Hz), that due to the ether at ~4.5 ppm is obscured by the $CH_3O-C(=O)-$ and CH_3-O- peaks. However, one can see its vicinal $Hg^{199}H$ side band 50 cps downfield which appeared as a doublet $J \cong 7.0$ Hz.

Addition to *endo*-5-Cyano-2-norbornene (XIII).—The reaction mixture of unsaturated compound (1.1908 g, 10.0 mmol) and mercuric acetate (3.1838 g, 10.0 mmol) in 100 ml of 25% acetone was worked up with a solution of 10 g of sodium chloride and 10 g of sodium bicarbonate in 200 ml of water. This mixture was continuously extracted with chloroform for 40 hr to yield 3.8236 g of a viscous orange oil. This product gave a precipitate with 2% ethanolic silver nitrate solution and a gray precipitate with ethanolic sodium borohydride. Its ir spectrum ($CHCl_3$) had bands at 2.79 and 5.79 μ (broad). Its nmr spectrum ($CHCl_3$) had doublets at 4.13 (J = 5.0 Hz), 3.98 (J = 6.8 Hz), and 5.0 ppm (J = 7 Hz). These were assigned to XVI, XV, and XIV, respectively. On standing in chloroform 3.1182 g of this product gave 1.7979 g of a white crystalline solid, mp 149.5–151.5°. Recrystallization from chloroform–*n*-heptane raised the melting point to 154–155°. Its ir spectrum (Nujol mull) had a band at 2.75 μ and showed no evidence of a carbonyl band. Its nmr spectrum (acetone-d_6) had a doublet at 3.94 ppm (J = 6.9 Hz), and therefore it was assigned structure XV.

Treatment of 0.3014 g of this product with 2 ml of acetic anhydride and 0.5 ml of dry pyridine yielded 0.2776 g of acetate (XIV), mp 170–170.2°, which was shown, by the method of mixture melting points and by exact correspondence of ir spectra, to be the same acetate obtained previously from the acetic acid-$Hg(OAc)_2$ treatment of *endo*-5-cyano-2-norbornene.

The reaction mixture from *endo*-5-cyano-2-norbornene (0.5979 g, 5.0 mmol), mercuric nitrate (1.7096 g, 5.0 mmol), and 50 ml of 20% acetone, after work-up with a solution of 1 g of sodium chloride and 1 g of sodium bicarbonate and extraction with chloroform, gave 2.1828 g of a gummy white solid. Slow crystallization from chloroform yielded 1.2679 g of alcohol XV, as indicated by the melting point (154–155°), mixture melting point, and ir and nmr spectra of the sample of alcohol previously obtained. The ir spectrum ($CHCl_3$) of the mother liquor had a carbonyl band at 5.83 μ. Its nmr spectrum showed a doublet at 4.12 ppm (J = 5.0 cps) and a multiplet at 7.65 ppm (olefin?). On the basis of this spectral evidence the lactam structure (XVI) was assigned to this residue (λ_{max} of γ-lactams, 5.88 μ). Further attempts to isolate this lactam by inducing crystallization or by chromatography on alumina (2% H_2O) failed to give a sample suitable for analysis.

Addition to Norbornene in Presence of Acetonitrile.—The reaction mixture of norbornene (0.3681 g, 4.0 mmol), mercuric nitrate (1.3516 g, 4.0 mmol), and 40 ml of 25% acetonitrile–water gave, after work-up with 1.2 g of sodium chloride and 1.2 g of sodium bicarbonate in 15 ml of water, 0.9517 g (69.4%) of 2-chloromercurinorborneol, mp 120–125° (lit.[24c] mp 131–131.5°). Chloroform extraction of the aqueous filtrate gave 0.3144 g (23%) more solid. The ir spectrum (Nujol mull) of this and the above product gave only a negligibly small carbonyl band, indicating less than 1% carbonyl-containing product present.

Registry No.—IV, 16487-00-6; VI, 16487-01-7; VII, 5257-51-2; VIII, 16487-03-9; IX, 16487-23-3; XI, 16487-24-4; XII, 16487-25-5; XIV, 16487-26-6; XV, 16487-27-7; XVI, 16487-28-8; product from *exo*-5-cyano-2-norbornene, 16487-04-0.

Acknowledgment.—The authors wish to thank the National Institutes of Health for a Postdoctoral Fellowship (A. F.), Varian Associates for several spectra, and the National Science Foundation for a grant (GP-242).

Oxymercuration of Strained Olefins.[1] The Effect of *syn*-7 Substituents

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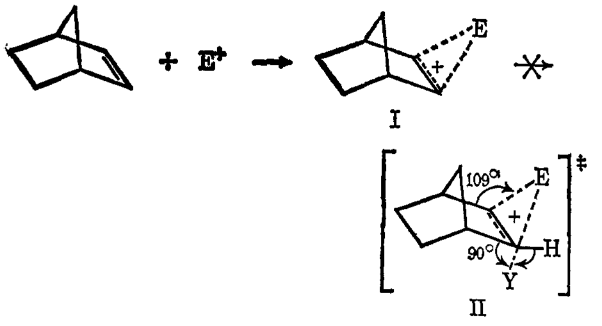
Oxymercuration of 1,4,7,7-tetramethylnorbornene produces 100% *cis-exo* product. Furthermore, *syn*-7-bromonorbornene oxymercurates completely *cis-exo*. These results are a strong indication that *cis-exo* electrophilic additions to norbornenes do not result from steric hindrance toward *endo* attack. Since the highly predominant *exo* attack on norbornenes by electrophiles is not of steric origin, it is concluded that it is an electronic effect.

The *cis* electrophilic additions to strained bicyclic olefins has been attributed to a twist strain introduced in the second step of the usual two-step *trans* addition.[3]

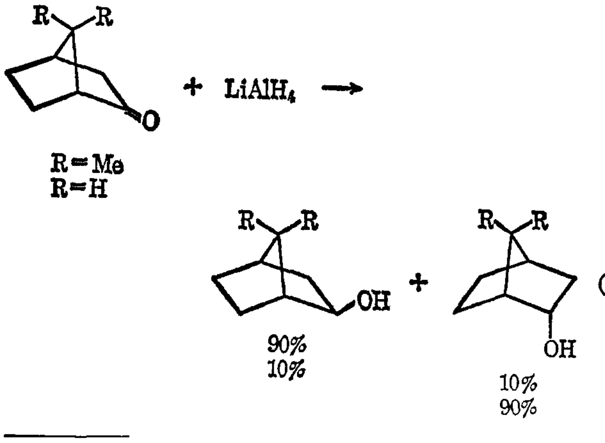


I

II

(1)

This postulate does not explain the highly selective *exo* attack by the electrophile to give I, and this selectivity is generally attributed to steric effects.[4] If this is true, then the addition to *syn*-7-substituted norbornene should occur *cis-endo*. Such substitution changes th stereochemistry of other reactions in the bicyclohepty system[4b] (eq 2 and 3).



(2)[5]

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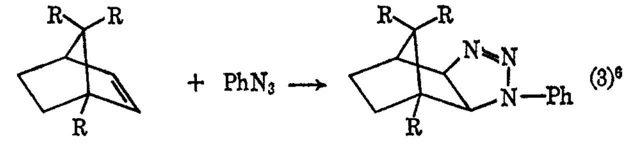
(1) Supported in part by the National Science Foundation, Grant GP-2829.

(2) National Institutes of Health Postdoctoral Fellow, 1964–1965.

(3) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

(4) (a) See, *e.g.*, J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 166; (b) p 129; (c) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(5) R. Howe, E. C. Friedrich, and S. Winstein, *J. Amer. Soc.*, **87**, 379 (1965).

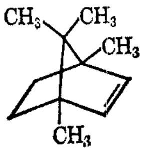


R = Me, no reaction
R = H, *exo* addition

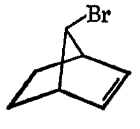
An alternative suggestion is that $Hg(OAc)_2$, HOAc, or HBr can add to norbornene by a simple four-center transition state which would be similar in steric effects to eq 3. This would also predict that *syn*-7-substituted norbornenes should give substantial *cis-endo* oxymercuration products. We have, therefore, investigated the effect of *syn*-7 substituents on oxymercuration of norbornene.

Results

We have prepared 1,4,7,7-tetramethylnorbornene (III)[7] and *syn*-7-bromonorbornene (IV)[8] by known methods. The structure of III was confirmed by its nmr spectrum and by its chemistry, described below.



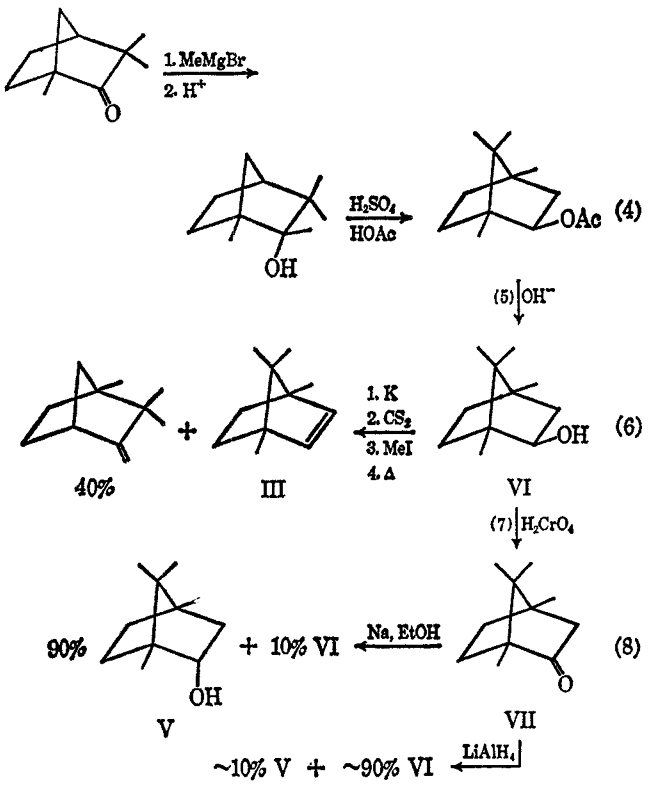
III



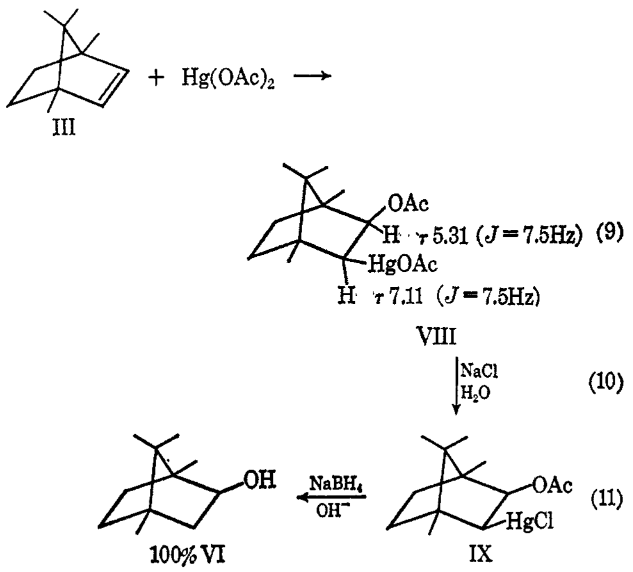
IV

Preparation of the 4-Methylborneol (V) and 4-Methylisoborneol (VI).—The method of Shavrygin[7b] was used to prepare 4-methylisoborneol (VI) from fenchone. This alcohol was converted to 1,4,7,7-tetramethylnorbornene and to the ketone and thence to the isomeric alcohols V and VI as shown in Scheme I. The reductions of 4-methylcamphor (VII) to V with Na in ethanol[9] and to VI with $LiAlH_4$ confirm the assigned structures.[4b]

Scheme I



Addition of Mercuric Acetate to III.—Combination of equimolar quantities of III and mercuric acetate in acetic acid and examination of the solution by nmr indicated formation of an acetoxymercuri acetate with the proton α to the OAc *cis* to the proton α to the Hg-OAc group as shown by clean doublets at τ 7.11 and 5.31 with coupling constants of $J = 7.5$ Hz.[3,10] (The nmr studies in this system are much simplified by the absence of 1,4,7,7 hydrogens.) The mercurial was isolated by dilution with aqueous sodium chloride and reduced with $NaBH_4$; the product was hydrolyzed and compared with V and VI by glpc. The alcohol proved to be VI and no trace of V was seen. The reactions just described therefore occur as is shown in eq 9–11.



The nmr spectrum of the reaction solution was identical with that of purified IX (except for the HgOAc hydrogens which are absent in IX and masked by the solvent peak in the reaction solution). Thus, not more than about 5% of isomeric mercurials was present. The positions of the sharp 7-methyl group resonances are very sensitive to 2 and 3 substitution.

In acetic acid the addition is slowly reversible. When an equimolar amount of norbornene was added to the solution of VIII, the nmr spectrum showed a reappearance of III, disappearance of norbornene, and formation of *exo*-3-acetoxy-*exo*-norbornylmercuric acetate.[3,11a–c] The half-life of this exchange was about 18 hr at 25°. Norbornene adds free mercuric acetate in acetic acid practically instantaneously. When a solution of VIII and norbornene was made 0.1 *M* in toluenesulfonic acid,[11d] the exchange half-time decreased to 30 min. On the other hand, an acetic acid solution of VIII was

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(6) K. Alder, G. Stein, and S. Schneider, *Ann.*, **515**, 185 (1935).

(7) (a) A. I. Shavrygin, *Zh. Obshch. Khim.*, **9**, 516 (1939); *Chem. Abstr.*, **34**, 404 (1940). (b) A. I. Shavrysin, *Zh. Obshch. Khim.*, **18**, 49 9(1948); *Chem. Abstr.*, **42**, 7276*h* (1948).

(8) H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

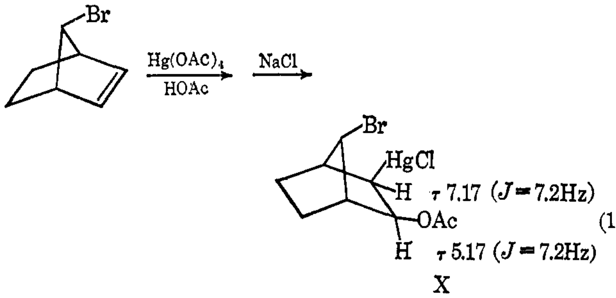
(9) S. Nametkin and A. Churchrikoff, *Ann.*, **432**, 207 (1923); see also S. Nametkin and L. Brüssoff, *ibid.*, **459**, 144 (1927).

(10) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 2709 (1963); J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

(11) (a) T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, No. 19, 15 (1959). (b) T. G. Traylor, *ibid.*, **86**, 244 (1964). (c) A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968). (d) Acid-catalyzed deoxymercuration has been studied by M. M. Kreevoy and M. A. Turner, *J. Org. Chem.*, **30**, 373 (1965), and previous papers.

found to retain its nmr spectrum for at least 50 days (65 half-lives). In the presence of toluenesulfonic acid, VIII isomerized to the other isomers, as shown by the disappearance of the original nmr absorptions and the appearance of new peaks at slightly different positions.

Addition of Mercuric Acetate to *syn*-7-Bromonorbornene.—The addition of equimolar mercuric acetate to *syn*-7-bromonorbornene[8] in acetic acid and pouring the resulting solution into aqueous sodium chloride produced an 86% yield of a mercurial whose melting point did not change upon recrystallization. The protons on carbons 2 and 3 exhibited simple doublets (J = 7.2 Hz) in the nmr spectrum. The fact that neither doublet was resplit by bridgehead protons (usually J = 4–5 Hz for *exo* protons) indicates that both protons were *endo*.[3,10] The splitting, J = 7.2 Hz, is also in agreement with the *cis-endo* configuration of these hydrogens. Thus addition occurred *cis-exo*.



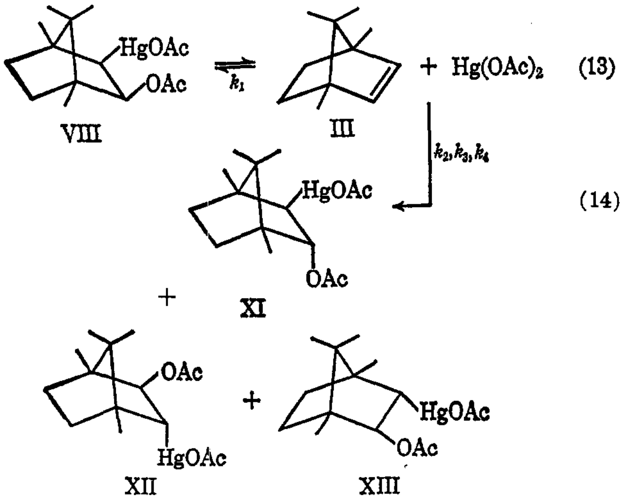
(12)

X

This structure proof was not carried further because we feared the toxicity of the bromohydrin which would result from the reduction of X.[12] However, the nmr spectrum alone is quite definitive.[10]

Discussion

The high degree of stereospecific *cis-exo* addition to III was demonstrated by a kinetic comparison using the reversible oxymercuration scheme shown in eq 13 and 14.



(13)

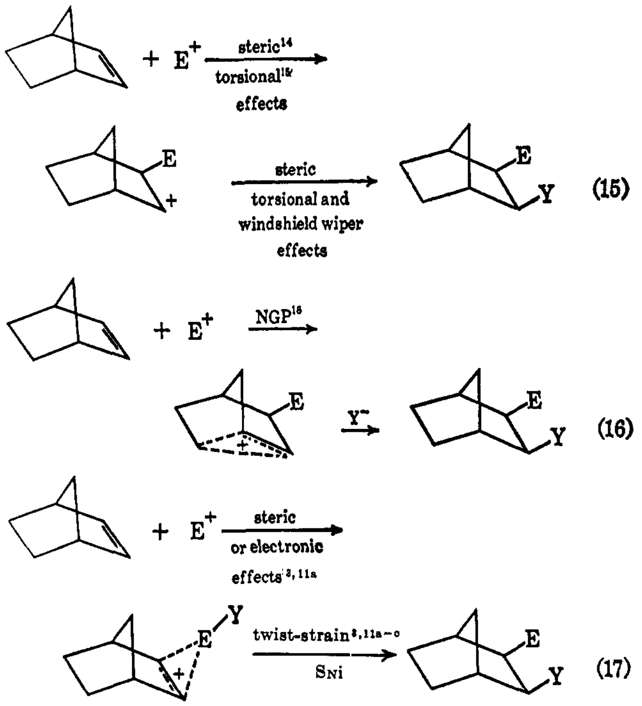
(14)

VIII III XI XII XIII

We have determined the rate of elimination from VIII under oxymercuration conditions by trapping the mercuric acetate with norbornene. After 65 half-lives for elimination followed by readdition (reaction 13), the nmr spectrum revealed no isomeric products. (With added acid to accelerate reaction such isomers were detected.)

Because borneol is more stable than isoborneol, it is reasonable to conclude that VIII is the least stable of the isomers VIII, XI, XII, and XIII. We therefore suggest that the rates of formation of XI, XII, and XIII (reaction 14) are so much slower than that of VIII (k_1) that during 65 half-lives for exchange of VIII no detectable amounts of the other isomers are formed. If $k_2 = 10^{-2}\ k_1$ then at least 25% of XIII should have been formed. In addition, we could not detect V in the product of the reduction of VIII with sodium borohydride. (As much as 0.5% could have been found.) Thus the preference for *exo* addition (*exo*/*endo* > 10^3) rivals that displayed by the bornyl cation.

It has therefore been established that bicyclo[2.2.1]heptenes react with electrophiles with high preference on the *exo* side *even in the presence of 7,7-dimethyl groups*.[13-15] Three different reasons have been offered for *exo* stereospecificity.



(15)

(16)

(17)

The literature abounds[3,11a-c] with evidence that resonance effects are not significant in oxymercuration and that oxymercuration does not proceed through classical carbonium ions such as that shown in reaction 15. Brown, Kawakami, and Ikegami[14a] have recently re-

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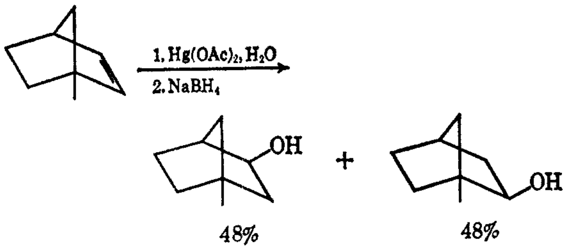
[12] S. Winstein, *J. Amer. Chem. Soc.*, **83**, 1516 (1961).

[13] Since this work was first submitted for publication, other examples of *cis-exo* electrophilic additions in the presence of 7,7-dimethyl groups have been reported[14a,b] and given interpretations[14a,b,15] with which the authors do not agree.[16] However, our priority in this discovery is acknowledged.[14a,15]

[14] (a) H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, **89**, 1525 (1967); (b) H. C. Brown and K.-T. Liu, *ibid.*, 3900 (1967); (c) see ref 14b, footnote 15.

[15] (a) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967); (b) *ibid.*, **89**, 3901 (1967).

[16] Note Added in Proof.—Professor Thomas Bond (private communication) has observed exclusive *cis*-hydroxymercuration of bicyclo[2.2.1]hexene. This result, predicted by the twist-strain theory of *cis* addition,[3,11a] is inconsistent with the proposals that torsional[15] or steric effects[14] are responsible for *cis* additions.

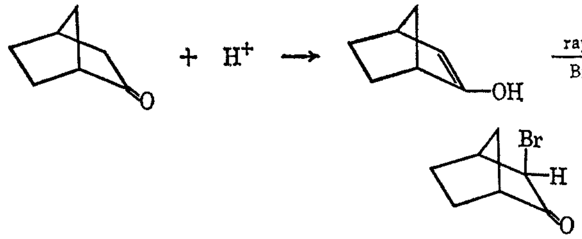


(18)

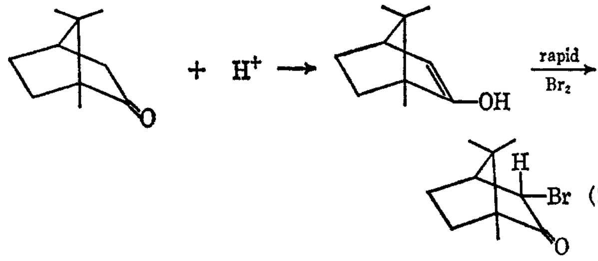
ported the result in eq 18 which reiterates these conclusions and indicates that resonance effects such as that shown in eq 16 do not account for *cis* oxymercuration of norbornenes. If oxymercuration involves neither reaction 15 nor 16, any discussion of classical *vs.* nonclassical carbonium ions can be omitted (see below).

The high stereospecificity in the addition to the sterically hindered olefins III and IV is not easily accommodated by reaction 17 which is similar to a molecular addition. Such processes either do not occur (phenylazide addition)[6] or lead to substantial *endo* product (hydroboration)[14c] when carried out on 7,7-dimethylbicyclo[2.2.1]heptenes. These observations seem to eliminate simple steric effects (which should have yielded some *endo* oxymercuration product) or torsional effects[15a] (according to which oxymercuration and hydroboration should give the same stereochemistry). It is therefore concluded that the stereochemistry in oxymercuration of bicycloheptenes is determined primarily by some electronic effect.

The acid-catalyzed brominations of camphor[17] and norcamphor[17a] agree with this postulate (with respect to the direction from which the electrophile attacks). In such brominations the rates are limited by enol formation, and the product is therefore determined kinetically.



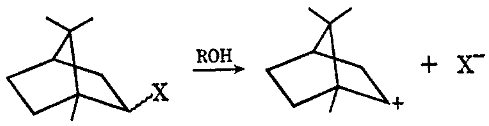
(19)



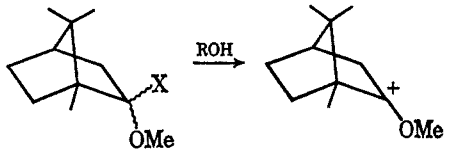
(20)

Such changes from *exo* to *endo* reactions upon external stabilization of positive charge have been observed previously.[18-20] There seems to be an electronic difference in the *exo* and *endo* sides of the norbornene which is removed (swamped out)[20] by external stabilization. This high stereospecificity holds only for electrophilic additions and carbonium ion reactions.

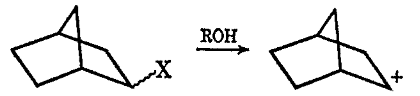
k_{exo}/k_{endo}



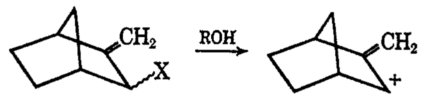
+ X^- 4×10^4 (21)[18]



0.1 (22)[19]

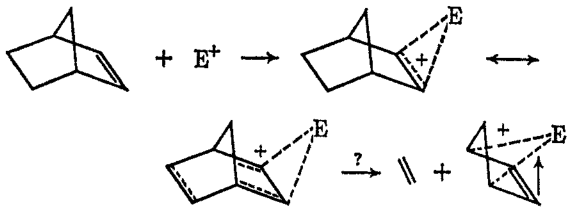


300 (23)[18]



3 (24)[20]

If effects such as those shown in eq 15 or 16 cannot be used, then an additional possibility for a stereospecific electronic effect must be offered (with some reluctance). One such possibility might be an electrophilic catalysis of a partial reverse Diels-Alder reaction. Such a formulation is symmetry allowed; it predicts neither rearrangement nor effects of 1-alkyl substitution but does require *exo* attack by electrophiles. However, neither this nor any other mechanism which has been suggested accommodates all the observations in a satisfactory manner, and the reason for the observed high *exo* stereospecificity in these *cis* electrophilic additions essentially remains obscure.



(25)

Effects of Added Sodium Acetate.—Of all the evidence against carbonium ion formation during oxymercuration the authors consider the effects of added sodium acetate[11a] to be the most decisive. When sodium acetate is included in an oxymercuration mixture in water or methanol, both *cis* and *trans* oxymercurations proceed more slowly owing to the reduced electrophilicity of the mercury salt. However this condition elicits completely different behavior from *cis* and *trans* oxymercurations. The inclusion of sodium acetate does not alter the *trans* oxymercuration product but causes *cis* oxymercurations to produce *cis*-acetoxyalkylmercury salts. Examples of both kinds of response are shown in Table I.[3,11b,21] These observations are not compatible with a mechanism of *cis* oxymercuration in which water and acetate ion compete for a carbonium ion. Rather they require that *cis* and *trans* oxymercurations involve different mechanisms.

We also observed that sodium acetate has a somewhat greater effect on product composition in oxy-

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[17] (a) W. G. Woods and J. D. Roberts, *J. Org. Chem.*, **22**, 1124 (1957). (b) F. S. Kipping and W. J. Pope, *J. Chem. Soc.*, **73**, 576 (1893); (c) F. H. Lees, *ibid.*, **83**, 145 (1903).

[18] A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 129, 131.

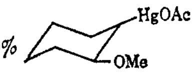
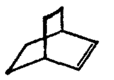
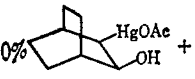
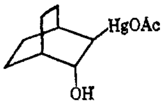
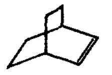
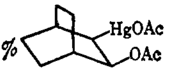
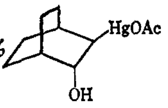
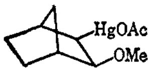
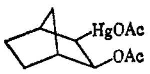
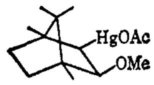
[19] T. G. Traylor and C. L. Perrin, *J. Amer. Chem. Soc.*, **88**, 4934 (1966).

[20] C. F. Wilcox, Jr., and R. G. Jesaitis, *Chem. Commun.*, 1046 (1967).

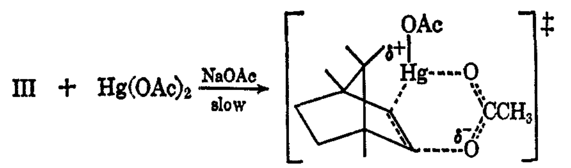
[21] M. J. Abercrombie, A. Rodgman, K. R. Bharucha, and G. F Wright, *Can. J. Chem.*, **37**, 1328 (1959).

Table I

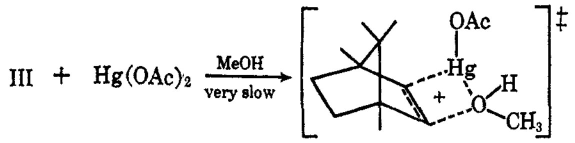
Effects of Added Sodium Acetate on the Products of Olefin Oxymercurations with $Hg(OAc)_2$

Olefin	Solvent	Concn of NaOAc, *M*	Products		Ref
Cyclohexene	MeOH	0.1	100% 		3
	H_2O–acetone	0	60%  +	40% 	11b
	H_2O–acetone	0.1	75%  +	25% 	11b
			 +		
Norbornene	MeOH	0	60–80%	20–40%	21, this work
Norbornene	MeOH	0.1	20–40%	60–80%	21, this work
			 +	VIII	
III	MeOH	0	70%	30%	This work
III	MeOH	0.1	0	100%	This work

mercuration of III than in oxymercuration of norbornene. This result at once confirms *cis* addition to III and suggests that methoxymercuration of norbornene proceeds through a four-center transition state. Such a four-center reaction would be retarded more by 7,7-dimethyl groups than would be the six-centered transition state for addition of the elements of mercuric acetate.[11a]



(26)



(27)

The *cis* additions of acids to norbornenes[22–24] have (with one exception)[14b] likewise been interpreted as rather polarized molecular additions. Unlike oxymercuration, acid additions are usually accompanied by some carbonium ion formation,[22,23] and this complicates the interpretations of such reactions.

Relationship to the Nonclassical Ion Problem.—The available data favor mechanisms of *cis-exo* additions in which both electrophile and nucleophile are strongly bonded to the respective carbons in the transition state. On the other hand, these results might be due to steric factors which respond only to electrophilic reagents and the intermediates might be classical carbonium ions which behave in a rather unprecedented manner. However, before these additions can be related to solvolysis reactions, it is necessary to prove that they indeed proceed through the same intermediates as those involved in solvolysis. Without this proof conclusions concerning the "need to reconsider the proposed σ-bonded intermediates"[14] derived from additions to olefins are invalid.

It might be asked whether the "polarized molecular addition" of eq 17 has a transition state whose charge distribution resembles that of the localized (eq 15) or σ-bridged (eq 16) carbonium ion. Equation 18 suggests that it resembles more closely the distribution in the localized (classical) carbonium ion, but this says nothing about the existence of nonclassical ions.

Experimental Section[25]

Reagents and Procedures.—Melting points were obtained using sealed capillaries in a Thomas-Hoover apparatus and are not corrected. Infrared spectra were determined in carbon tetrachloride solution using a Perkin-Elmer 137 Infracord spectrophotometer. Nmr spectra were determined on a Varian HR-60 instrument; chemical shifts are reported in units of τ and were calibrated by the side-banding technique. Tetramethylsilane was used as an internal standard in carbon tetrachloride solutions; alkyl resonances calibrated in this way were used as internal standards in acetic acid solutions. Gas chromatographic analyses and separations were carried out on a Wilkens "Autoprep" instrument using the columns named.

Acetic acid was purified by distillation from potassium permanganate followed by distillation from triacetyl borate.[26] Tetrahydrofuran was purified by stirring over potassium hydroxide and distilling from lithium aluminum hydride. [7]

Preparation of 1,4,7,7-Tetramethylnorbornene (III).[7]—Crude 4-methylisoborneol (VI) was prepared by treating Eastman Organic Chemicals fenchone (85% pure by glpc) with methylmagnesium bromide, treating the crude product of this reaction with acetic acid–sulfuric acid at 65° for 24 hr and saponifying the resulting acetate. A recrystallized sample of this product melted at 188.5–191 (lit.[7b] mp 190–191°). The crude alcohol

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(22) (a) S. J. Cristol, W. R. Seifert, D. W. Johnson, and J. B. Jurale, *J. Amer. Chem. Soc.*, **84**, 3918 (1962); (b) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Lett.*, 185 (1963).

(23) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstke, *J. Amer. Chem. Soc.*, **88**, 4922 (1966).

(24) S. Winstein, private communication.

(25) Analyses were performed by Schwartzkopf Microanalytical Laboratory and by F. Pascher Microanalytical Laboratory.

(26) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955.

(27) K. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(338 g, 2 mol) was added to 82 g (2.1 g-atoms) of potassium metal in 1 l. of dry toluene and heated at reflux after the initial reaction subsided. The resulting solution was treated with 160 g (2.1 mol) of carbon disulfide in 2 hr, then with 269 g (1.9 mol) of methyl iodide and 300 ml of ether. After filtration and removal of solvent by distillation, the residue was distilled through a short-path column first at atmospheric pressure and temperatures up to 160° and then at aspirator pressure and 160° to give (after redistillation of foreruns and residues) 71.6 g of white solid (0.47 mol, 21% based on fenchone). There was also obtained in the distillation about 100 ml of a higher boiling liquid whose infrared spectrum showed no olefinic absorption.

The solid reaction product was recrystallized three times from acetonitrile to give 42 g of white solid (mp 115°) which was shown by glpc (on a 0.375-in column, packed with Carbowax 20M on Chromosorb P and operated at 100°) to consist of two components in the ratio 61:39 having retention times of 20 and 45 min. The first of these was collected and identified by its spectral properties as 1,4,7,7-tetramethylnorbornene (III): infrared spectrum, 6.15 μ (weak),[28,29] 14.00 (strong);[28,29] nmr (CCl_4) τ 9.38 (s, three protons of a 7-methyl group), 9.33 (s, three protons of a 7-methyl group), 9.00 (s, six protons of the two bridgehead methyl groups), 8.3–9.3 (m, four protons of the 2-methylene groups), 4.49 (s, two vinyl protons). Samples of this olefin used in later experiments were purified by glpc in this way.

The second component was assumed to be a trimethyl-*exo*-methylenenorbornane on the basis of its spectral properties: infrared spectrum 6.05 μ (strong),[30] 11.33 (strong);[30] nmr (CCl_4) τ 9.12 (s, three protons of a methyl group), 9.08 (s, three protons of a methyl group), 9.04 (s, three protons of a methyl group), 8–9 (m, four protons of two methylene groups), 7.57 (d, J = 4 cps, vague, one bridgehead proton), 5.81 and 5.63 (s, two vinyl protons of a terminal methylene group).

Oxidation of *exo*-1,4,7,7-Tetramethylnorborneol with Chromic Acid.—Chromium trioxide (2.5 g, 0.025 mol) was dissolved in 10 ml of water and 15 ml of actic acid was added. The alcohol (VI) (2.0 g, 0.0119 mol) was dissolved in 10 ml of acetic acid and cooled in an ice bath while the cooled chromic acid solution was added slowly to keep the temperature below 15°. The solution was stirred 4 hr while warming to room temperature and then was poured into 500 ml of water and filtered. The collected solid was dried in a desiccator to give 1.35 g (0.0081 mol, 68%) of a white solid, mp 149–168°. Recrystallization from petroleum ether (bp 30–60°) gave 0.106 g of material with mp 168.0–168.6° (lit.[9] mp 168–168.5°).

Reduction of 1,4,7,7-Tetramethylnorbornanone with Sodium in Alcohol.—The ketone (0.2 g, 0.0012 mol) was dissolved in 50 ml of absolute ethanol and sodium (0.6 g, 0.026 g-atom) was added with stirring in small pieces over a period of 24 hr. After the sodium was completely dissolved, the solution was poured into 500 ml of water which was then extracted twice with petroleum ether which was then removed on the rotary evaporator. The residue, a white solid (0.134 g, 0.0008 mol, 70%), was shown by ir spectroscopy to contain alcohol but no ketone and was assumed to be *endo*-1,4,7,7-tetramethylnorborneol. Recrystallization from acetonitrile yielded 4 mg of material, mp 167–178° (lit.[9] mp 183–184°), with the same infrareds pectrum as that of the crude material. Glpc analysis of crude alcohol indicated about 10% VI and 90% the *endo* isomer (V).

Reduction of 1,4,7,7-Tetramethylnorbornanone with Lithium Aluminum Hydride.—Reduction of this ketone (1.1 g) with ethereal lithium aluminum hydride produced 85% (VI) which melted at 182–187.5° before and 188.5–192.5° after recrystallization from acetonitrile. Glpc analysis of the crude alcohol indicates about 90% VI and 10% the *endo* isomer (V). These results agree with the usual *endo* attack on 7,7-disubstituted norbornanones.[4b]

Reaction of 1,4,7,7-Tetramethylnorbornene with Mercuric Acetate in Acetic Acid.—Pure 1,4,7,7-tetramethylnorbornene (0.0671 g, 0.000446 mol), dissolved by warming in acetic acid in an nmr tube, gave the characteristic spectrum of the olefin. Mercuric acetate (0.145 g, 0.000455 mol) was added and the tube was shaken 10 min until the solid dissolved. The nmr spectrum now corresponded exactly to that of the purified mercurial (see below). The contents of the tube were poured into sodium chloride solution which was extracted twice with methylene chloride. The methylene chloride layers were combined, washed with sodium bicarbonate, dried over Drierite, and evaporated to give a gum which gradually solidified to a white solid, mp 92–100° (0.137 g, 0.000308 mol, 69%), identified as *exo*-2-chloromercuri-*exo*-3-acetoxy-1,4,7,7-tetramethylnorbornane. One recrystallization from heptane–ethyl acetate gave 0.0485 g of stubby white crystals: mp 100–101.5° (second recrystallization from heptane raised the melting point to 101.8–103.2°); infrared spectrum 5.72 μ; nmr (CCl_4) τ 9.30 (s, three protons of a methyl group), 9.16 (s, three protons of a methyl group), 8.97 (s, three protons of a methyl group), 8.89 (s, three protons of a methyl group), 8.06 (s, three protons of the methyl group of the acetate), 9.1–8.4 (m, four protons of the two methylene groups), 7.11 (d, J = 7.5 Hz, one proton attached to mercury-bearing carbon), 5.31 (d, J = 7.5 Hz, one proton attached to acetoxy-bearing carbon).

Anal. Calcd for $C_{13}H_{21}HgO_2Cl$: C, 35.06; H, 4.75; Cl, 7.97. Found: C, 35.44; H, 5.18; Cl, 8.40.

Exchange Reaction between the Mercuric Acetate–1,4,7,7-Tetramethylnorbornene Adduct and Norbornene.—The addition of mercuric acetate to 1,4,7,7-tetramethylnorbornene in an nmr tube was carried out as before; then 1 equiv of norbornene was added giving the superimposed spectra of the unsubstituted olefin and the original mercurial. Addition of 0.2 equiv of toluenesulfonic acid led to complete disappearance (half-life, 30 min) of the spectra of norbornene and of the mercurial (VIII) and simultaneous regeneration of the spectrum of the tetramethylnorbornene (VI). In addition there appeared the typical spectrum of the addition product from norbornene.

Repetition of the above experiment without the addition of toluenesulfonic acid led to the same result but with the half-life lengthened to 18 hr.

The mercuric acetate–1,4,7,7-tetramethylnorbornene adduct (VIII) alone in acetic acid showed no change in its nmr spectrum after 50 days. When toluenesulfonic acid (0.2 M) was added, the two doublets at τ 7.11 and 5.31 slowly disappeared and were replaced by two doublets at slightly lower field (J = 10 Hz) and two doublets at slightly higher field ($J \cong 3$ Hz). While these isomers were not isolated, the nmr spectrum indicates that both *cis-endo* and *trans* products were formed.

Reduction of *exo*-2-Chloromercuri-*exo*-3-acetoxy-1,4,7,7-tetramethylnorbornane with Sodium Borohydride.—A purified sample of IX (0.924 g) in 2.5 ml of 2 N sodium hydroxide was treated with sodium borohydride (0.7 g) for 5 hr and extracted with ether; the ether was washed, dried, and evaporated to yield a mixture of acetate and alcohol. This mixture was treated with a refluxing solution of 0.5 N sodium hydroxide in 50% methanol for 2 hr, diluted with aqueous sodium chloride, extracted with ether, and the extract dried and evaporated to yield 82 mg (23%) of solid product, mp 176–193°. Glpc analysis (see below) of this product showed only VI and no trace of the *endo* product (V) was observable.

When the entire oxymercuration solution (containing VIII) was treated with enough base to neutralize the acetic acid, then reduced with sodium borohydride in ether, direct examination of the ethereal solution by glpc revealed an 8% yield of VI and no trace of V. The low yield of VI is not significant here because the exchange experiments, and the nmr results above establish that only one product was produced. However, Bordwell and Douglass[31] have greatly improved this reduction and Brown, Kawakami, and Ikegami[14a] have obtained greater than 98% yield of 7,7-dimethyl-*exo*-norborneol from oxymercuration of apobornylene followed by reduction.

Reaction of *syn*-7-Bromonorbornene with Mercuric Acetate in Acetic Acid.—*syn*-7-Bromonorobornene (IV) (1.10 g, 0.00635 mol), prepared by the method of Kwart and Kaplan,[8] was dissolved in 25 ml of glacial acetic acid in a 125-ml erlenmeyer flask and mercuric acetate (2.03 g, 0.00637 mol) was added with 10-min shaking to dissolve the solid. After standing 20 min the solution was poured into sodium chloride solution and let stand overnight. The solid was collected and dried in a desiccator to give white crystals (2.57 g, 86.3%), mp 123–124.5°, identified as *exo*-2-chloromercuri-*exo*-3-acetoxy-*syn*-7-bromonorbornane (X): (recrystallization from heptane–ethyl acetate gave mp 121.2–123.8°); infrared 5.74 and 5.80 μ; nmr ($CDCl_3$) τ 8.0–8.8

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(28) Characteristic of 1,2-disubstituted olefins.[29]

(29) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 36, 48.

(30) Characteristic of 1,1-disubstituted olefins: ref 29, pp 36, 51.

(31) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966).

(m, four protons of two methylene groups), 7.97 (s, three protons of the acetoxy methyl group), 7.35 (s, broad, two bridgehead protons), 7.17 (d, J = 7.2 Hz, proton on mercury-bearing carbon), 5.94 (s, broad, bridge proton), 5.17 (d, J = 7.2 Hz, proton on acetoxy-bearing carbon).

Anal. Calcd for $C_9H_{12}O_2HgClBr$: C, 23.09; H, 2.58; Hg, 42.85; Cl, 7.57; Br, 17.07. Found: C, 23.04; H, 2.57; Hg, 42.69; Cl, 7.82; Br, 16.94.

Effects of Sodium Acetate Addition.—A solution of III (0.075 g, 0.00050 mol) and mercuric acetate (0.159 g, 0.00050 mol) in 1.0 ml of absolute methanol was allowed to stand overnight, poured into 10 ml of sodium chloride solution (~0.5 M), and extracted with six 5-ml portions of methylene chloride. After drying over calcium chloride and evaporating to dryness the product weighed 0.06 g (30% yield). The infrared spectrum showed a carbonyl peak at 5.8 μ which, by comparison with the 3.4-μ absorption both in this product and in pure VIII, indicated about 30% VIII in the product. When this experiment was repeated with 0.1 M sodium acetate in the methanol, the crude product had a spectrum identical with that of the product obtained in acetic acid. When this latter experiment (0.1 M NaOAc) was carried out with norbornene, the reaction was very fast (complete in 10 min) and the product contained about 60% acetate and 40% methoxymercurial. This ratio was obtained by comparing the infrared spectrum of the product with those of various mixtures of 3-*exo*-chloromercuri-2-*exo*-norbornyl acetate and 3-*exo*-methoxy-2-*exo*-norbornylmercuric chloride.[11a]

Both III and norbornene were oxymercurated in the presence of 0.1 M sodium acetate at the same concentrations given above but using 50 vol. % water–tetrahydrofuran as solvent. The results corresponded rather closely to those obtained in methanol. Thus, the product from III was almost pure VIII but that from norbornene contained 40–50% hydroxymercurial.

Registry No.—III, 16487-05-1; VII, 10309-50-9; IX, 16487-07-3; X, 16487-08-4.

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The Reaction of Sulfur Dichloride with Linear Diolefins. Stereochemical Aspects in the Formation of Cyclic Sulfides[1]

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Additions of sulfur dichloride to linear diolefins, such as pentadiene-1,4, hexadiene-1,5, diallyl sulfide, and diallyl ether, which lead to cyclic β,β′-dichlorosulfides is reported. Only in one case an alternative synthesis had been reported previously. Stereochemical aspects of that addition are discussed, which are characterized by the predominant formation of the *cis* products in that reaction. The addition reaction is compared with the hydrogen sulfide addition to several linear diolefins. An outstanding feature of the reaction is the influence of steric effects on the reaction products, which cause the formation of predominantly anti-Markovnikov products. In one example, ring expansion from a tetrahydrothiophene ring system to a thiacyclohexane system occurs both during oxidation and reduction of the sulfur dichloride addition product. An alternative synthesis to the cyclic β,β′-dichlorosulfides is provided by the addition of chlorine to the corresponding olefinic episulfides.

Although sulfur monochloride and 2,3-dimethylbutadiene were reported to give 3,4-dichloro-3,4-dimethyltetrahydrothiophene in a yield of 1%[2] and although transannular additions of sulfur dichloride to cyclic diolefins occur readily, the possibility that cyclic derivatives may result in reactions of sulfur dichloride with linear diolefins has not been investigated. This reaction is an approach to a variety of cyclic sulfides. In the absence of special geometric arrangements of the olefinic double bonds, which would favor such an intramolecular addition, the use of high dilutions of equimolar amounts of reagents is required to reduce the yield of intermolecular addition which leads to polymer formation.[3-6] In this report, only monomeric components of the addition reaction are investigated, which consist exclusively of cyclic β,β′-dichlorosulfides.

The products of that addition reaction are of mechanistic and stereochemical interest with respect to the size of the resulting heterocyclic ring system and the configuration of its substituents. In principle, three possible ring systems can be envisaged to result from that reaction with linear diolefins, which differ in the number of atoms in the sulfur-containing ring (Scheme I). In addition, and contrary to the reaction of sulfur dichloride with cyclic diolefins[3-6] where only a single stereoisomer was obtained, the reaction with linear diolefins could conceivably lead to two stereoisomers, one *meso* (*cis*) and a *dl* pair (*trans*). With one exception, the products described here have not been reported in the earlier literature.

Results and Discussion

The addition reaction of sulfur dichloride was investigated on seven diolefins. The structures of the isolated addition products were primarily assigned on the basis of their nuclear magnetic resonance spectra, specifically on the relative proportion of CH_2Cl and CHCl *vs.* CH_2S and CHS protons, which distinguishes the various ring systems.

Additional support for several of the assigned structures results from the reduction of the cyclic dichlorosulfides to known sulfides with lithium aluminum hydride. In addition, several of these sulfides can be synthesized in low yield by the reaction of hydrogen sulfide with the corresponding linear diolefins.[7,8]

The addition of sulfur dichloride to diallyl ether leads to 1 in a yield of 42%. No isomeric products of differ-

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[1] Presented in part at the Intra-Science Research Symposium, Santa Monica, Calif., Nov 30, 1967.

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