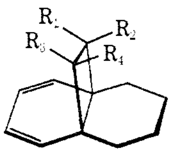
Functionalization Reactions of [4.4.2]Propella-3,11-diene

Leo A. Paquette* and Gerald L. Thompson[1]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received February 23, 1972*

Abstract: Electrophilic additions to [4.4.2]propella-3,11-diene have been found to proceed only at the cyclohexene double bond and exclusively from the endo direction. Methods for indirect functionalization of the cyclobutene ring have been devised. The various sequences have allowed the stereospecific introduction of deuterium atoms and methoxyl groups at C_{11} and C_{12} with retention of a conjugated diene unit in ring A. The high degree of selectivity encountered in a number of transformations is briefly rationalized in conformational terms.

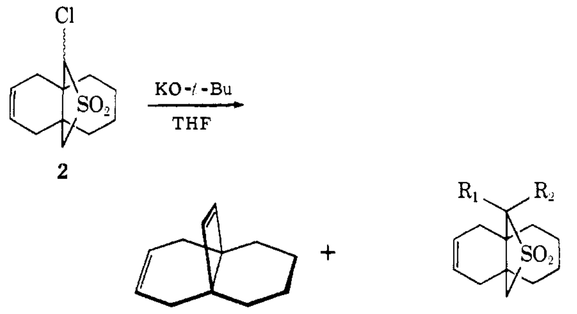
To render inoperative the symmetry-controlled [${}_\sigma2_s + {}_\sigma2_a$] scission of a cyclobutane to a pair of olefinic components, the four-membered ring must be conformationally constrained to prevent attainment of the requisite state of structural distortion. Denial of the concerted fragmentation pathway to a cyclobutane will then force the cleavage to proceed in stepwise fashion *via* transient 1,4 diradicals. Our combined interest in the stereochemical consequences of 1,4-diradical production[2] and in propellane chemistry[3] has prompted an investigation of the stereochemical consequences attending the pyrolysis of several specifically substituted [4.4.2]propella-2,4-dienes of general structure **1**. Such tricyclic molecules are incapable of extensive twisting and appeared ideally suited for the present purpose. The previously reported [4.4.2]-propella-3,11-diene (**3**)[3b] offered promise as a potential precursor to various derivatives of **1** and we report here appropriate functionalization reactions of this diene. The ensuing paper details the thermal and photochemical fragmentation reactions of **1**.[4]



1

Results

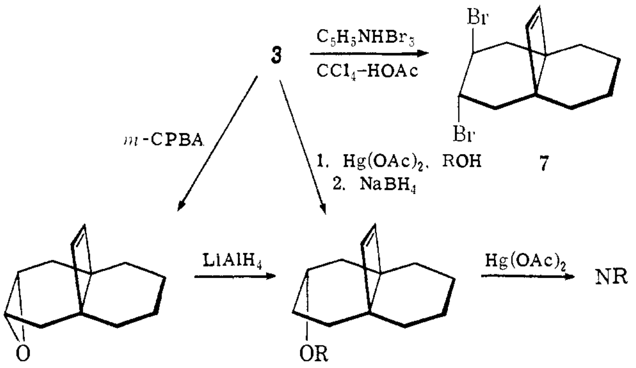
Exposure of a mixture of the two epimeric 11-chloro-12-thia[4.4.3]propell-3-ene 12,12-dioxides (**2**) to excess potassium *tert*-butoxide in refluxing tetrahydrofuran gave predominantly **3** (76%) together with lesser quantities of *tert*-butoxy sulfones **4a** and **4b**.[3b] When **3** was epoxidized with *m*-chloroperbenzoic acid in methylene chloride solution, a single epoxide **5** was produced. Its nmr spectrum, in particular the characteristic cyclobutene olefinic singlet (area 2) at δ 6.10, established that reaction had occurred exclusively at the cyclohexene double bond. In confirmation of the endo stereochemistry for the oxirane ring, **5** was reduced with lithium aluminum hydride to give an alcohol **6a** which proved unreactive to the action of mercuric acetate.[5] Oxymercuration of **3** with mercuric acetate in tetrahydrofuran-water (1:1) and subsequent demercuration[6] led also to **6a**. Execution of the mercuric acetate sequence in methanol[7] gave rise uniquely to ether **6b** whose configurational assignment follows from spectral similarities with **6a** and by analogy. It was also found that treatment of **3** with 1 equiv of freshly prepared pyridinium hydrobromide perbromide afforded exclusively the trans dibromide **7**. The presence in **7** of a cyclobutene ring was again consistent with the nmr spectrum. In this instance, however, the trans disposition of the two bromine atoms places the two olefinic protons in distinctly different environ-



2

3

4a, $R_1 = H$; $R_2 = O$-*t*-Bu
b, $R_1 = O$-*t*-Bu; $R_2 = H$



7

5

6a, R = H
b, R = CH_3

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[1] Philips Petroleum Fellow, 1970–1971; University Dissertation Fellow, 1971–1972.

[2] (a) L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, 92, 1763 (1970); (b) L. A. Paquette and J. A. Schwartz, *ibid.*, 92, 3215 (1970); (c) L. A. Paquette, M. R. Short, and J. F. Kelly, *ibid.*, 93, 7179 (1971); (d) L. A. Paquette and G. L. Thompson, *ibid.*, 93, 4920 (1971); (e) L. A. Paquette and L. M. Leichter, *ibid.*, 93, 4922 (1971).

[3] (a) L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *ibid.*, 93, 4508 (1971); (b) L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *ibid.*, 93, 4516 (1971); (c) L. A. Paquette and R. W. Houser, *ibid.*, 93, 4522 (1971); (d) earlier references cited in these papers.

[4] L. A. Paquette and G. L. Thompson, *ibid.*, 94, 7127 (1972).

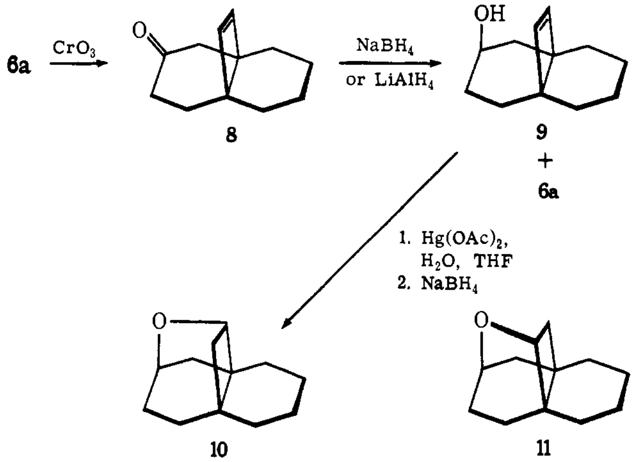
[5] F. G. Bordwell and M. L. Douglass, *ibid.*, 88, 993 (1966).

[6] H. C. Brown and P. J. Geoghegan, Jr., *ibid.*, 89, 1522 (1967).

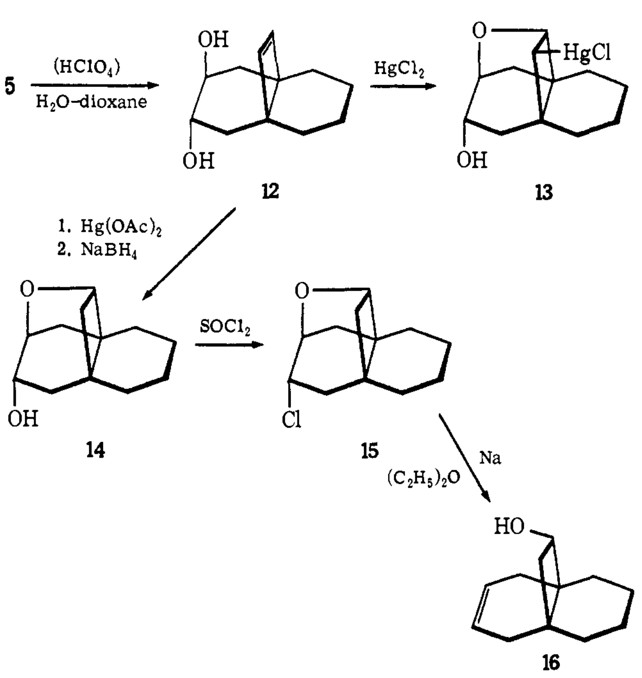
[7] H. C. Brown and M.-H. Rei, *ibid.*, 91, 5646 (1969).

ments; as a result, these hydrogens appear as an AB quartet at δ 6.10 and 6.47 with $|J_{AB}| = 3.0$ Hz.

Further proof for the correctness of these assignments was derived from Jones oxidation of **6a** to ketone **8**. The thin reservation that **8** could have been a cyclobutanone cannot be maintained against the observation of an infrared carbonyl band at 1720 cm^{-1} and a two-proton olefinic singlet in the nmr at δ 6.15. Reduction of **8** either with lithium aluminum hydride or sodium borohydride afforded chiefly (see Experimental Section) exo alcohol **9**. Cyclization of **9** by means of mercuric acetate led quantitatively to a cyclic ether. Although the available evidence does not distinguish between **10** and **11**, the former structure is preferred by analogy to the established cyclization mode of the closely related diol **12** (see below).



As experimental work progressed, it appeared increasingly unlikely that the cyclobutane ring in **3** could be *directly* functionalized.[8] Therefore, our attention became directed to the pursuit of methods for *indirect* substitution at C_{11} and C_{12}. To this end, epoxide **5** was converted to trans diol **12** with perchloric acid in aqueous dioxane. From an AB quartet at δ 6.06 and 6.27 ($J_{AB} = 3.0$ Hz) in the nmr spectrum, the trans relationship of the two hydroxyl groups can be inferred. Diol **12** underwent ready cyclization in the presence of mercuric chloride to yield adduct **13**. All available evidence indicates trans addition to the cyclobutene double bond.[9] When treated consecutively with $Hg(OAc)_2$ and $NaBH_4$ as before, **12** was converted quantitatively to **14**. The question of 3,12 or 3,11 bonding (as shown in **13–15**) of the ether oxygen is considered in detail below. Of more immediate import was the finding that conversion of **14** to chloride **15** with thionyl chloride–pyridine in benzene and subsequent treatment of **15** with sodium in refluxing ether led to stereocontrolled introduction (syn) of a hydroxyl function on the four-membered ring with retention of unsaturation in ring A. The absence of any gross structural change during these interconversions was attested to by the close similarity of the nmr spectra of **16** and [4.4.2]propell-3-ene (**46**).



The direction of cyclization of trans diol **12** under conditions of mercuration was unambiguously determined in the following manner. Although the olefinic protons in **16** are seen as overlapping multiplets of considerable complexity at both 60 and 100 MHz, the addition of 22 mol % $Eu(fod)_3$[10] in carbon tetrachloride produces a greater downfield shift of H_3 than of H_4 due to the closer proximity of the former to the *syn*-hydroxyl group. At this particular concentration the olefinic absorptions are quite distinctly separated and not yet obscured by other more rapidly shifting peaks. In view of this capability to distinguish between the two sp^2-bound hydrogens, it remained to label one of these selectively. The desired transformations were achieved as illustrated in the ensuing scheme. Quite unexpectedly, treatment of **18a** with thionyl chloride–pyridine in benzene or with triphenylphosphine dichloride in refluxing dimethylformamide[11] returned only ketone **17**. This difficulty was bypassed by reaction of derived mesylate **19a** with sodium iodide in hexamethylphosphoramide (HMPA) at 100° for 2 days.[12] The nmr spectrum of **21** in carbon tetrachloride containing 22 mol % $Eu(fod)_3$ was nearly superimposable upon that of **16** with the exception that the vinyl region of the spectrum had been reduced to a broad singlet due only to H_3 centered at δ 6.93. No absorption was detectable at δ 6.56, the chemical shift for H_4. As a consequence, the cyclization of diol **12** (and presumably also alcohol **9**) is necessarily unidirectional toward the more proximate cyclobutene carbon atom.

The penultimate step in the synthesis of **23** involved O-methylation of the alkoxide derived from **16** with methyl iodide. This methoxypropellene **22** then underwent ready conversion to diene **23** when subjected to the combined action of *N*-bromosuccinimide and potassium *tert*-butoxide.

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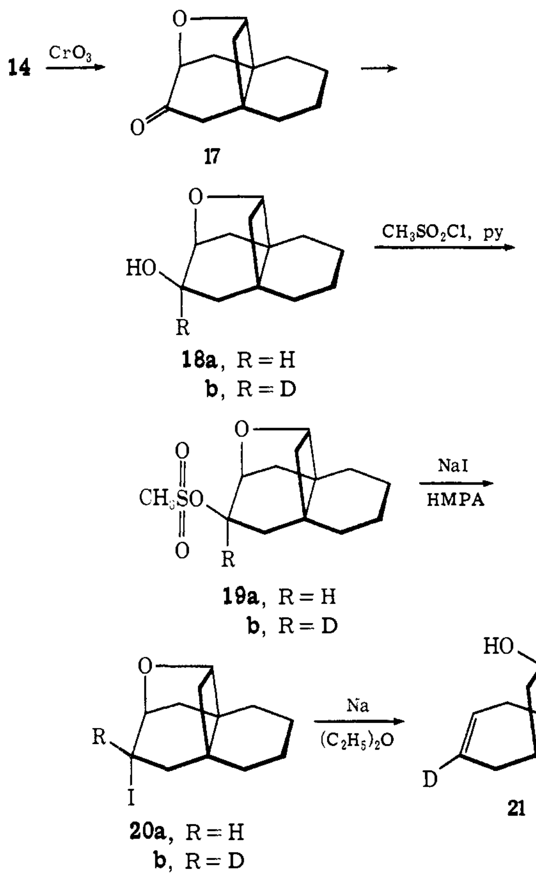
(8) Additionally, the solvomercuration–demercuration in methanol of epoxide **5** was seen to fail, even when a 100% excess of mercuric acetate was used. Likewise the further bromination of **7** with pyridinium hydrobromide perbromide could not be achieved.

(9) R. K. Bly and R. S. Bly, *J. Org. Chem.*, 28, 3165 (1963); (b) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Amer. Chem. Soc.*, 89, 880 (1967); (c) A. Factor and T. G. Traylor, *J. Org. Chem.*, 33, 2607 (1968); (d) W. L. Waters, *Tetrahedron Lett.*, 3769 (1969).

(10) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93, 1522 (1971).

(11) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *ibid.*, 86, 964 (1964).

(12) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967).



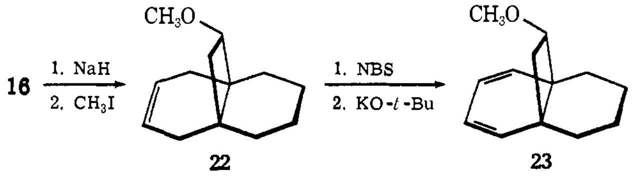
17

18a, R = H
b, R = D

19a, R = H
b, R = D

20a, R = H
b, R = D

21



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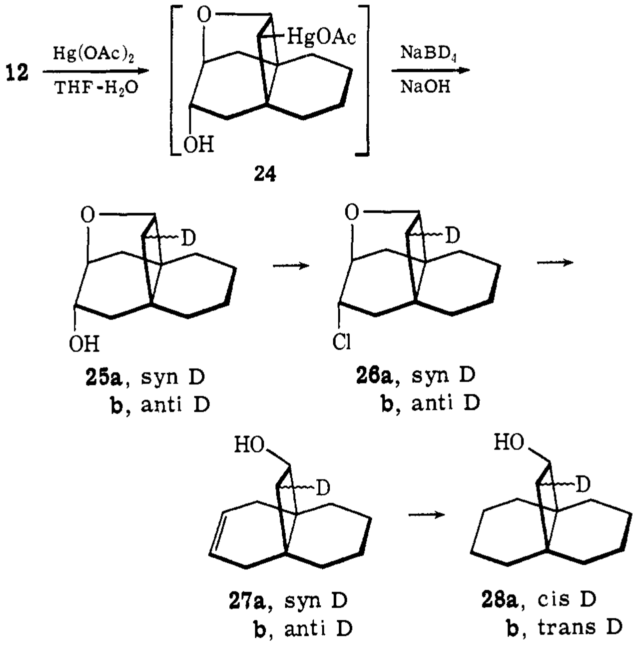
23

Having achieved efficient functionalization at C_{11}, we next sought to simultaneously introduce deuterium stereospecifically at C_{12}. An attractive sequence for consideration was deemed to be the *in situ* reduction of organomercurial **24** with alkaline sodium borodeuteride. When **24** was treated in this fashion, hydroxy ether **25** was obtained in quantitative yield. However, because demercuration with sodium borohydride involves the generation of intermediate alkyl radicals,[13] the stereochemical disposition of the deuterium atom in **25** was not entirely predictable.[14] Accordingly, it was imperative that the precise nature of the deuterium substitution be established. To this end, **25** was converted sequentially to labeled cyclobutanol **28**.

The point of this sequence was to arrive at a molecule, in this instance **28**, which could be realistically expected to be capable of unequivocal synthesis in its two stereoisomeric forms. Unquestionably, the most promising avenue for exploration lay in the direction of lanthanide-induced pseudocontact-shifted proton nmr spectra of these isomers. For this purpose, [4.4.2]propell-11-ene (**30**) was prepared. With diborane and diborane-d_6, **30** yielded **32** and **28a**, respectively, as the sole products. Also, cyclobutene **30** was readily converted to epoxide **33** which yielded **28b** upon lithium aluminum deuteride reduction. A second minor substance was noted (vpc analysis) but not characterized; in view of the established behavior of cyclobutene epoxides under conditions of hydride reduction,[15] this by-product has been tentatively formulated as **34**.



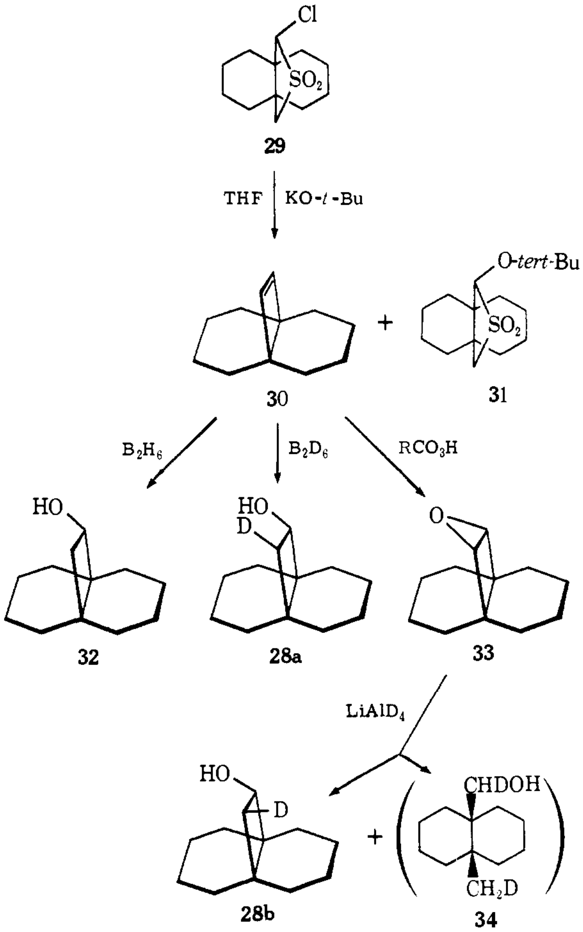
24

25a, syn D
b, anti D

26a, syn D
b, anti D

27a, syn D
b, anti D

28a, cis D
b, trans D



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32

28a

33

28b

34

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[13] G. M. Whitesides and J. S. Filipo, Jr., *J. Amer. Chem. Soc.*, 92, 6111 (1970).

[14] J. J. Miller, Ph.D. Thesis, University of California (Berkeley), 1966.

[15] L. A. Paquette, A. A. Youssef, and M. L. Wise, *J. Amer. Chem. Soc.*, 89, 5246 (1967).

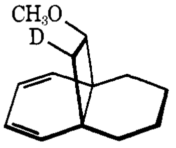
Table I. Chemical Shifts (δ Values) and Multiplicities Recorded for the More Downfield Shifted Protons (Excluding -OH) in **28a**, **28b**, and **32** [0.66 M Solutions in CCl_4 Containing 45 mol % $Eu(DPM)_3$][a]

Compd	$H_{11\,cis}$	$H_{12\,cis}$	$H_{12\,trans}$	Cyclohexyl ring protons		
32	15.3 (1, br t, $J \approx 7$ Hz)	8.93 (1, dd, $J = 8$, 10.5 Hz)	5.65 (1, dd, $J = 7$, 10.5 Hz)			
28a	15.3 (1, d, $J = 7$ Hz)		5.65 (1, d, $J = 7$ Hz)	9.75 (1, t, $J = 13$ Hz)	6.37 (1, d, $J = 13$ Hz)	5.38 (1, d, $J = 13$ Hz)
28b	15.3 (1, d, $J = 8$ Hz)	8.93 (1, d, $J = 8$ Hz)				
28a + **28b**[b]	15.3 (1, d, $J = 8$ Hz)	8.93 (0.74, d, $J = 8$ Hz)	5.65 (0.26, m)			

[a] Spectra were determined at 1000-Hz sweep width. [b] As obtained from the solvomercuration–demercuration ($NaBD_4$) of **12** (see text).

As expected, the chemical shifts of the two H_{12} protons in **32** are very similar. Furthermore, the coupling constants of these hydrogens with H_{11} are nearly identical. However, by the use of trisdipivalomethanatoeuropium(III) [$Eu(DPM)_3$],[16] the location of deuterium can be unequivocally established. Through-space distances from the hydroxyl group to $H_{12\,cis}$ (~2.7 Å) and $H_{12\,trans}$ (~3.3 Å)[17] were anticipated from plots of log Δppm *vs.* log R[18] to give rise to shift differences of approximately 6 ppm for the two protons in the presence of 100 mol % $Eu(DPM)_3$. During preliminary studies, it was observed that 0.66 M solutions of **32** in carbon tetrachloride containing 45 mol % $Eu(DPM)_3$ exhibited a series of well-separated peaks. Not only were H_{11}, $H_{12\,cis}$, and $H_{12\,trans}$ sufficiently downfield shifted and separated, but three protons on the cyclohexane ring were influenced quite dramatically by the complex as well (Table I).

Assignments to the cyclobutyl protons follow convincingly from the data in Table I. As can be seen, the [4.4.2]propellan-11-ol obtained from the solvomercuration–demercuration of **12** is actually a mixture of **28a** and **28b** in a ratio of 26:74. Since this epimeric composition would suffice for certain of our anticipated studies,[2d,4] conversion to a mixture of monodeuterated methoxydienes **35** (26%) and **36** (74%) was performed as discussed previously.



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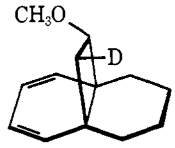

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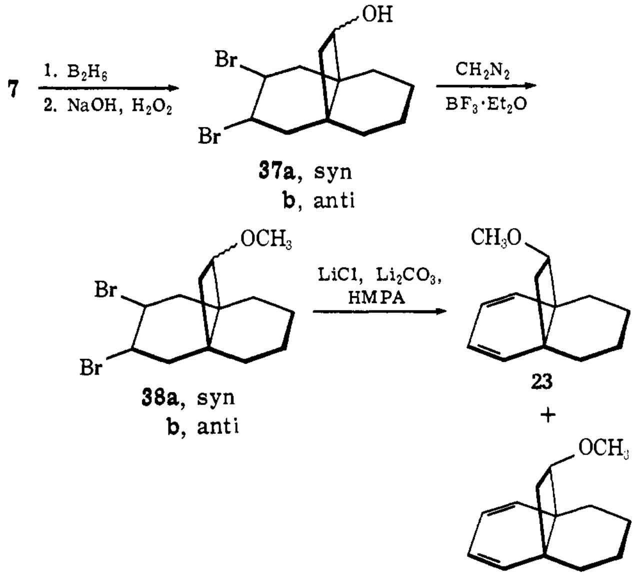
Because the need for greater stereospecificity persisted, attempts were next made to improve the stereochemical outcome of the demercuration of **24**. A number of reports[19] have touted the sodium amalgam reduction of organomercurials as a reaction of high stereospecificity. However, when **24** was treated with 1% sodium amalgam in 1:1 D_2O-CH_3OD,[20] ring opening was evidenced and trans diol **12** was obtained in 84% yield. Conditions were not found to circumvent this propensity for concomitant C–O bond cleavage.

At this point, we returned to dibromide **7** for this molecule appeared to offer the maximum opportunity for synthetic and stereochemical control. The hydroboration of **7**, not unexpectedly,[8] was quite sluggish, requiring heating to 55°. Also, as determined later in the sequence, there was surprisingly little selectivity in the direction of approach, *syn*- and *anti*-**37** being produced in a ratio of 40:60. This mixture of alcohols (**37**) was alkylated[21] and dehydrobrominated[22] to give a mixture of **23** (40%) and **39** (60%).



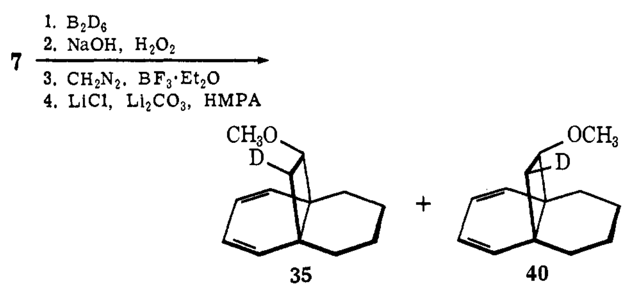
37a, syn
b, anti

38a, syn
b, anti

23

39

Repetition of this scheme except for substitution of B_2D_6 led similarly to **35** (40%) and **40** (60%). The



35

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(16) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970); *J. Amer. Chem. Soc.*, **93**, 641 (1971).

(17) Estimated from Prentice-Hall molecular models.

(18) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

(19) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963); J. K. Stille and S. K. Stinson, *Tetahedron*, **20**, 1387 (1964); S. Wolfe and P. Campbell, *Can. J. Chem.*, **43**, 1184 (1965).

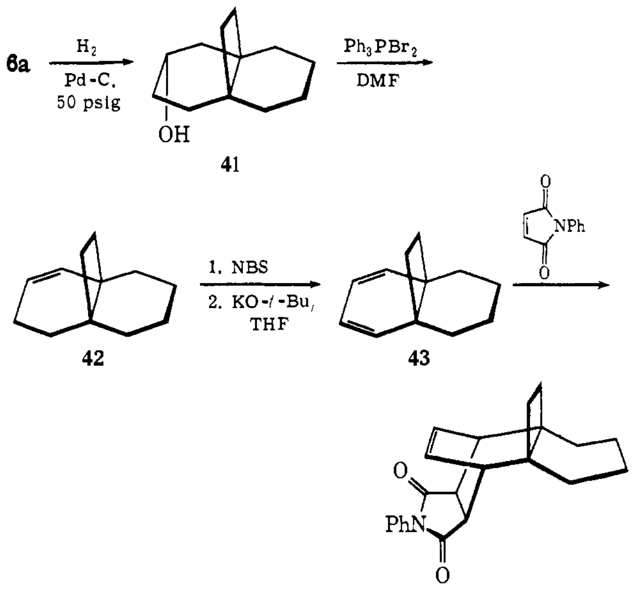
(20) V. I. Sokolov, N. B. Rodina, and D. H. Reutov, *J. Organometal. Chem.*, **17**, 477 (1969).

(21) M. Neeman and W. S. Johnson, *Org. Syn.*, **41**, 9 (1961).

(22) J. F. Normant and H. Deshayes, *Bull. Soc. Chim. Fr.*, 2455 (1967).

distribution of syn and anti isomers from repeated hydroborations of **7** remained invariant and did not seem to be affected by slight changes in reaction conditions. These observations were of direct importance to related studies which are detailed below. The epimeric nature of the methoxyl groups in **23** and **35** on the one hand and **39** and **40** on the other was clearly revealed by their nmr spectra, the former exhibiting a methoxyl singlet at δ 3.25 and the latter at δ 3.15. The cis orientation of the deuterium atoms in **35** and **40** was assigned on the basis of extensive precedent,[23] the behavior of structurally related cyclobutene **30** under analogous conditions, and the individual nmr spectra.[24]

Synthetic efforts were next addressed to the proper introduction of deuterium at C_{11} and C_{12}. Initial pilot studies were made with unlabeled diene **43**. Reaction



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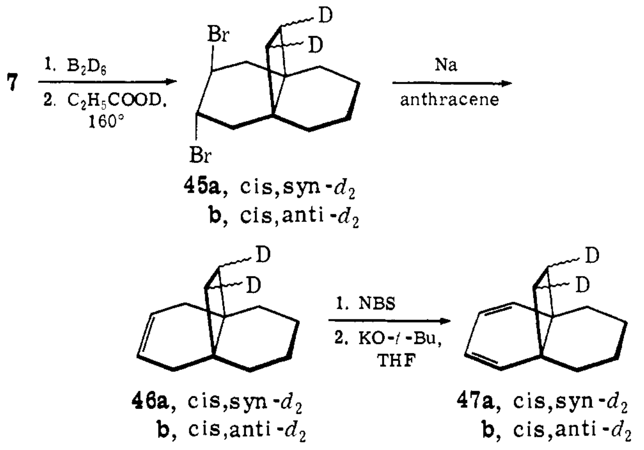
of alcohol **41** with triphenylphosphine dibromide in dimethylformamide at 150° proceeded to give olefin **42** directly in good (75%) yield. Presumably the bromide is produced as an unstable intermediate under these reaction conditions. The product was the 2-olefin as evidenced from the unsymmetrical olefinic signal in the nmr spectrum and from comparison with **46** (see below). The conversion to diene **43** was completed by allylic bromination (NBS) and subsequent dehydrobromination. Adduct **44** was prepared by heating **43** with *N*-phenylmaleimide in refluxing toluene in an attempt to distinguish by nmr analysis the syn and anti protons on the ethano bridge (not possible in **43**). However, both pairs of protons in **44** again appeared at the same chemical shift.

The analogous introduction of deuterium [tris(triphenylphosphine)rhodium(I) chloride as catalyst] was, however, not free of isotopic scrambling.[25] Conversely, addition to an olefin of deuteriodiborane followed by deuterolysis with a carboxylic acid-d_1 represents an exceptionally reliable method of introducing two deuterium atoms in a cis 1,2 relationship.[23] Along these lines, treatment of the B_2D_6 addition product mixture from **7** (see above) with propionic acid-d_1 proved somewhat sluggish but proceeded satisfactorily at 160° (3.5 hr). The mixture of **45a** and **45b** so produced

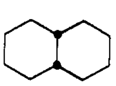


(ratio 40:60)[26] was debrominated with sodium anthracene in tetrahydrofuran[27] and subsequently dehydrogenated in the customary manner to furnish dienes **47a** and **47b**.

Despite the high levels of isotopic purity of the sodium borodeuteride (99% d_4) and propionic acid-*d* (>97%), labeled diene **47** was found to possess approximately 2.5 protons on the ethano bridge (nmr analysis). A more accurate analysis of the deuterium content of **47** was not possible by mass spectrometry because this substance does not exhibit a parent ion. However, pyrolysis studies[4] revealed the composition to be 55% d_2, 40% d_1, and 5% d_0. However, because ethylene-d_0 and -d_1 do not interfere with nmr analysis of the mixture of *cis*- and *trans*-1,2-dideuterioethylenes,[4] this result was acceptable.

Discussion

The remarkable stereoselectivity with which [4.4.2]-propella-3,11-diene (**3**) undergoes addition reactions is worthy of comment. The results are best interpreted in terms of conformational factors. In this context, it has been previously demonstrated that the interconversion of one *cis*-decalin form into its conformational isomer requires an activation energy only slightly larger than for cyclohexane.[28] It would appear therefore that the "second ring" of *cis*-decalin **48** exerts only



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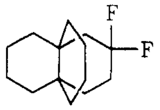

49

a minimal effect on the rotation–inversion process. 9-Substituted *cis*-decalins exhibit lower activation energies for ring inversion than the parent system, presumably because of ground-state destabilization.[29]

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[23] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962; G. Zweifel and H. C. Brown, *Org. React.*, 13, 1 (1963).

[24] The coupling constants for the H_{11}–H_{12} spin-spin interaction in 35, 36, and 40 were found to be 6.8, 8.2, and 8.0 Hz, respectively. In the case of 40, the magnitude of the splitting is of little true diagnostic value *per se* because $J_{11,12\ \mathrm{cis}} = J_{11,12\ \mathrm{trans}}$ in this isomer.

[25] J. A. Atkinson and M. O. Luke, *Can. J. Chem.*, 48, 3580 (1970), and references contained therein.

[26] Established by separate oxidation (NaOH, H_2O_2) of the organoborane and ultimate conversion to **35** and **40**.

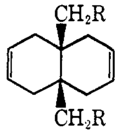
[27] L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, 93, 5735 (1971).

[28] (a) F. R. Jensen and B. H. Beck, *Tetrahedron Lett.*, 4523 (1966); (b) R. E. Lack, C. Ganter, and J. D. Roberts, *J. Amer. Chem. Soc.*, 90, 7001 (1968).

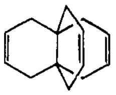
[29] (a) J. T. Gerig and J. D. Roberts, *ibid.*, 88, 2791 (1966); (b) W. B. Scott and R. E. Pincock, *J. Org. Chem.*, 32, 3374 (1967); (c) J. Altman, H. Gilboa, D. Ginsburg, and A. Loewenstein, *Tetrahedron Lett.*, 1329 (1967).

More recently, Gilboa, *et al.*,[30] have noted that the $\Delta G^{\ddagger}$ for ring inversion in saturated [4.4.4]propellane (**49**) is quite similar to that obtained for 9,10-disubstituted *cis*-decalins. These observations have been interpreted to mean that each cyclohexane moiety in this tricyclic molecule is free to adopt a conformation independent of the remaining two rings.

The introduction of unsaturation into such molecules is not without effect. In cyclohexene, for example, the energy difference between the boat and half-chair forms is reduced below that in cyclohexene.[31] Theoretical studies[31c,32] have shown additionally that the interconversion mechanism in cyclohexene may be quite different from that in cyclohexane, the latter displaying a minimum in the energy profile. In contrast, the $\Delta G^{\ddagger}$ values for 9,10-disubstituted *cis*-hexalins **50** are approximately twice those observed and calculated for cyclohexene. The reasonable interpretation advanced in explanation of these data is founded upon the higher rigidity (*cf.* molecular models) of the hexalin system which requires both rings to invert simultaneously.[28] That is to say, when one ring is in the boat form, the second one must also be in the boat form. This is in direct contrast to the conformational situation in the saturated analogs. What there is to say about [4.4.4]-propella-3,8,12-triene (**51**) is totally analogous. The value of $\Delta G^{\ddagger}$ for **51** is approximately three times larger than that witnessed for cyclohexene and 1.5 times that obtained for the *cis*-hexalins.[30] Accordingly, conformational interconversion in **51** appears to involve the simultaneous movement of all three rings, the implication being that the reaction profile consists of a lone maximum.

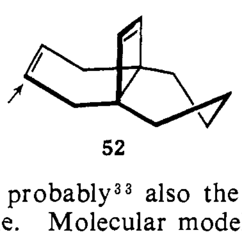


50

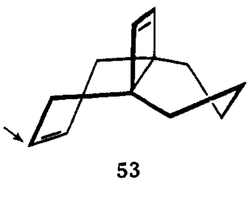


51

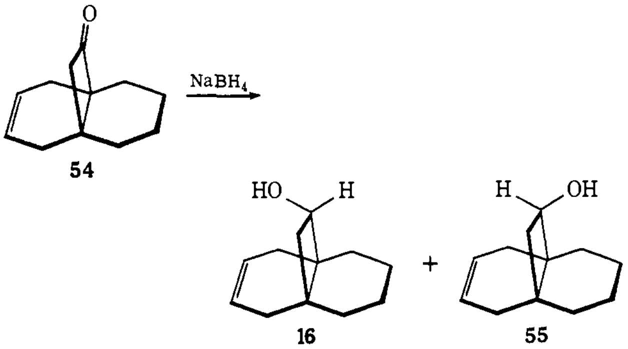
The conformational status of **3** can intuitively be expected to be intermediate between those prevailing in **49** and **51**. In view of Brown's demonstration[6] that addition of water in oxymercuration–demercuration reactions occurs from the less hindered side, the exclusive endo addition of mercuric acetate (and other electrophiles) to **3** reveals that **52** is the most reactive, and probably[33] also the dominant, conformer of this diene. Molecular models clearly show that attack on the alternative boat conformation of the cyclohexene ring (**53**) would lead only to exo product. A similar propensity for endo attack, albeit not quite as overwhelming, was also seen in the hydride reduction of ketone **8**. The more stable conformation of the cyclohexane unit (ring B) in **3** cannot, of course, be ascertained from the reactivity of ring A. However, the behavior of ketone **54** toward sodium borohydride in methanol at −78° would appear to argue against the exo boat configuration of the tetramethylene bridge. Under the stated conditions, **16** is formed more rapidly than **55** (ratio 62:38).[34] Interestingly, the ratio of these alcohols becomes 1:1 when the reaction is conducted at room temperature. The twist–boat conformation for ring B has been accepted tentatively because of its lower energy relative to the endo-boat structure.[35]



52



53



54

16

55

Experimental Section

[4.4.2]Propella-3,11-diene (**3**). To an ice-cold mechanically stirred solution of 65.3 g (0.250 mol) of **2**[3a] in 1 l. of anhydrous tetrahydrofuran was added 140 g (1.25 mol) of potassium *tert*-butoxide, and the mixture was stirred at reflux for 21 hr. Water (1 l.) and petroleum ether (30–60°, 500 ml) were added to the cooled mixture, the layers were separated, and the aqueous layer was extracted with petroleum ether (3 × 500 ml). The combined organic layers were washed with water (2 × 1 l.) and saturated sodium chloride solution (150 ml), dried, and concentrated under a packed column. The residue was vacuum distilled to give 30.5 g (76.3%) of **3**, bp 100–102° (30 mm), with spectra identical with those reported previously.[3b]

The nonvolatile component (16.9 g) was chromatographed on silica gel (elution with ether–hexane, 1:9) to give a mixture of **4a** and **4b** as a white solid, mp 91–93° (from hexane). There was isolated 11.8 g (16%) of the purified *tert*-butoxy sulfones. To preclude enrichment of either isomer during chromatography, the nmr spectrum of the crude material was recorded. By integration of the singlets at δ 4.64 and 5.00 which correspond to **4a** and **4b**, respectively, the ratio of these two sulfones was found to be 35:65.

Anal. Calcd for $C_{16}H_{26}O_3S$: C, 64.40; H, 8.78; S, 10.72. Found: C, 64.40; H, 8.81; S, 10.57.

3,4-Epoxy[4.4.2]propell-11-ene (**5**). An ice-cold mixture of 0.163 g (1.02 mmol) of **3**, 0.254 g (89.7%, 1.11 mmol) of *m*-chloroperbenzoic acid, and 10 ml of methylene chloride was stirred for 2 hr. Pentane (100 ml) was added and the organic solution was washed with 20% sodium bisulfite (2 × 100 ml) and 10% sodium carbonate solutions (2 × 100 ml), water (50 ml), and saturated sodium chloride solution (50 ml). The resulting solution was dried and carefully concentrated *in vacuo* to give 0.177 g (99%) of **5** as a colorless oil. Analysis of this oil by vpc indicated the presence of only one component. An analytical sample was obtained by preparative scale vpc (0.25 in. × 12 ft 10% SF-96, 125°): $\nu_{\max}^{\text{neat}}$ 2870 and 775 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.10 (s, 2, olefinic) and 3.0–1.3 (m including br s at 1.55, 12).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.51; H, 9.15.

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(30) H. Gilboa, J. Altman, and A. Loewenstein, *J. Amer. Chem. Soc.*, 91, 6062 (1969).

(31) (a) F. A. L. Anet and M. Z. Haq, *ibid.*, 87, 3147 (1965); (b) F. R. Jensen and C. H. Bushweller, *ibid.*, 87, 3285 (1965); (c) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *ibid.*, 90, 5773 (1968).

(32) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *ibid.*, 70, 4227 (1948).

(33) Although likely, this need not necessarily be so; similar considerations form part of the Curtin-Hammett principle.

(34) G. L. Thompson, unpublished observations.

(35) For a related discussion based on the spectral properties of [4.4.2]-propella-3,8-diene-11,12-dione, see J. J. Bloomfield and R. E. Moser, *J. Amer. Chem. Soc.*, 90, 5625 (1968); S. C. Neely, R. Fink, D. van der Helm, and J. J. Bloomfield, *ibid.*, 93, 4903 (1971).

endo-**3-Hydroxy[4.4.2]propell-11-ene (6a). A. Solvomercuration–Demercuration of 3.** To a stirred mixture of 6.38 g (20.0 mmol) of mercuric acetate, 20 ml of water, and 20 ml of tetrahydrofuran was added 1.60 g (10.0 mmol) of **3**. The yellow mixture was allowed to stir at ambient temperature for 1 hr. Aqueous sodium hydroxide (20 ml, 3 *N*) was added, followed by another 20 ml of base containing 0.76 g (20 mmol) of sodium borohydride. The mixture was stirred for 2 hr to coagulate the mercury and the supernatant liquid was extracted with ether. The ethereal solution was washed with sodium bicarbonate solution, water, and sodium chloride solution and dried. The solvent was evaporated and the residue was chromatographed on silica gel. Unreacted **3** was eluted with pentane, the alcohol with ether. The yield of **6a** was 1.24 g (70%); the unreacted starting material was quantitatively recovered (0.5 g). Purification by preparative scale vpc (0.25 in. × 5 ft 10% SF-96, 143°) afforded **6a** as a colorless oil: $\nu_{\max}^{\text{neat}}$ 3250, 2880, 1460, 1035, and 780 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.11 (s, 2, olefinic), 3.5–4.3 (m, 1, >CHO), 2.34 (s, 1, OH), and 1.2–2.3 (m including br s at 1.52, 14).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.64; H, 10.13.

B. Hydride Reduction of 5. The epoxide obtained from 5.25 g (32.8 mmol) of **3** was reduced directly with 3.8 g (100 mmol) of lithium aluminum hydride in 150 ml of refluxing ether during 10 hr. An alkaline work-up was employed, the salts were separated by filtration, and the solvent was removed *in vacuo* to give 5.84 g (100%) of **6a**, identical spectrally and in purity to the sample obtained above.

endo-**3-Methoxy[4.4.2]propell-11-ene (6b).** To a stirred solution of 319 mg (1.00 mmol) of mercuric acetate and 10 ml of methanol was added 166 mg (1.04 mmol) of **3**. The mixture was allowed to stir at ambient temperature for 20 min. Sodium hydroxide solution (3 *N*, 1 ml) was added, followed by 1 ml of 3 *N* sodium hydroxide solution containing 38 mg (1.00 mmol) of sodium borohydride. The mercury was allowed to coagulate; the solution was decanted and extracted with pentane (3 × 10 ml). The combined organic layers were dried and concentrated. The residue (one component) was subjected to preparative scale vpc (0.25 in. × 6 ft 10% SF-96, 150°) for ultimate purification. There was obtained 120 mg (64%) of **6b**: $\nu_{\max}^{\text{neat}}$ 2860, 1460, 1090, and 775 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.15 (s, 2, olefinic), 3.3–3.9 (m, 1, >CHO), 3.30 (s, 3, OCH_3), and 1.2–2.4 (m including br s at 1.57, 14).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.35; H, 10.52.

trans-**3,4-Dibromo[4.4.2]propell-11-ene (7).** A mixture of 1.76 g (11.0 mmol) of **3** and 3.52 g (11.0 mmol) of freshly prepared pyridinium hydrobromide perbromide in 30 ml each of carbon tetrachloride and acetic acid was stirred at 25° for 6.8 hr. Ether (100 ml) was added and the organic layer was washed with water (3 × 100 ml) and saturated sodium bicarbonate solution (100 ml), dried, and concentrated *in vacuo*. There was obtained 3.55 g (100%) of **7** as an unstable yellow oil. An analytical sample was obtained by molecular distillation: $\nu_{\max}^{\text{neat}}$ 2880 and 780 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.10 and 6.47 (AB quartet, J_{AB} = 3 Hz, 2, olefinic), 4.3–5.0 (m, 2, >CHBr), and 1.2–2.5 (m including br s at 1.55, 12).

Anal. Calcd for $C_{12}H_{16}Br_2$: C, 45.03; H, 5.04. Found: C, 45.66; H, 5.07.

[4.4.2]Propell-11-en-3-one (8). To an ice-cold stirred solution of 0.792 g (4.50 mmol) of **6a** in 50 ml of acetone was added Jones' reagent (2.67 mmol/ml) until a brown color persisted for 5–10 min. The mixture was filtered, concentrated, dissolved in pentane, washed with saturated sodium bicarbonate solution, and dried. Solvent removal *in vacuo* afforded a quantitative yield (0.784 g) of **8** as a colorless oil. An analytical sample was obtained by preparative scale vpc (0.25 in. × 5 ft 10% SF-96, 140°): $\nu_{\max}^{\text{neat}}$ 2870, 1720, and 785 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.15 (s, 2, olefinic) and 1.5–2.5 (m including br s at 1.60, 14).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.94; H, 9.19.

exo-**4-Hydroxy[4.4.2]propell-11-ene (9). A. NaBH$_4$ Reduction.** A mixture of 47 mg (0.27 mmol) of **8** and 47 mg (1.2 mmol) of sodium borohydride in 2 ml of absolute ethanol was stirred at 25° for 1.2 hr. The solvent was stripped, the residue was taken up in dilute hydrochloric acid and ether, and the organic phase was dried and concentrated to give 54 mg of **9** and **6a** as a colorless oil. Nmr analysis of the olefinic signals (**9** appears as an AB quartet at δ 6.07 and 6.30, $|J|$ = 3 Hz) established the exo:endo ratio to be 76:24.

B. LiAlH$_4$ Reduction. A mixture of 49 mg (0.28 mmol) of **8** and 49 mg (1.3 mmol) of lithium aluminum hydride in 2 ml of ether was heated at reflux with stirring for 1.0 hr. An alkaline work-up was employed and the filtrate was concentrated *in vacuo* to give 48 mg (98%) of **9** and **6a** in a 67:33 ratio.

3,11-Epoxy[4.4.2]propellane (10). A 335-mg (1.88 mmol) sample of **9** was treated with 977 mg (3.06 mmol) of mercuric acetate in 1:1 THF–H_2O (18 ml) and then 116 mg (3.06 mmol) of sodium borohydride as described previously. There was obtained a quantitative yield (0.335 g) of **10** which was purified by chromatography on silica gel and by preparative scale vpc (0.25 in. × 5 ft 10% SF-96, 140°): $\nu_{\max}^{\text{neat}}$ 2880 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 4.33–4.58 (m, 1, >CHO in 6-ring), 4.03 (d, $|J|$ = 5.0 Hz, >CHO in 4-ring), and 1.1–2.5 (m, 16).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.09; H, 10.29.

trans-**3,4-Dihydroxy[4.4.2]propell-11-ene (12).** A solution of 2.50 g (14.2 mmol) of **5**, 225 ml of 67% aqueous dioxane, and 10 drops of 60% perchloric acid was heated at reflux with stirring for 10 hr. The dioxane and some water were removed on the rotary evaporator, and the aqueous mixture was extracted with ether (3 × 100 ml). The ether extract was washed with 100 ml of saturated sodium bicarbonate solution, dried, and concentrated *in vacuo* to give **12** as hard white crystals: mp 82.5–83° (from benzene–cyclohexane); $\nu_{\max}^{\text{CHCl}_3}$ 3300, 2880, 1450, and 1060 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.06 and 6.27 (AB quartet, J_{AB} = 3.0 Hz, 2, olefinic), 3.3–4.2 (m, 4, >CHO and OH), and 1.1–2.2 (m including br s at 1.55, 12).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.19; H, 9.42.

Mercuric Chloride Adduct of 12 (13). To a stirred solution of 287 mg (0.90 mmol) of mercuric acetate in 4.0 ml of water was added 3.4 ml of tetrahydrofuran and 172 mg (0.89 mmol) of **12**. The clear solution was allowed to stir at 25° for 30 min, and then 4.0 ml of water containing 53 mg (0.90 mmol) of sodium chloride was added. The mixture was stirred for an additional 15 min and the precipitated solid was filtered, washed with water, and dried *in vacuo* (70°) to give 350 mg (92%) of **13** as a white powder, mp 228° dec. Two recrystallizations from methanol raised the decomposition point to 229.5–230°.

Anal. Calcd for $C_{12}H_{17}ClHgO_2$: C, 33.57; H, 3.99; Cl, 8.26. Found: C, 33.62; H, 4.08; Cl, 8.27.

endo-**5-Hydroxy-3,11-epoxy[4.4.2]propellane (14).** Tetrahydrofuran (12 ml) was added to a magnetically stirred solution of 1.595 g (5.00 mmol) of mercuric acetate in 12 ml of water. To this yellow suspension was added 0.970 g (5.00 mmol) of **12**. The mixture became homogeneous and clear within 10 sec. After 20 min, 12 ml of 3 *N* sodium hydroxide solution was added, followed by 12 ml of base containing 0.190 g (5.00 mmol) of sodium borohydride. Work-up as before afforded 0.970 g (100%) of crude **14**. Preparative scale vpc (0.25 in. × 5 ft 10% SF-96, 177°) furnished pure **14** as a colorless oil: $\nu_{\max}^{\text{neat}}$ 3280, 2850, 1460, 1035, and 995 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.9–4.3 (m, 3, >CHO), 3.8 (br s, 1, OH), and 0.9–2.5 (m, 14).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.34; H, 9.32.

endo-**4-Chloro-3,11-epoxy[4.4.2]propellane (15).** To a cold stirred solution of 970 mg (5.00 mmol) of **14** and 0.41 ml (5.00 mmol) of pyridine in 25 ml of benzene was added dropwise a solution of 0.37 g (5.05 mmol) of thionyl chloride in 5 ml of benzene and heated at 60° for 4.5 hr. Ice water and ether were added, and the organic layer was separated, washed with saturated sodium bicarbonate solution (2 × 30 ml) and 30 ml of 1% hydrochloric acid solution, dried, and concentrated. There was obtained 1.06 g (100%) of crude **15**. An analytical sample was obtained by preparative scale vpc (0.25 in. × 5 ft 10% SF-96, 177°): $\nu_{\max}^{\text{neat}}$ 2870, 1450, and 1135 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.8–4.6 (m, 3, >CHCl and >CHO) and 0.8–2.6 (m, 14).

Anal. Calcd for $C_{12}H_{17}ClO$: C, 67.75; H, 8.06; Cl, 16.67. Found: C, 68.09; H, 8.14; Cl, 16.26.

syn-**11-Hydroxy[4.4.2]propell-3-ene (16).** A magnetically stirred mixture of 1.86 g (8.69 mmol) of **15** and 2.0 g (87 mg-atoms) of sodium metal cut into small pieces in 50 ml of anhydrous ether was heated at reflux for 2.5 days. The excess sodium was destroyed with methanol. Water (50 ml) was added, the layers were separated, and the aqueous phase was extracted with ether (50 ml). The combined organic layers were washed with 50-ml portions each of 10% hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride solutions. Drying and concentration *in vacuo* gave 1.50 g (96%) of **16** as white crystals: mp 64.5–65° (from pentane); $\nu_{\max}^{\text{CHCl}_3}$ 3300 and 2880 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.5–6.1 (m, 2, olefinic), 4.1–4.4 (t, $|J|$ = 7.5 Hz, 1, >CHO), and 1.0–2.9 (m including s at 2.83 for OH, 15).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.68; H, 10.16.

3,11-Epoxy[4.4.2]propellan-4-one (17). A solution of 203 mg (1.05 mmol) of **14** in 25 ml of acetone held at 0° was treated with 0.37 ml of 2.67 *M* Jones' reagent. Processing of the mixture as before gave 190 mg (95%) of **17**: $\nu_{\max}^{\text{neat}}$ 2880 and 1730 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 4.18 (pseudotriplet, 2, >CHO) and 1.0–2.7 (m, 14).

A 2,4-dinitrophenylhydrazone derivative was prepared, mp 141.5–143° (from 95% ethanol).

Anal. Calcd for $C_{18}H_{20}N_4O_5$: C, 58.06; H, 5.41; N, 15.05. Found: C, 57.78; H, 5.36; N, 14.89.

Reduction of 17. A. With Sodium Borohydride. A solution of 246 mg (1.28 mmol) of **17** and 56 mg (1.5 mmol) of sodium borohydride in 5 ml of absolute ethanol was stirred at 25 for 1.5 hr, poured into dilute hydrochloric acid, and extracted with ether. The combined organic phase was washed with saturated sodium chloride solution, dried, and evaporated to give 214 mg (86%) of **18a** as a viscous oil. Treatment with methanesulfonyl chloride (see below) provided the corresponding mesylate (**19a**) which exhibited methyl singlets due to **19a** (δ 3.08) and its epimer (δ 3.06) in the ratio of 96:4.

B. With Lithium Aluminum Hydride. A mixture of 223 mg (1.16 mmol) of **17** and 57 mg (1.5 mmol) of lithium aluminum hydride in 25 ml of ether was heated at reflux with stirring for 2 hr. An alkaline work-up was employed and the filtrate was concentrated *in vacuo* to give 220 mg (98%) of **18a** and **14** in a 10:1 ratio. Pure **18a** was obtained by preparative scale vpc (0.25 in. × 10 ft XF-1150, 152°): $\nu_{\max}^{\text{neat}}$ 3400 and 2900 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 4.50 (t, $|J|$ = 5.0 Hz, 1, H_3), 4.08 (d, $|J|$ = 5.0 Hz, 1, H_{11}), 3.92 (m, 1, H_4), 3.27 (br s, 1, OH), 2.22 and 2.43 (dd, $|J|$ = 13 and 5 Hz, 1, $H_{12\,\text{syn}}$), and 0.9–2.1 (m, 13).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.32; H, 9.31.

Conversion of 18a to 16. Methanesulfonyl chloride (0.35 g, 3.0 mmol) was added dropwise to a magnetically stirred solution of **18a** (179 mg, 0.923 mmol) in 5 ml of pyridine kept at 0–5° with an ice–salt bath. After 1.5 hr at this temperature, the contents were poured onto ice and dilute hydrochloric acid and the aqueous mixture was extracted twice with pentane. The pentane solution was washed with dilute hydrochloric acid, dried, and evaporated to yield 284 mg (100%) of **19a** as a colorless viscous oil: $\nu_{\max}^{\text{neat}}$ 2900, 1350, 1170, 975, and 930 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 4.52–5.08 (m, 2, H_3 and H_4), 4.07–4.20 (m, 1, H_{11}), 3.08 (s, 3, CH_3SO_3), and 0.9–2.6 (m, 14). Presence of endo isomer contaminant was indicated by an additional methyl singlet at 3.06.

A stirred mixture of 210 mg (0.77 mmol) of **19a** and 1.0 g (7 mmol) of sodium iodide in 10 ml of anhydrous hexamethylphosphoramide was heated at 107° under a nitrogen atmosphere for 27 hr. Water was added and the mixture was extracted with pentane. The combined organic layers were washed with water and saturated sodium bicarbonate solution, dried, and concentrated. The residue was chromatographed on silica gel; elution with 10% ether–petroleum ether (30–60°) provided 111 mg (49%) of **20a**.

A mixture of 79 mg (0.26 mmol) of **20a** and 0.1 g (4 mg-atoms) of sodium (in small pieces) was stirred at reflux for 1.2 days. The customary work-up furnished a quantitative yield of impure **16** which after preparative scale vpc isolation (0.25 in. × 4 ft 5% SF-96, 140°) exhibited spectral properties superimposable upon the authentic sample.

Conversion of 17 to 21. Lithium aluminum deuteride (164 mg, 3.90 mmol) reduction of **17** (1.41 g, 7.34 mmol) gave 1.51 g (100%) of an alcohol mixture consisting chiefly of **18b**. Reaction of this material with 2.5 g (22 mmol) of methanesulfonyl chloride in 25 ml of pyridine at 0–5° as before yielded 1.12 g (56%) of **19b** admixed with a small quantity of its epimer. When the labeled mesylate was heated with sodium iodide (6.2 g, 41 mmol) in 20 ml of dry HMPA at 103° for 2 days, there was obtained 0.60 g (49%) of **20b** after silica gel chromatography. Lastly, exposure of **20b** to 0.5 g (20 mmol) of small pieces of sodium in 15 ml of ether at reflux for 1.2 days led quantitatively (390 mg) to **21**. Chromatography of the crude product on silica gel, followed by preparative scale vpc purification, furnished the analytical sample of **21**: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.70–6.00 (br s, 1, olefinic), 4.1–4.4 (t, $|J|$ = 7.5 Hz, 1, >CH), and 1.0–2.9 (m, 14).

***syn*-11-Methoxy[4.4.2]propell-3-ene (22).** To a stirred slurry of 830 mg (35 mmol, mineral-oil free) of sodium hydride in 40 ml of anhydrous dimethylformamide was added 3.08 g (17.3 mmol) of **16**. The mixture was stirred for 1 hr during which time the temperature was raised to 60°. After cooling, 5 ml of methyl iodide was slowly added and stirring was maintained for another hour. Water and ether were added, the aqueous layer was extracted with ether, and the combined ether extracts were washed with dilute acid and base, water, and saturated sodium chloride solution. After drying, the solution was evaporated *in vacuo* to yield 3.32 g (100%) of **22** as a light yellow oil. An analytical sample was obtained by preparative scale vpc (0.25 in. × 5 ft 10% SF-96, 143°, and then 0.25 in. × 5 ft 5% Carbowax 20M, 143°): $\nu_{\max}^{\text{neat}}$ 2880, 1450, 1215, 1125, and 1110 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.5–6.1 (m, 2, olefinic), 3.8–4.1 (dd, $|J|$ = 7.0 and 8.0 Hz, 1, >CHO), 3.26 (s, 3, OCH_3), and 1.1–3.0 (m, 14).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48 Found: C, 81.44; H, 10.51.

***syn*-11-Methoxy[4.4.2]propella-2,4-diene (23).** A mixture of 195 mg (1.01 mmol) of **22**, 199 mg (1.12 mmol) of *N*-bromosuccinimide, 4 grains of benzoyl peroxide, and 3 ml of carbon tetrachloride was refluxed with stirring for 15 min. The mixture was cooled to 25°, filtered through a glass wool plug, and concentrated *in vacuo* to give 276 mg of a pale yellow oil which was not further purified.

A slurry of this crude bromide (256 mg, 0.94 mmol) and 560 mg (5.0 mmol) of potassium *tert*-butoxide in 5 ml of dry tetrahydrofuran was stirred at reflux for 3 hr, cooled, and treated with 10 ml of water. The solution was extracted with pentane (3 × 10 ml) and the combined pentane layers were washed with 10% hydrochloric acid (10 ml) and water (6 × 10 ml), dried, and concentrated *in vacuo* to yield 154 mg of a yellow oil. This residue when purified by vpc (0.25 in. × 6 ft 10% XF-1150, 128°) gave 105 mg (59%) of **23**: $\nu_{\max}^{\text{neat}}$ 2880, 1450, 1215, 1125, 1110, and 705 cm^{-1}; $\lambda_{\max}^{\text{isooctane}}$ 269 nm (ϵ 3060); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.1–6.1 (m, 4, olefinic), 4.0–4.3 (dd, $|J|$ = 6.8 and 8.2 Hz, 1, >CH), 3.25 (s, 3, OCH_3), and 0.7–2.3 (m, 10).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.22; H, 9.53.

Solvomercuration–Demercuration ($NaBD_4$) of 12. To a stirred solution of 5.79 g (18.1 mmol) of mercuric acetate in 20 ml of water was added 20 ml of tetrahydrofuran. The yellow suspension was cooled to 0°, and 3.51 g (18.1 mmol) of **12** was added during 3 min. The clear solution was allowed to stir at ambient temperature for 0.5 hr during which time a white precipitate formed. The mixture was cooled to 0°, and 40 ml of 3 *N* sodium hydroxide solution was added. While the two-phase liquid was still cold, 0.38 g (9.1 mmol) of sodium borodeuteride was added in one portion. The mercury was allowed to coagulate at ambient temperature with stirring, and the supernatant liquid was extracted with ether (4 × 40 ml). The combined ether extracts were washed with 0.1 *N* hydrochloric acid (2 × 50 ml) and saturated sodium chloride solution (50 ml), dried, and concentrated *in vacuo* to give 3.57 g (100%) of **25** as a colorless oil which was used without further purification.

To a stirred solution of 3.53 g (18.1 mmol) of **25** and 1.79 g (22.6 mmol) of pyridine in 100 ml of anhydrous benzene cooled to near the freezing point was added slowly a solution of 2.69 g (22.6 mmol) of thionyl chloride in 20 ml of benzene. The white suspension was allowed to stir at 60° for 20 hr. The reaction mixture was worked up as before to give 3.75 g (97%) of yellow oil. This sample of **26** and 4 g (175 mg-atom) of sodium (small pieces) in 80 ml of anhydrous ether was heated at reflux for 24 hr. The usual processing and chromatography on silica gel (elution with 10% ether in hexane) led to the isolation of 2.59 g (83%) of **27** as white crystals, mp 64.5–65°.

A solution of 0.026 g (0.14 mmol) of **27** in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure using 50 mg of Adams catalyst (3.5 ml of hydrogen was immediately taken up). The catalyst was removed by filtration and the filtrate was concentrated to give 0.026 g (100%) of white crystals. An nmr sample was obtained by sublimation *in vacuo*.

11-Chloro-12-thia[4.4.3]propellane 12,12-Dioxide (29). A solution of 10.4 g (40.0 mmol) of **2** in 80 ml of ethyl acetate was hydrogenated at atmospheric pressure over Adams' catalyst for 12 hr. Removal of the catalyst and concentration of the filtrate afforded 10.2 g of crude product. This material was chromatographed on silica gel and recrystallized from ethyl acetate to give 8.06 g (77%) of **29**: mp 178–179°; $\nu_{\text{TMS}}^{\text{CHCl}_3}$ 2880, 1320, and 1130 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.38 (s, 1, >CHCl), 3.57 and 2.87 (AB q, $|J_{AB}|$ = 13.5 Hz, 2, CH_2SO_2), and 0.9–2.4 (m, 16).

Anal. Calcd for $C_{12}H_{19}ClO_2S$: C, 54.84; H, 7.29; S, 12.20. Found: C, 54.92; H, 7.28; S, 12.16.

[4.4.2]Propell-11-ene (30) and 11-(*tert*-Butoxy)-12-thia[4.4.3]-propellane 12,12-Dioxide (31). To a cold stirred solution of 4.00 g (15.2 mmol) of **29** in 50 ml of dry tetrahydrofuran was added 8.5 g (76 mmol) of powdered potassium *tert*-butoxide. This mixture was refluxed for 2 hr, cooled, and treated with water and pentane.

The organic layer was washed with water (3 × 50 ml) and saturated sodium chloride solution (50 ml), dried, and concentrated under a packed column. The crystalline residue was washed with pentane leaving 0.76 g (17%) of **31**: mp 130–131° (from ethyl acetate); $\nu_{\max}^{\mathrm{CHCl_3}}$ 2930, 1300, 1130, and 1090 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.02 (s, 1, >CHO), 3.45 and 2.67 (AB q, $|J_{AB}|$ = 13 Hz, 2, CH_2SO_2), and 0.9–2.2 (m including s at 1.32, 25).

Anal. Calcd for $C_{16}H_{28}O_3S$: C, 63.97; H, 9.40; S, 10.55. Found: C, 63.88; H, 9.40; S, 10.55.

The filtrate was concentrated and vacuum distilled to give 1.64 g (67%) of **30**, bp 105° (15 mm). An analytical sample was obtained by preparative scale vpc (0.25 in. × 10 ft 10% Carbowax 20M, 120°): $\nu_{\max}^{\mathrm{neat}}$ 2900, 1450, 835, and 770 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.13 (s, 2, vinyl) and 1.47 (br s, 16).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.98; H, 11.09.

[4.4.2]Propellan-11-ol (32). To a stirred solution of 1.00 g (6.18 mmol) of **30** and 0.281 g (7.41 mmol) of sodium borohydride in 20 ml of dry tetrahydrofuran under nitrogen was added 1.40 g (9.87 mmol) of freshly distilled (from CaH_2) boron trifluoride etherate. The solution was stirred at 25° for 3 hr and then warmed to 40°. Sodium hydroxide (3.1 ml of 3 *N*) and 30% hydrogen peroxide (3.1 ml) solutions were added, and after several minutes 10 ml of saturated sodium chloride solution was introduced and the organic material was extracted with ether (3 × 20 ml). The processed organic phase furnished 1.21 g (100%) of **32**, mp 111–113° (from hexane).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.62; H, 11.00.

The *cis*-12-deuterio derivative **28a** was prepared analogously using sodium borodeuteride.

11,12-Epoxy[4.4.2]propellane (33). A mixture of 335 mg (2.07 mmol) of **30** and 480 mg (2.48 mmol, 89.5%) of *m*-chloroperbenzoic acid in 20 ml of chloroform was stirred at reflux for 4 hr. Pentane (40 ml) was added and the organic phase was processed as previously described. The viscous oil so obtained (386 mg, 100%) was purified by preparative scale vpc (0.25 in. × 6 ft 5% SF-96, 120°) to give **33** as a waxy solid: mp 30°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.53 (s, 2, >CHO) and 0.9–2.2 (m, 16).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.15; H, 10.12.

Hydride Reduction of 33. Treatment of 74 mg (0.41 mmol) of **33** in 5 ml of dry tetrahydrofuran with 16 mg (0.41 mmol) of lithium aluminum hydride (reflux for 65.5 hr) and subsequent acidic work-up (10% H_2SO_4) afforded 79 mg of crude white crystals. Vpc analysis (0.25 in. × 6 ft 5% SF-96, 140°) indicated a 5:1 ratio of two products. Isolation of the major product showed it to be **32**; the minor product was not characterized.

The *trans*-12-deuterio derivative **28b** was prepared in analogous fashion using lithium aluminum deuteride.

Conversion of 27a,b to 35 and 36. O-Alkylation of 2.59 g (14.5 mmol) of a 26:74 mixture of **28a** and **28b** with 1.8 g (75 mmol) of sodium hydride and 10 ml of methyl iodide in 50 ml of anhydrous dimethylformamide afforded 2.60 g (93%) of yellow oil. A mixture of 1.32 g (6.84 mmol) of this labeled ether mixture, 1.34 g (7.52 mmol) of *N*-bromosuccinimide, and several grains of benzoyl peroxide in 25 ml of carbon tetrachloride was refluxed with stirring for 40 min. The contents were cooled to 5° and filtered, and the filtrate was concentrated *in vacuo*. A slurry of the residue and 3.8 g (34 mmol) of potassium *tert*-butoxide in 25 ml of anhydrous tetrahydrofuran was heated at reflux for 4.5 hr. Water was added and the mixture was extracted with ether. The ether solution was washed twice with water and chromatographed without concentration on neutral alumina to give 1.28 g (98%) of a 26:74 mixture of **35** and **36**.

syn- **and** *anti*-**11-Methoxy[4.4.2]propella-2,4-dienes (23 and 39).** The hydroboration of **7** (2.40 g, 7.50 mmol) with 290 mg (7.5 mmol) of sodium borohydride and 1.4 g (10 mmol) of boron trifluoride etherate in 40 ml of dry tetrahydrofuran at 55° for 3.5 hr was performed as previously described. There was obtained 2.64 g of **37** as an immobile paste. An ether solution (200 ml) of diazomethane (from 10.3 g of *N*-methyl-*N*-nitrosourea, undistilled) was added in three portions to a stirred ice-cold solution of the dibromo alcohol mixture and 0.05 ml of boron trifluoride etherate in 100 ml of ether. After 1.5 hr, the polymethylene was removed by filtration through a pad of anhydrous magnesium sulfate and the solvent was removed to furnish 2.66 g of residual oil. This material, together with 1.3 g (30 mmol) of anhydrous lithium chloride and 2.2 g (30 mmol) of dry lithium carbonate in 40 ml of distilled (from CaH_2) HMPA was heated at 95° for 17 hr under nitrogen with stirring. The contents were cooled, water and pentane were added, and the layers were separated. The organic phase was washed well with water, dried, and concentrated to give 1.35 g (95%) of crude **3** and **4**. Preparative vpc (0.25 in. × 10 ft 10% XF-1150, 117°) provided **39** (t_R = 19 min): $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.3–6.0 (m, 4, olefinic), 3.93 (t, J = 8.0 Hz, 1, >CHO), 3.15 (s, 3, CHO), 2.22 and 2.28 (m, 2, H_{12}), and 0.8–2.2 (m, 8).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.05; H, 9.52.

The second component (t_R = 26 min) was shown to be identical with **23**. The ratio of **39** to **23** was 60:40.

cis-**Deuterio**-*syn*- **and** -*anti*-**11-methoxy[4.4.2]propella-2,4-dienes (35 and 40).** From 2.48 g (7.75 mmol) of **7**, 620 mg (15 mmol) of sodium borodeuteride, and 2.84 g (20 mmol) of boron trifluoride etherate in 10 ml of anhydrous tetrahydrofuran, there was obtained 2.53 g (96%) of heavy oil. Methylation of this material with excess diazomethane as before yielded 2.74 g (100%) of an equally thick oil. Exposure of this material to 1.7 g (40 mmol) of lithium chloride and 3.0 g (40 mmol) of lithium carbonate in 35 ml of HMPA at 95° for 25 hr led to the isolation of 1.35 g (91%) of residue which consisted of 90% of **35** and **40** (syn-anti ratio of 40:60) and 10% of an unidentified component. Preparative scale vpc separation (³/₈ in. × 15 ft 20% XF-1150, 130°) provided 412 mg of **40** and 224 mg of **35** (43% combined yield based upon dibromide **7**).

endo-**[4.4.2]Propellan-3-ol (41).** A solution of 3.99 g (22.4 mmol) of **6a** in 100 ml of methanol containing 0.4 g of 85% platinum oxide was hydrogenated at 50 psig for 21 hr. The catalyst was separated by filtration, and the filtrate was concentrated *in vacuo* to give 3.96 g (98%) of **41** as white crystals: mp 79–80° (from pentane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3250 and 2880 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.6–4.2 (m, 1, >CHO), 2.8–3.0 (br s, 1, OH), and 0.9–2.4 (m, 18).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.86; H, 11.06.

[4.4.2]Propell-2-ene (42). Bromine was slowly added to a magnetically stirred solution of 1.93 g (10.7 mmol) of **41** and 3.12 g (11.8 mmol) of triphenylphosphine in 30 ml of dimethylformamide, until a yellow color persisted. The solution was heated at 150° for 0.5 hr and then cooled. Water (30 ml) was added and the precipitated triphenylphosphine oxide was removed by filtration and washed with pentane. The filtrate was extracted with pentane (2 × 50 ml) and the combined organic layers were washed with water (2 × 50 ml), dried, passed through a short column of alumina, and concentrated *in vacuo* to give 1.31 g (75%) of **42**. An analytical sample was obtained by preparative scale vpc (0.25 in. × 6 ft 5% SF-96, 122°): $\nu_{\max}^{\mathrm{neat}}$ 2920 and 1460 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.36–5.87 (m, 2, olefinic) and 0.9–2.3 (m, 16).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.85; H, 11.25.

[4.4.2]Propella-2,4-diene (43). A mixture of 1.19 g (7.35 mmol) of **42**, 1.44 g (8.09 mmol) of *N*-bromosuccinimide, and several grains of benzoyl peroxide in 25 ml of carbon tetrachloride was heated at reflux with stirring for 0.7 hr. After the usual work-up, the residue was dissolved in 40 ml of dry tetrahydrofuran, to which solution was added 3.29 g (29.4 mmol) of potassium *tert*-butoxide. After 4 hr at reflux, water and pentane were added. Customary processing led to the obtention of a residue which was chromatographed on alumina (elution with pentane) to give 411 mg of an oil composed of **43** (80%) and two unidentified minor components (10% each). Pure **43** was obtained by preparative scale vpc (0.25 in. × 6 ft 5% SF-96, 122°): $\nu_{\max}^{\mathrm{neat}}$ 2920 and 1460 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.2–6.0 (A_2B_2, 4, olefinic), 1.8–2.2 (m, 4, cyclobutyl), and 1.45 (br s, 8).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06: Found: C, 89.90; H, 10.11.

Adduct **44** was prepared by refluxing **43** with an equimolar amount of *N*-phenylmaleimide in toluene for 20 hr, white crystals, mp 207.5–208° (from benzene–ether).

Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.11; H, 6.95; N, 4.01.

[4.4.2]Propell-3-ene. To a stirred mixture of 3.52 g (11.0 mmol) of **7** and 0.46 g (11 mmol) of sodium borohydride in 50 ml of dry diglyme under nitrogen was added 2.09 g (14.7 mmol) of boron trifluoride etherate. The mixture was allowed to stir at 25° for 1 hr, 5.0 ml (66 mmol) of propionic acid was added, and the mixture was stirred at reflux for 3.5 hr. To the cooled mixture was added water (150 ml) and ether (100 ml) and the organic layer was separated, washed with water (3 × 100 ml) and sodium bicarbonate solution (100 ml), dried, and concentrated. To a magnetically stirred solution of the residue in 30 ml of dry tetrahydrofuran under nitrogen was added a 0.57 *M* tetrahydrofuran solution of sodium anthracene until the blue color persisted. This solution was allowed to stir for 2 hr and was subsequently quenched by exposure to the atmosphere. Pentane (100 ml) was added and the resulting mixture was filtered. The filtrate was washed with water (4 × 250 ml), dried, and evaporated under a packed column. The residue was chromatographed on an alumina column (pentane elution) and the eluate was again carefully concentrated. This residue was purified by preparative scale vpc (0.25 in. × 6 ft 5% SF-96, 120°) to give 670 mg (37%) of [4.4.2]propell-3-ene: $\nu_{\max}^{\text{neat}}$ 2900 and 1450 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.68–5.80 (m, 2, olefinic) and 1.2–2.1 (m, 16).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.68; H, 11.26.

The *cis*-11,12-dideuterio derivative **46** was prepared analogously using sodium borodeuteride and propionic acid-d_1.

The conversion of **46** to **47** was achieved by the same procedure as that utilized in the transformation of **42** to **43** with identical results.

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Stereochemical Features of the Thermal and Photochemical Fragmentations of [4.4.2]Propella-2,4-dienes

Leo A. Paquette* and Gerald L. Thompson[1]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received February 23, 1972*

Abstract: Vapor-phase pyrolysis of several 11,12-disubstituted [4.4.2]propella-2,4-dienes has been found to result in clean fragmentation to tetralin and an olefinic component. Photofragmentation under singlet conditions also leads to substantial tetralin formation, although some ($_\sigma 2 + {}_\sigma 2$) cleavage in the opposite direction is now encountered. The isomer distributions of the methyl 2-deuteriovinyl ether and 1,2-dideuterioethylene so produced have been measured and significant stereoselectivity is observed. The level of stereocontrol is seen, however, to vary with the method of inducing fragmentation and with the geometry of the starting propelladiene. These observations are discussed in terms of the behavior of 1,4-diradical intermediates.

By 1961, preliminary insight into the mechanism of the thermal fragmentation of cyclobutanes to ethylenes began to emerge as the direct result of the pioneering studies of Walters.[2] In particular, Gerberich and Walters noted that although *cis*-1,2-dimethylcyclobutane did experience partial isomerization to its trans counterpart in the temperature region 380–430°,[3] the isolated 2-butene (64% cis and 36% trans) differed significantly in stereochemical composition from that of the equilibrium mixture (43–47% cis at these temperatures). Additionally, pyrolysis of *trans*-1,2-dimethylcyclobutane was seen to afford 2-butene composed chiefly, but not exclusively, of the trans isomer (89%).[4] The reasonable argument was advanced "that if a biradical exists momentarily as an intermediate, it decomposes before the original geometry is completely converted to the equilibrium distribution."

Nearly a decade later, Woodward and Hoffmann called attention to the theoretical possibility that the fragmentations of four-membered rings could proceed concertedly by the simultaneous stretching of two opposite bonds to furnish olefinic products directly.[5] This particular application of orbital symmetry theory revealed convincingly, however, that simple [$_\sigma 2_s + {}_\sigma 2_s$] fragmentation was unallowed for the concerted thermal reaction. Rather, synchronous rupture was demonstrated to require appreciable prior twisting of the cyclobutane ring in a manner which effectively inverts the stereochemistry of one of the constituent carbons at the transition state. At the time, *bona fide* experimental tests of this intriguing stereochemical implication were not available because of a lack of cyclobutane derivatives bearing sufficient stereochemical labeling.

The recent studies of Baldwin,[6] Frey,[7] and Paquette[8] with fused ring systems have given evidence that 1,4-diradical intermediates are likely involved, except when the proper juxtapositioning of an additional weak σ bond effectively obviates the need for the [$_\sigma 2_a + {}_\sigma 2_s$] mechanism. By and large, the structural features present in the cyclobutane derivatives pyrolyzed to date[9] have been such, however, that bond rotation, ring closure, and bond scission processes are reasonably competitive.[10]

Unfortunately, the inherently transient nature of 1,4 diradicals renders their detection and study by standard methods exceedingly difficult. Consequently, their intervention is frequently surmised on the basis of thermodynamic,[11] kinetic, and stereochemical grounds.

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