–55.2° (sealed capillary, lit.[52] mp 54°) gave an nmr spectrum identical with that of authentic v prepared by lithium aluminum hydride reduction of **34**:[52] $\delta_{TMS}^{CDCl_3}$ broad absorption from δ 1.2–1.8 with maxima at 1.49 and 1.26.

Anal. Calcd for $C_{10}H_{18}O$: *m/e* 154.1358. Found: *m/e* 154.1359.

Alcohol iv, mp 81–82° (lit.[54,55] mp 84–86°), was identified by comparison of its ir spectrum with that published and by its pmr spectrum: $\delta_{TMS}^{CDCl_3}$ 5.45 (m, 1, olefinic) and 1.1–2.6 (m, 15).

Anal. Calcd for $C_{10}H_{16}O$: 152.1201. Found: *m/e* 152.1204.

Alcohol **35**, mp 50.2–50.8° (sealed capillary), was characterized by the following pmr signals: $\delta_{TMS}^{CDCl_3}$ 1.1–1.8 (m, 19) and 0.72 (t, $|J|$ = 7.5 Hz, methyl).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16; *m/e* 182.1671. Found: C, 79.44; H, 12.20; *m/e* 182.1674.

Conversion of 35 to 36. To 660 mg (3.0 mmol) of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt[33] in 15 ml of dry tetrahydrofuran was added dropwise with stirring a solution of 250 mg of **35** in 15 ml of the same solvent. The mixture was stirred with heating at 55–60° overnight and worked up as described above to give the olefin as a colorless oil:[56] $\delta_{TMS}^{CDCl_3}$ 5.35 (m, 1, olefinic), 0.9–2.3 (m, 16), and 0.75 (t, $|J|$ = 7 Hz, methyl). For analysis, see above.

Hydrogenation of the crude hydrocarbon over Adams' catalyst in 75 ml of ethyl acetate at atmospheric pressure and purification by preparative vpc (12% Carbowax 20M column, 148°) gave the cis–trans 9-ethyldecalin mixture **36**: $\delta_{TMS}^{CDCl_3}$ 0.9–2.0 (m), 0.76, and 0.72 (overlapping t, methyl groups).

Anal. Calcd for $C_{12}H_{22}$: *m/e* 166.1721. Found: *m/e* 166.1724.

Solvolysis of 24b. A solution of 300 mg (0.811 mmol) of **24b** and 176 mg (1.64 mmol) of 2,6-lutidine in 50 ml of 80:20 acetone–water was heated at 100° for 58.3 hr (11.4 half-lives). Customary work-up gave an oil, vpc analysis of which showed it to consist of two components: **37** (77%) and **38** (23%). Additional experiments gave ratios ranging to 91% of **37** and 9% of **38**.

The pmr spectrum of **37**, mp *ca.* 37°, showed signals at δ 6.02 (4 lines, 1, X part of ABX), 5.67 (m, 4, olefinic), 5.24, 5.05, 4.93 (8 lines, 2, AB part of ABX), 2.12 (br s, 8), and 2.03 (s, 1, O*H*).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15; *m/e* 176.1201. Found: C, 81.30; H, 9.16; *m/e* 176.1203.

The pmr spectrum of **38** is discussed in the text.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92; *m/e* 158.1095. Found: C, 90.84; H, 8.97; *m/e* 158.1098.

Control experiments established that, under the solvolysis and work-up conditions employed, **37** was stable but **38** decreased to 44% of its original amount.

Hydrogenation of 37. Hydrogenation of 85 mg of **37** in ethyl acetate solution over 5% Pd–C and preparative vpc isolation (12% Carbowax 20M column, 150°) gave material identical with authentic **35**.

Anal. Calcd for $C_{12}H_{22}O$: *m/e* 182.1670. Found: *m/e* 182.1674.

Dehydration of 37. A solution of 96.4 mg (0.546 mmol) of **37** in 10 ml of dry tetrahydrofuran was added dropwise with stirring to 242 mg (1.10 mmol) of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt[33] and the mixture was heated at 60° for 2 hr. Processing as described above furnished **39** as a thermally unstable oil: $\delta_{TMS}^{CDCl_3}$ 5.5–6.3 (m, 6, X part of ABX and olefinic ring protons), 4.85–5.21 (6 lines, 2, AB of ABX), 2.87 (m, 2, doubly allylic protons), and 2.28 (m, 4, allylic).

Anal. Calcd for $C_{12}H_{14}$: *m/e* 158.1095. Found: *m/e* 158.1098.

Attempted vpc purification (150°) of **39** gave a mixture composed chiefly of **39** and **38**. Reprocessing through the gas chromatograph (150°) resulted in complete conversion to **38**.

Hydrogenation of 39. A 132-mg sample (0.75 mmol) of crude tetraene **39** in ethyl acetate solution was reduced over Adams' catalyst and the product was isolated by vpc. Its nmr spectrum was identical with that of the isomeric 9-ethyldecalins prepared earlier.

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34; *m/e* 166.1721. Found: C, 87.00; H, 13.30; *m/e* 166.1724.

11-Hydroxymethyl[4.4.1]propella-3,8-diene-*11,11-d*$_2$ 3,5-Dinitrobenzoate (44). To a stirred slurry of 448 mg (10.7 mmol) of lithium aluminum deuteride in 10 ml of dry ether was added dropwise a solution of 1.00 g (5.26 mmol) of **23** in 15 ml of ether. The mixture was refluxed overnight and processed in the predescribed fashion, and the resulting alcohol (740 mg) was converted directly to the ester. The pmr spectrum lacked the absorption at δ 4.62.

Solvolysis of 44. Identical solvolysis of **44** gave **37-*d*$_2$** (87%) and **54** (13%) which were separated by vpc techniques. The pmr spectrum of the alcohol lacked the AB portion of the ABX pattern and exhibited a broad singlet at δ 6.00 for the X part of the ABX pattern, thus indicating that the deuterium labeling is in fact totally in the terminal methylene group.

The pmr spectrum (C_6D_6) of **54** showed the absence of the signal at δ 1.63 due to H_{9b} and, by inference, the signal due to H_{9a} (not totally distinguishable from H_{7a}). A quantitative determination of the location of deuterium was not made in this instance.

11-Hydroxymethyl[4.4.1]propellane-*11,11-d*$_2$ 3,5-Dinitrobenzoate (53). An ethyl acetate solution containing 490 mg of 11-hydroxymethyl[4.4.1]propella-3,8-diene-*11,11-d*$_2$ was hydrogenated over Adams' catalyst and the resulting tetrahydro alcohol was transformed without purification to the 3,5-dinitrobenzoate. This ester lacked the absorption at δ 4.67.

Solvolysis of 53. Solvolysis of **53** gave a mixture of **31-*d*$_2$**, **32-*d*$_2$**, and **33-*d*$_2$**. Nmr analysis of the mixture showed broad singlets at δ 6.40 (due to **33**) and 6.11 (due to **32**) for the X portions of the respective ABX patterns and at 5.53 for both the X part of the ABX pattern and the olefinic ring proton of **31**. No signals for the AB portions of the spectra of **31–33** were present and thus the deuterated products contain the CH=CD$_2$ and are unscrambled with regard to the isotopic label.

Solvolysis of 20c in Tetrahydrofuran–Methanol. A solution of 100 mg (0.270 mmol) of **20c** and 58 mg (0.540 mmol) of 2,6-lutidine in 17 ml of tetrahydrofuran–methanol (3:1) was heated at 130° for 23 hr. Pmr analysis showed the presence of unrearranged alcohol **20a** (8%), methyl 3,5-dinitrobenzoate (**55**, 11.7%), and 5-vinyltetralin (**29**, 88.3%), These were separated gas chromatographically and individually characterized.

For **55**: mp 107–108.5°; $\delta_{TMS}^{CDCl_3}$ 9.03 (s) and 4.00 (s, 1:1).

Solvolysis of 28b. Heating of 60 mg (0.16 mmol) of **28b** and 178 mg (1.65 mmol) of 2,6-lutidine in 50 ml of tetrahydrofuran–methanol (3:1) at 100° for 18 hr gave 55 mg of a yellow liquid. Pmr analysis indicated the mixture to be composed of unrearranged alcohol **28a** (46.5%), recovered **28b** (53.5%), and **55** (37.1%). No pmr signals for 1-vinylnaphthalene were observed. Both **28a** and **55** proved stable to the reaction conditions. Unreacted **28b** could be recovered readily by trituration of the mixture with pentane.

In another experiment at 130° an additional substance was produced. It was identified as 1-vinylnaphthalene (**56**) by comparison of its ir spectrum with that published and its pmr spec-

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trum:[57] $\delta_{TMS}^{CDCl_3}$ 7.2–8.2 (m, 8, aromatic and X part of ABX), 5.91, 5.63, 5.57, and 5.38 (8 lines, 2, AB portion of ABX). The entire product distribution is given in Table III.

11-Methoxymethyl-1,6-methanocyclodecapentaene (57). To a suspension of sodium hydride (139 mg, 5.8 mmol, 244 mg of 57% oil dispersion) in 5 ml of dry dimethylformamide was added 200 mg (1.16 mmol) of **28a** dissolved in 5 ml of the same solvent. After 1 hr, 825 mg (5.8 mmol) of methyl iodide was introduced *via* syringe, the mixture was allowed to stir for 20 hr, and subsequently pipetted over ice and pentane (40 ml). The pentane layer was washed with water (3 × 50 ml) and the individual water portions were extracted with pentane (3 × 30 ml). The combined organic layers were dried and evaporated, and the residue was recrystallized from hexane and sublimed (45°, 0.01 mm) to give a white solid: mp 54.2–55.5°; $\delta_{TMS}^{CDCl_3}$ 7.16–7.46 (m, 4), 6.74–7.08 (m, 4), 2.90 (s, OCH_3), 2.04 (d, J = 6.9 Hz, $-CH_2O-$), and −0.06 (t, J = 6.9 Hz, H_{11}).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58; *m/e* 186.1045. Found: C, 83.68; H, 7.49; *m/e* 186.1047.

(57) Sadtler spectrum no. 3566.

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Barriers to Internal Rotation in 1,3,5-Trineopentylbenzenes. VI. Correlation between Barriers to Internal Rotation ($\Delta G^{\ddagger}$) and Substituent Size

Bertil Nilsson,*[1] Per Martinson,[2] Kåre Olsson,[2] and Robert E. Carter*[1]

Contribution from Organic Chemistry 2, Chemical Center, S-220 07 Lund 7, Sweden, and The Department of Organic Chemistry, University of Göteborg and Chalmers Institute of Technology, Fack, S-402 20 Göteborg 5, Sweden.
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Abstract: Relative "effective sizes" of the substituents H, F, Cl, Br, CH_3, and I in the 1,3,5-trineopentylbenzene system have been estimated from $\Delta G^{\ddagger}$ values obtained by dynamic nmr measurements of rotational barriers, ranging from 5.4 to 18.8 kcal/mol. An increase in barrier height with increasing substituent van der Waals volume was observed. The methyl group was found to be between chlorine and bromine in size in the trineopentylbenzene system. Linear free-energy relationships between the barriers for the trineopentylbenzenes and those for two other systems, in which the barriers arise from nonbonded interactions between an alkyl group and halogens, are presented.

At the molecular level, the significance of the term "size" when applied to a covalently bound atom or group is apparently not unequivocal. It may depend upon the molecular environment, especially in the case of atoms containing only a few electrons[3] (H, F, etc.), and perhaps upon the geometry of the particular interaction used to measure the "size" in question, since bond polarizabilities are in general anisotropic,[4] and the shape of a bound atom (or group) may be effectively nonspherical, as proposed by Nyburg and Szymański[5] for the covalently bound fluorine atom. The careful determination of barriers to internal rotation in a series of molecules, in which a change in the substituent "size" is the most important factor in determining a change in barrier height, offers in principle a means of experimentally establishing the relative "effective sizes" of the substituents in the series. However, there are apparently few molecular systems which allow such a study over a sufficiently wide range of substituent "sizes" by the same method of measurement, and which have barriers whose relative heights are primarily determined by differences in effective substituent "sizes."

The nmr kinetic method has been extensively used for the measurement of barriers to internal rotation,[6] and in some cases[7-13] (see Discussion) it has been possible to determine the barrier as a function of substituent "size" for a limited number of substituents.

In the 1,3,5-trineopentylbenzene series **1**, we have available a molecular system in which barriers of the same group (*tert*-butyl) past the substituents H, F, Cl, Br, I, and CH_3 could be determined. We have previously reported the determination (by complete lineshape analysis) of barriers past chlorine,[14,15] bro-

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(2) Department of Organic Chemistry, University of Göteborg and Chalmers Institute of Technology.
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