Table V. GLC–Mass Spectral Analysis of the Quinoline Reaction Solution (Run 8, Table IV)

probable compd	wt, %	probable compd	wt, %
tetrahydroquinoline dimer	0.01	hexahydro-quinoline	0.7
dihydroquinoline dimer	0.04	tetrahydro-quinoline	26.4
quinoline dimer	0.6	dihydroquinoline	1.7
tetrahydromethyl-quinoline	0.02	quinoline	63.2
dimethylquinoline	0.3	dimethylaniline	0.5
tetrahydromethyl-quinoline	1.1	indan	0.6
dihydromethyl-quinoline	0.3	methylaniline	3.3
methylquinoline	0.4	aniline	0.6
methylnaphthalene	0.2		

Acknowledgment. We gratefully acknowledge that this research was supported by the United States Department of Energy on Contract No. E (49-18)-2211.

Registry No.—1,2,3,4-Tetrahydronaphthalene, 119-64-2; 1,2,3,4-tetrahydroanthracene, 2141-42-6; anthracene, 120-12-7; 9,10-dihydroanthracene, 613-31-0; methylbenzohydrindene, 37977-37-0; quinoline, 91-22-5; 1,2,3,4-tetrahydroquinoline, 635-46-1; CO–H_2O, 40217-37-6; CO–H_2O–H_2, 66402-63-9; H_2, 1333-74-0.

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Chemistry of Allene Oxides[1,2]

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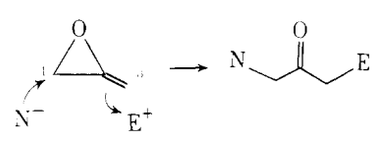
A general and facile method to the highly reactive allene oxides has been developed. 1-*tert*-Butylallene oxide is isolated and characterized. 1-Alkyl-, 3-alkyl-, and 3-aryl-substituted allene oxides, when similarly generated, suffer regiospecific nucleophilic epoxide opening to give substituted ketones. On the other hand, 1-aryl- and 1,1-dialkyl-substituted allene oxides give products characteristic of cyclopropanones. These allene oxides, once generated, are believed to have undergone facile isomerization to cyclopropanones. The mechanism of the isomerization process is discussed.

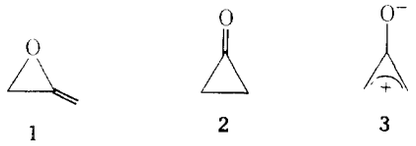
Allene oxide (1) is an extremely unusual molecule. Within its simple framework, it has encompassed the structural features of epoxide, double bond, and enol ether. Allene oxide is also highly strained. Several quantum mechanical calculations[3–8] have concluded that it has a higher energy content than cyclopropanone (2), a molecule already notorious for its instability and reactivity.[9] It is not surprising, therefore, to find that allene oxide is very reactive and has eluded isolation. Prior to our work, only two substituted allene oxides, 1,1-di-*tert*-butyl[10] and 1,1,3-tri-*tert*-butyl,[11,12] both sterically encumbered, have been properly characterized. There are reasons, however, other than its intrinsic interest, to investigate the chemistry of allene oxide. Reactions at carbon-1 and carbon-3 of the allene oxide molecule should render it a useful synthon (eq 1). Furthermore, allene oxide is linked structurally to its valence tautomers, cyclopropanone (2)[8,9] and oxyallyl (3),[13] interesting species in their own right. The relationships between these isomers have not been entirely clear and are a problem of much current interest.[14] There are two aspects to the problem; one is the relative stability of these structures and the other is the mechanism of the isomerization



(1)

process. An understanding of this problem would inevitably lead to a better understanding of the fundamental nature of bonding in small-ring compounds and may cast light on the validity of some of the theoretical calculations.

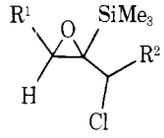
One difficulty associated with the study of the chemistry of allene oxides is the lack of an adequate method of synthesis. A generally employed approach is by way of epoxidation of allenes, which, for all practical purposes, means the reaction of allenes with peracids (eq 2).[15] This approach suffers the



1 2 3

0022-3263/78/1943-2994$01.00/0

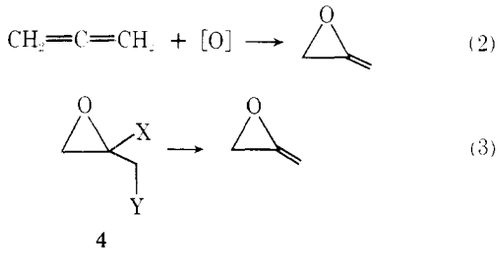
Table I. Physical Data of Epoxides 9



	R^1	R^2	registry no.	bp, °C (mmHg)	^1H NMR, δ	anal.
9a	*t*-Bu	H	61628-67-9 (cis) 61628-68-0 (trans)	87–90 (9)	cis 0.35 (s, 9 H), 1.05 (s, 9 H), 2.5 (s, 1 H), 3.25 (AB, 2 H); trans 0.15 (s, 9 H), 1.1 (s, 9 H), 2.5 (s, 1 H), 3.7 (AB, 2 H)[b]	C, H
9b	H	H	61628-45-3	81–83 (35)	0.2 (s, 9 H), 2.65 (s, 2 H), 3.5 (AB, 2 H)	C, H
9c	CH_3	H	61628-46-4	96–98 (48)	0.2 (s, 9 H), 1.3 (d, 3 H), 2.8 (g, 1 H), 3.25 (AB, 2 H)	C, H
9d	*i*-Pr	H	61628-47-5	86–87 (14)	0.25 (s, 9 H), 1.1 (d, 6 H), 1.5 (m, 1 H), 2.45 (d, 1 H), 3.35 (AB, 2 H)	C, H
9e	n-$C_{10}H_{21}$	H	61628-48-6	107–109 (0.1)	0.25 (s, 9 H), 0.7–1.8 (m, 21 H), 2.75 (t, 1 H), 3.35 (AB, 2 H)	C, H
9f	c-C_6H_{11}	H	61628-59-2	59–60 (0.03)	0.2 (s, 9 H), 0.8–2.2 (m, 11 H), 2.45 (m, 1 H), 3.3 (AB, 2 H)	C, H
9g	H	n-$C_{10}H_{21}$	61628-49-7	*a*	0.0 (s, 9 H), 0.6–1.8 (m, 21 H), 2.4–2.8 (m, 2 H), 4.0 (m, 1 H)	*c*
9h	Ph	H	61628-52-2	62–64 (0.05)	0.2 (s, 9 H), 3.25 (AB, 2 H), 3.95 (s, 1 H), 7.25 (s, 5 H)	C, H
9i	*p*-MeC_6H_4	H	61628-53-3	80–83 (0.1)	0.2 (s, 9 H), 2.3 (s, 3 H), 3.25 (AB, 2 H), 4.0 (s, 1 H), 7.1 (s, 4 H)	C, H
9j	H	n-$C_{10}H_{21}$	66374-60-5 (R*, R*) 66374-62-7 (R*, S*)	*a*	0.0 (s, 9 H), 0.6–1.8 (m, 21 H), 2.4–2.8 (m, 2 H), 4.0 (m, 1 H)	*b,c*

[a] Decomposed on attempted distillation. [b] A mixture of diastereomers as determined for NMR. [c] Its molecular weight was determined by mass spectrometry.

inherent disadvantage that the epoxide structure is easily ruptured under acidic conditions.[15] We recognized that an alternative approach is to generate the double bond subsequent to the formation of the epoxide ring (eq 3). This ap-



(2)

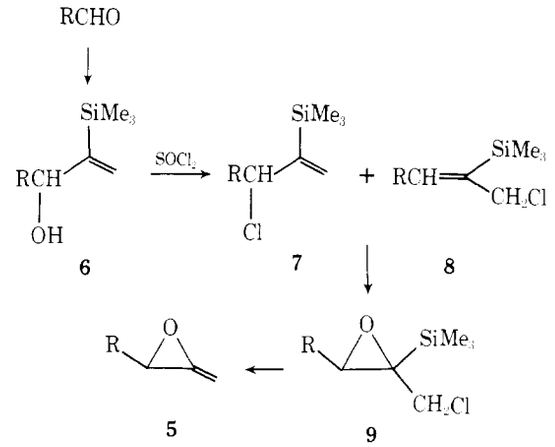
(3)

4

proach is, of course, not without complications. The reagent (e.g., base) necessary to effect the elimination of YX (e.g., Y = H, X = Cl) may react with the product allene oxide, or indeed, with the precursor **4**. What is required is a method of elimination sufficiently mild and selective so that the allene oxides generated have a reasonable chance of survival, or, at the very least, undergo reactions which are chemically meaningful. Our work in the use of β-functionalized organosilicon compounds as a method of alkene synthesis[16] has led us to examine the β elimination of **4** (Y = R_3Si–, X = good leaving group) as an entry to allene oxides.[2a]

In this publication, we wish to show that: (1) the approach defined by eq 3 is a viable one, and is demonstrated by the generation and characterization of 1-*tert*-butylallene oxide;[2b] (2) other allene oxides are too reactive to be isolated; their generation was, however, demonstrated by reactions with external nucleophiles;[2c] (3) the course of the reaction of allene oxides depends critically on the nature of the substituents on carbon-1; and (4) the relevance of these observations to the mechanism of the allene oxide–cyclopropanone isomerization process is discussed.

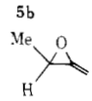
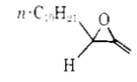
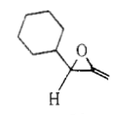
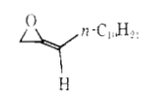
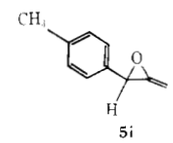
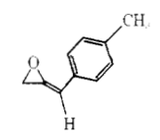
Scheme I



Results and Discussion

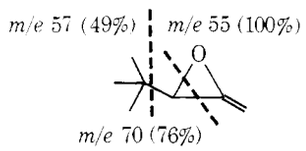
1-*tert*-Butylallene Oxide: Isolation and Characterization.[2a] The synthesis of 1-*tert*-butylallene oxide (**5a**) has been achieved according to Scheme I (R = *t*-Bu). The preparation of the isomeric chlorides **7** and **8** has been detailed elsewhere.[17] Epoxidation of the mixture of isomeric chlorides (**7a** + **8a**, R = *t*-Bu) with 40% peracetic acid yielded the epoxide **9a** (R = *t*-Bu) as a mixture of two geometric isomers (cis and trans) in a ratio of 62:38. The chloride **7a** (R = *t*-Bu) was apparently resistant to epoxidation under the reaction conditions. The epoxide **9a** was stirred at room temperature with a slight excess of cesium fluoride in acetonitrile or diglyme for 1 day. On workup, it was observed that the trimethylsilyl–carbon bond in the epoxide had been cleaved. The product was, however, polymeric in nature. The reaction was, therefore, carried out in diglyme with a slow stream of dried nitrogen bubbling into the reaction mixture so that any volatile

Table II. Physical Data of Compounds[a] 10, 11, 12, 13, 14, and 17. Derived from the Reaction of Allene Oxides with Nucleophiles

precursor	registry no.	nucleophile	product	registry no.	spectroscopic data[b]
 5a	51211-86-0	H_2O	*t*-BuCH(OH)C(=O)CH_3 (**10a**)	7737-47-5	NMR 1.0 (s, 9 H), 2.2 (s, 3 H), 2.8 (br, 1 H), 3.85 (s, 1 H); IR 3400, 1710 cm^{-1}
		C_2H_5SH	*t*-BuCH(SC_2H_5)C(=O)-CH_3 (**10b**)	61628-65-7	NMR 1.05 (s, 9 H), 1.2 (t, 3 H), 2.25 (s, 3 H), 2.45 (g, 2 H), 3.05 (s, 1 H); IR 1700 cm^{-1}
		CCl_3CO_2H	*t*-BuCH($OCOCCl_3$)C(=O)-CH_3 (**10c**)	66374-61-6	NMR 1.05 (s, 9 H), 2.2 (s, 3 H), 4.75 (s, 1 H); IR 1720, 1780 cm^{-1}
 5b	40079-14-9	PhOH	$PhOCH_2C(=O)CH_3$ (**10d**)	621-87-4	NMR 2.15 (s, 3 H), 4.4 (s, 2 h), 6.7–7.4 (m, 5 H); IR 1720 cm^{-1}
 5c	66202-65-1	Cl^- [c]	$CH_3CH(Cl)C(=O)CH_3$ (**11a**)	4091-39-8	NMR 1.5 (d, 3 H), 2.2 (s, 3 H), 415 (g, 1 H); IR 1710 cm^{-1}
		PhOH	$CH_3CH(OPh)C(=O)CH_3$ (**10e**)	6437-85-0	NMR 1.4 (d, 3 H), 2.0 (s, 3 H), 4.4 (g, 1 H), 6.7–7.3 (m, 5 H); IR 1720 cm^{-1}
		$(i\text{-Pr})_2NH$	$CH_3CH[N(i\text{-Pr})_2]C(=O)$-$CH_3$ (**10f**)	61628-54-4	NMR 0.9–1.2 (m, 15 H), 2.15 (s, 3 H), 2.6–3.3 (m, 2 H), 3.4 (g, 1 H); IR 1705 cm^{-1}
 5d	66202-66-2	Cl^- [c]	*i*-PrCH(Cl)C(=O)CH_3 (**11b**)	2907-70-2	NMR 0.9–1.2 (m, 15 H), 2.15 (s, 3 H), 2.6–3.3 (m, 2 H), 3.4 (g, 1 H); IR 1705 cm^{-1}
		PhOH	*i*-PrCH(OPh)C(=O)CH_3 (**10g**)	61628-56-6	NMR 0.9–1.2 (2 d, 6 H), 2.1 (s, 3 H), 1.9–2.4 (m, 1 H), 4.15 (d, 1 H), 6.7–7.5 (m, 5 H); IR 1715 cm^{-1}
		C_2H_5SH	*i*-PrCH(SC_2H_5)C(=O)CH_3 (**10h**)	61628-55-5	NMR 0.9–1.3 (m, 9 H), 2.15 (s, 3 H), 2.0 (br, 1 H), 2.45 (g, 2 H), 2.9 (d, 1 H); IR 1700 cm^{-1}
		PhSH	*i*-PrCH(SPh)C(=O)CH_3 (**10i**)	27872-69-1	NMR 1.1 (2d, 6 H), 2.0 (br, 1 H), 2.25 (s, 3 H), 3.3 (d, 1 H), 7.3 (br, 5 H); IR 1700 cm^{-1}
 5e	66202-67-3	Cl^- [c]	$C_{10}H_{21}CH(Cl)C(=O)CH_3$ (**11c**)	66374-43-4	NMR 0.7–2.0 (br, 21 H), 2.1 (s, 3 H), 3.95 (t, 1 H); IR 1708 cm^{-1}
		CH_3OH	$C_{10}H_{21}CH(OCH_3)C(=O)$-$CH_3$ (**12**)	61628-57-7	NMR 0.7–1.7 (br, 21 H), 2.15 (s, 3 H), 3.4 (s, 3 H), 3.55 (t, 1 H); IR 1720 cm^{-1}
 5f	66202-68-4	Cl^- [c]	$C_6H_{11}CH(Cl)C(=O)CH_3$ (**11d**)	18956-02-0	NMR 0.8–2.2 (br, 11 H), 2.3 (s, 3 H), 4.0 (d, 1 H); IR 1710 cm^{-1}
 5g	66374-44-5	CH_3OH	$CH_3OCH_2C(=O)CH_2$-*n*-$C_{10}H_{21}$ (**13a**)	61628-58-8	NMR 0.7–1.7 (br, 21 H), 2.3 (t, 2 H), 3.3 (s, 3 H), 3.65 (s, 2 H); IR 1720 cm^{-1}
		PhOH	$PhOCH_2C(=O)CH_2$-*n*-$C_{10}H_{21}$ (**13b**)	66374-45-6	NMR 0.7–1.9 (br, 21 H), 2.4 (t, 2 H), 4.35 (s, 2 H), 6.6–7.3 (m, 5 H); IR 1720 cm^{-1}
 5h	36808-13-6	CH_3OH	$PhCH_2CH_2C(=O)OCH_3$ (**14a**)	103-25-3	NMR 2.4–3.1 (m, 4 H), 3.6 (s, 3 H), 7.2 (s, 5 H); IR 1735 cm^{-1}
		C_2H_5SH	$PhCH_2CH_2C(=O)SC_2H_5$ (**14b**)	30911-16-1	NMR 1.2 (t, 3 H), 2.6–3.1 (m, 6 H), 7.2 (s, 5 H); IR 1685 cm^{-1}
		$PhNH_2$	$PhCH_2CH_2C(=O)NHPh$ (**14c**)	3271-81-6	NMR 2.3–3.05 (m, 4 H), 6.7–7.4 (m, 10 H), 8.0 (br, 1 H); IR 3410, 1680 cm^{-1}
 5i	66202-69-5	PhOH	*p*-$CH_3C_6H_4CH_2CH_2C(=O)$-OPh (**14d**)	61628-60-2	NMR 2.3 (s, 3 H), 2.65–3.1 (m, 4 H), 6.9–7.5 (m, 9 H); IR 1750 cm^{-1}
 5j	66374-46-7	C_2H_5SH	*p*-$CH_3C_6H_4CH_2C(=O)$-$CH_2SC_2H_5$ (**17a**)	61628-59-9	NMR 1.35 (t, 3 H), 2.4 (s, 3 H), 2.6 (s, 2 H), 3.35 (s, 2 H), 3.95 (s, 2 H), 7.2 (s, 4 H); IR 1700 cm^{-1}
		PhOH	*p*-$CH_3C_6H_4CH_2C(=O)$-CH_2OPh (**17b**)	66445-06-9	NMR 2.3 (s, 3 H), 3.75 (s, 2 H), 4.5 (s, 2 H), 6.6–7.3 (m, 9 H); IR 1720 cm^{-1}

[a] All compounds have correct molecular weights according to their mass spectra. [b] NMR was obtained in CCl_4 as solvent and IR was measured neat. [c] The product was obtained after hydrolytic workup.

products could be carried over into a cold trap at −78 °C. After 1 day, a colorless liquid was collected in the cold trap. Purification by reduced pressure (15 mm) bulb-to-bulb distillation twice at room temperature into another cold trap afforded a reasonably pure compound which was identified to be 1-*tert*-butylallene oxide on the basis of its spectroscopic data and chemical behavior. The ^1H NMR spectrum of **5a** displayed peaks at δ 1.0 (s, 9 H), 3.25 (s, 1 H), and 4.15 (AB, J = 4 Hz, 2 H), in agreement with the designated structure.[10] Its ^{13}C NMR spectrum, which exhibited peaks at 25.94 (CH_3, q, J_{CH} = 127.3 Hz), 31.89 (*t*-BuC, s), 68.01 (CH, multiplicity obscured), 70.32 (CH_2=, t, J_{CH} = 167.5 Hz), and 144.32 (-C=, s), is compatible with the structure. The mass spectrum of **5a**

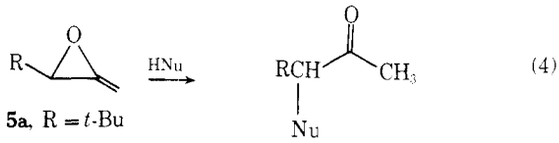


was informative. It showed a weak molecular ion at *m/e* 112 (3%) and fragments (*m/e*, relative intensity) indicative of the structure.

1-*tert*-Butylallene oxide (**5a**) was stable in dilute CCl_4, $CHCl_3$, and CH_2Cl_2 solutions at room temperature for about 1.5 h but polymerization was observed after 3 h. No sign of isomerization to 2-*tert*-butylcyclopropane could be detected spectroscopically when **5a** was heated in dilute solution or treated with boron trifluoride. In either case, polymer was obtained. The polymer showed strong carbonyl absorptions in the IR spectrum (~1710 cm^{-1}) and ^1H NMR signals around 2 ppm (except *tert*-butyl signal at 1 ppm). It, therefore, appeared not to have the polycyclopropanone structure similar to that which resulted from the polymerization of cyclopropanone.[18]

1-*tert*-Butylallene oxide undergoes reactions with protic nucleophiles (HNu) such as water, thiol, and acid to give the addition products **10a–c** (Table II) in good yields. In all cases, the reactions were regiospecific in that only products with the nucleophile attached to the substituted carbon were observed.

It should be noted that this is the first time that reaction of an isolated allene oxide has been demonstrated. Previously isolated allene oxides, such as 1,1-di-*tert*-butyl-[10] or 1,1,3-tri-*tert*-butylallene oxide,[11] either underwent isomerization[10] or resisted reactions[11] altogether. The steric factor, which contributed to the lack of reactivity, is precisely the reason which led to their isolation. The presence of only one *tert*-butyl group in **5a**, it seems, renders the molecule sufficiently stable to be isolated, but does not mask its reactivity completely. The addition products, especially **10c**, bear resem-



(4)

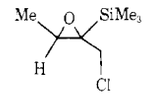
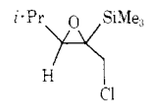
5a, R = *t*-Bu

10a, R = *t*-Bu, Nu = OH
b, R = *t*-Bu, Nu = SEt
c, R = *t*-Bu, Nu = CCl_3CO_2

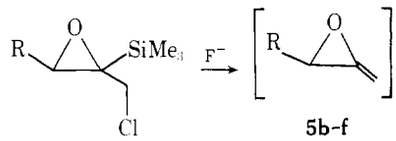
blance to those obtained from the peracid oxidation of allenes, where the intermediacy of allene oxides have been postulated.[15] Our observation then lends strong support to this postulation.

It is also appropriate at this point to comment briefly on the mechanisms of the addition reaction (eq 4). A S_N2 displacement of the epoxide by the nucleophile at C-1 can account readily for the product as well as the regiochemistry. The alternative possibility, involving first opening of the allene oxide to an oxyallyl species, followed by capture of the nucleophile, is deemed to be less likely in view of the regiochemistry of the product. We shall return to the mechanistic question later.

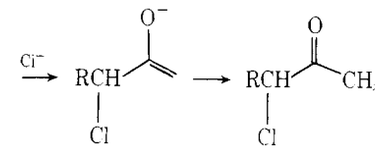
Table III. Reaction Conditions and Yields of 10

epoxide precursor	reaction conditions 25 °C, 3 days	10 R	10 Nu	% isolated yield
 9c	CsF/diglyme	Me	OPh	58
	CsF/Me_2SO	Me	OPh	61
	Et_4NF/CH_3CN	Me	OPh	75
	CsF/CH_3CN	Me	OPh	78
 9d	Et_4NF/glyme	*i*-Pr	OPh	70
	Et_4NF/glyme	*i*-Pr	SEt	74
	KF/benzene/18-crown-6 (0.5 equiv)	*i*-Pr	SEt	51

1- and 3-Monosubstituted Allene Oxides: Reactions with Nucleophiles. The isolation and characterization of 1-*tert*-butylallene oxide demonstrated convincingly the efficacy of the fluoride ion-promoted β elimination of the epoxide **9** as a method of generating allene oxide. A number of epoxides (**9b–f**), where the alkyl group R was sterically less bulky than the *tert*-butyl group, were synthesized. The epoxides were treated with a variety of alkali and tetraalkylammonium fluorides in several polar aprotic solvents. While the cleavage of the trimethylsilyl–carbon bond occurred readily, in no case were the attempts to isolate the allene oxides successful. Instead, 3-chloro-2-ketones **11a–d** were ob-



9b–f **5b–f**



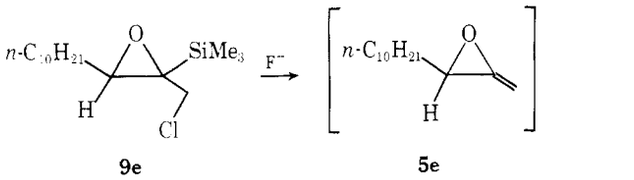
11a–d

tained in moderate to good yields (Table II). These results suggest that the desired β elimination of trimethylsilyl and chloro functions have occurred, giving the expected allene oxides.[19] Subsequent nucleophilic attack by the chloride ion on the generated allene oxides could then account for the formation of **11**. The existence of the allene oxides was also demonstrated by trapping with other nucleophiles. Thus, when the epoxide **9** (**b–f**) was stirred at 25 °C with a slight excess of cesium fluoride in acetonitrile in the presence of a threefold excess of a protic nucleophile (HNu), the sole product was the 3-substituted-2-ketone **10** (**d–i**) (Table II).

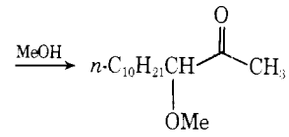
A few brief comments should be made concerning the reagents and solvents. The yields of the products did not vary greatly from one solvent to another (Table III). In general, the reaction with tetraethylammonium fluoride in dimethyl sulfoxide proceeded at a faster rate. However, cesium fluoride in acetonitrile was more convenient in experimental operation. Potassium fluoride in benzene with 18-crown-6 was also effective.

The reactions of the nucleophiles (HNu) with the intermediate allene oxides are again regiospecific. The regiospecificity was demonstrated by comparing the reactions of the two isomeric epoxides **9e** and **9g**. Under identical reaction

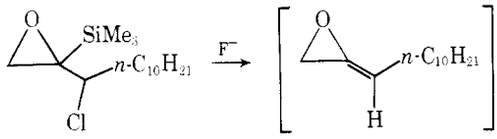
conditions with methanol as the nucleophile, **9e** gave only the 3-methoxy-2-ketone **12**, whereas **9g** afforded the 1-methoxy-2-ketone **13a** exclusively. The regiospecific nature of



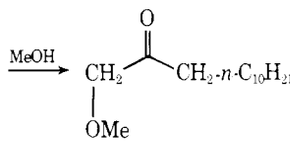
9e **5e**



12



9g **5g**

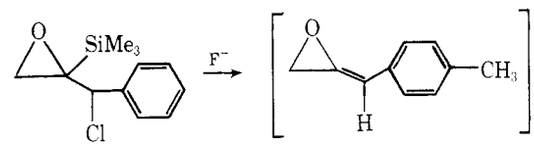


13a

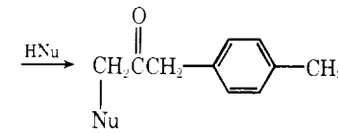
the reaction argues convincingly for the nucleophilic opening of the epoxide structure in the isomeric allene oxides **5e** and **5g** as the mechanism. Conversely, it also rules out any common species, either the cyclopropanone or the oxyallyl, as the necessary intermediate for these reactions.

A dramatic change in the course of the reaction occurred when the substituent of the epoxide was an aryl group (**9h,i**, R = Aryl). The epoxides **9h** or **9i**, on treatment with cesium fluoride in the presence of a protic nucleophile under identical conditions, yielded quantitatively a product identified to be dihydrocinnamate **14** (**a–d**, Table II). A reasonable pathway for the formation of **14** is through the intermediary of the allene oxide **5** (**h,i**), then to the cyclopropanone **15** (R = Ph or p-$CH_3C_6H_4$–), followed by a Favorski type reaction of the nucleophile with **15**[20] (Scheme II). The reaction of cyclopropanone with nucleophile to form the hemiketal of structure **16** (R = Ph or p-$CH_3C_6H_4$–) is well known.[9] The hemiketal can open to give the observed dihydrocinnamate.[9] Indeed, the formation of dihydrocinnamate from phenylcyclopropanone and a nucleophile has been reported previously.[21]

On the other hand, an aryl substitution at C-3 of the epoxide **9j** did not lead to the formation of dihydrocinnamate. Reaction of the epoxide **9j** with the cesium fluoride and a nucleophile yielded exclusively the 1-substituted-2-ketone **17** (**a,b**, Table II).



9j **5j**



17a, Nu = SEt
b, Nu = OPh

It appears, therefore, that the nature of the substituent at C-1 of allene oxide has a decisive effect on its fate. When the substituent was either an alkyl group (as in **5c–f**) or a hydrogen (as in **5b,g,j**), the allene oxide suffered nucleophilic attack. When the substituent is sufficiently bulky, as in 1-*tert*-butylallene oxide (**5a**), the nucleophilic attack was slow enough so that its isolation was possible. However, when the substituent at C-1 was an aryl group (as in **5h** and **5i**), the allene oxide isomerized first to cyclopropanone before the nucleophilic attack.

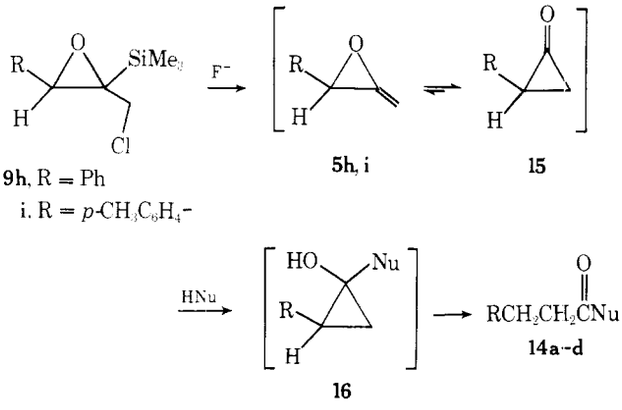
Mechanism of the Allene Oxide–Cyclopropanone Isomerization Process. We must digress for the moment to fill in the background on the allene oxide–cyclopropanone isomerization problem. Several theoretical studies[3–8] at various levels of approximation have been reported on the valence tautomers of C_3H_4O. Of primary concern in most of the calculations was which of the three tautomers, cyclopropanone (**2**), allene oxide (**1**), or oxyallyl (**3**), is the most stable. The computed results differ widely, but they do generally agree (except that of the extended Hückel method[3]) that oxyallyl (**3**) is the highest energy form, and cyclopropanone (**2**), the lowest energy species.[4–8] Various spectroscopic studies[22–24] leave no doubt that cyclopropanone has the closed structure indicated by **2**. The isolation of 1,1-di-*tert*-butyl-,[10] 1,1,3-tri-*tert*-bytyl-,[11] and from the present work, 1-*tert*-butylallene oxides suggests that **1** is also a viable species.

Experimentally, it is known that 1,3-di-*tert*-butylallene oxide isomerizes to the corresponding cyclopropanone upon heating, thus establishing the cyclopropanone form to be more stable than allene oxide for that particular case.[10] On the other hand, 1,1,3-tri-*tert*-butylallene oxide[11] has been found not to isomerize to the cyclopropanone even on prolonged heating. In our case, 1-*tert*-butylallene oxide suffers destruction without evidence of having been transformed into the corresponding cyclopropanone. The cause for the lack of isomerization could have been either kinetic or thermodynamic in nature.

There is the further question concerning the mechanism of the allene oxide–cyclopropanone isomerization process. The crux of the question is whether oxyallyl (**3**) is involved as an intermediate in the isomerization or not. The latest CNDO/2 calculation[8] indicated a mechanism through the intermediacy of oxyallyl (Scheme III, path a) to be energetically unlikely. Instead, a novel pathway involving bending of the molecule has been suggested (Scheme III, path b). Prior experimental evidence[10] does not allow a distinction to be made between these two possibilities.

Our observation that the presence of an aryl group at C-1 of allene oxide has a decisive effect on its rate of isomerization to cyclopropanone does not appear to be compatible with a mechanism based solely on the bending of the molecule as

Scheme II

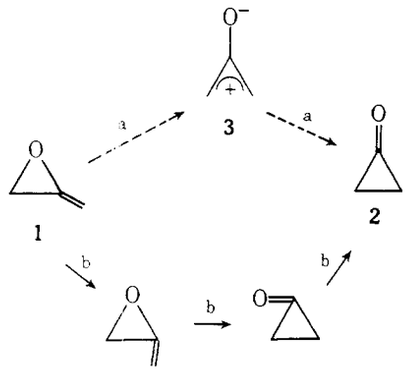


9h, R = Ph
i, R = p-$CH_3C_6H_4$-

5h, i **15**

16 **14a–d**

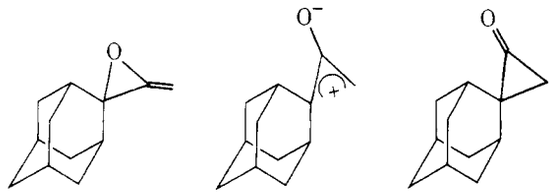
Scheme III



outlined by path b, Scheme III. A reasonable interpretation of the substituent effect is that, in the allene oxide–cyclopropanone isomerization process, the rate-determining step must involve rupture of the C-1 oxygen bond with considerable charge developing at C-1. An oxyallyl intermediate, as outlined by path a, Scheme III, would be in agreement with such a substituent effect.

One may argue that the presence of a phenyl group could often modify substantially the mechanism of a reaction and one should not generalize this to include the alkyl system.[25] What is required is the positive observation of an alkyl-substituted allene oxide isomerizing to the cyclopropanone under identical conditions. We proceeded to do so.

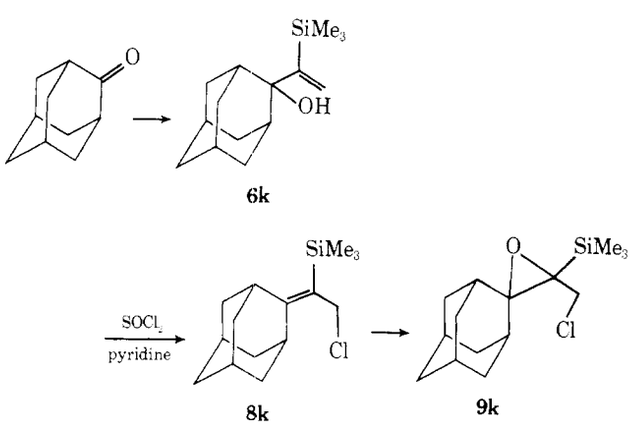
3′-Methylenespiro[adamantane-2,2′-oxirane] (5k). We feel that the allene oxide **5k** can serve as an ideal candidate to test the mechanism. The nucleophilic attack on the allene oxide should be suppressed and the formation of the oxyallyl intermediate 18 should be facilitated. If the oxyallyl intermediate is not involved in the isomerization process, **5k** should be isolable under our reaction conditions in view of the fact that **5a** could be isolated. If, on the other hand, the oxyallyl intermediate 18 is involved, the products should be the cyclopropanone **19** or its derivatives. Another advantage of the admantyl system is the knowledge that side reactions due to carbocation rearrangement would be minimized.[26]



5k 18 19

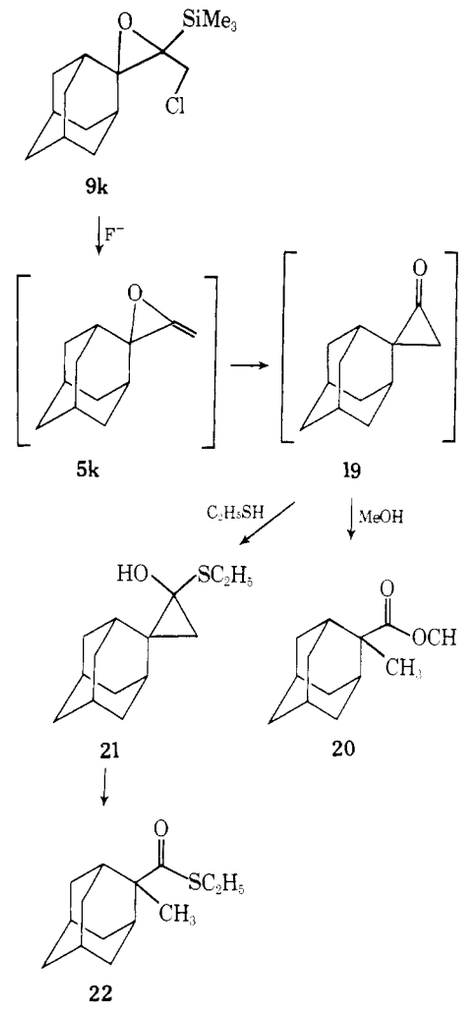
The precursor epoxide **9k** was prepared from adamantanone in several steps according to Scheme IV. In the conversion of the alcohol **6k** to the chloride **8k,** as well as in the epoxidation step (**8k** → **9k**), acidic conditions had to be avoided. When the epoxide **9k** was treated with fluoride ion in the presence of methanol, the methyl ester **20** was obtained as the exclusive product in quantitative yield. A reasonable interpretation for the formation of the ester **20** is that the allene oxide **5k,** once generated, undergoes a fast isomerization to the cyclopropanone **19,** which on reaction with methanol gave the ester **20** (Scheme V).

Scheme IV



6k 8k 9k

Scheme V



9k 5k 19 21 20 22

Definite proof of the participation of cyclopropanone was obtained when the reaction of **9k** with fluoride ion was carried out in the presence of ethanethiol. The hemithioketal **21** was isolated in reasonable purity in 65% yield. The structure of **21** was evident from its ^1H NMR spectrum, which showed the AB quartet at δ 0.75 (J = 5 Hz) indicative of the cyclopropane structure, and its IR spectrum with strong OH absorption at 3300 cm^{-1}. On standing at room temperature, **21** slowly rearranged to the thiol ester **22.** The rearrangement process was accelerated by heating above 50 °C.

Conclusion

It is clear that a consistent picture has emerged. In the conversion of allene oxide (**1**) to cyclopropanone (**2**), a rate-determing step leading to the formation of oxyallyl (**3**) is most likely involved (path a, Scheme III). For allene oxide itself,[10] or monoalkyl-substituted ones, the kinetic barrier to the isomerization is relatively high; the allene oxides suffer nucleophilic attack or polymerization more readily. If the substituent is bulky, so that the bimolecular nucleophilic substitution reaction is slowed down, as in the case of 1-*tert*-butyl

or 1,3-di-*tert*-butyl, the allene oxides can be isolated. For aryl-substituted or disubstituted allene oxides, the rate of isomerization to cyclopropanone is faster than the attack of nucleophile, and they undergo reactions characteristic of the cyclopropanone. Finally, 1,1,3-tri-*tert*-butylallene oxide[11] most likely owes its stability to a thermodynamic factor as originally suggested.[11,27]

These results have important synthetic consequences. We have already observed that aryl-substituted allene oxides undergo cycloaddition reactions with 4π systems,[1,2a] reactions typical of cyclopropanones[9] and oxyallyls,[13] whereas monoalkyl substituted allene oxides do not.[1] Other reactions of allene oxides, as they unfold in the future, must take these results into consideration.

Experimental Section

Common chemicals were obtained from commercial sources and were purified as necessary. Melting points were obtained on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 257 or Unicam SP1000 grating infrared spectrometers. Spectra were calibrated with the 1601-cm^{-1} band of a polystyrene film. Nuclear magnetic resonance spectra were recorded on Varian Associates T-60 or Brucker WH90 spectrometer. Mass spectra were recorded either by direct insertion on an AEI-MS-902 mass spectrometer or by GC–MS with an LKB-9000 spectrometer at 70 eV. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Gas chromatographic (GC) analyses were performed on an F & M Model 5751-A Research Chromatograph. Two 6 ft × ⅛ in. stainless steel columns were used: 10% SE-30 Ultraphase on Chromosorb W A/W-DMCS, or 10% Apiezon-L on Chromosorb W A/W-DMCS. Preparative thin-layer and column chromatography were done on silica gel.

1-Substituted-2-(trimethylsilyl)-2-propen-1-ols (6). The title alcohols were prepared from the reaction of α-(trimethylsilyl)vinyl carbanion with appropriate carbonyl compounds as described.[17] Compounds **6a** (R = *t*-Bu), **6d** (R = *i*-Pr), **6e** (R = *n*-$C_{10}H_{21}$), **6f** (R = c-C_6H_{11}), and **6h** (R = Ph) have been previously reported.[17] The following new compounds have been prepared. 2-(Trimethylsilyl)-2-propen-1-ol (**6b**): bp 74–75 °C (30 mm); 65% yield; ^1H NMR (CCl_4) δ 0.0 (s, 9 H), 3.95 (s, 1 H), 4.1 (m, 2 H), 5.5 (AB, 2 H). Anal. ($C_6H_{14}OSi$) C, H. 3-(Trimethylsilyl)-3-buten-2-ol (**6c**): bp 72–74 °C (28 mm); 81% yield; (CCl_4) δ 0.1 (s, 9 H), 1.15 (d, 3 H), 3.0 (s, 1 H), 4.3 (q, 1 H), 5.45 (AB, 2 H). Anal. ($C_7H_{16}OSi$) C, H. 1-*p*-Tolyl-2-(trimethylsilyl)-2-propen-1-ol (**6i**): bp 86–88 °C (0.3 mm); 78% yield; ^1H NMR (CCl_4) δ 0.2 (s, 9 H), 2.5 (s, 3 H), 3.2 (s, 1 H), 5.4 (m, 1 H), 5.8 (AB, 2 H), 7.25 (s, 4 H). Purity and molecular weight were established by GC–MS.

Reaction of 1-Substituted-2-(trimethylsilyl)-2-propen-1-ols (6) with Thionyl Chloride to Give 7 and/or 8. The reaction of **6** with thionyl chloride to give **7** and/or **8** has been described.[17] Compounds **7a** + **8a** (R = *t*-Bu), **8d** (R = *i*-Pr), **8e** (R = *n*-$C_{10}H_{21}$), **8f** (R = c-C_6H_{11}), and **8h** (R = Ph) have been previously reported.[17] The following new compounds have been prepared. 3-Chloro-2-(trimethylsilyl)-1-propene (**7b**): bp 53–55 °C (35 mm); 80% yield; ^1H NMR (CCl_4) δ 0.15 (s, 9 H), 4.05 (m, 2 H), 5.5 (AB, 2 H). Anal. ($C_6H_{13}ClSi$) C, H. 1-Chloro-2-(trimethylsilyl)-2-butene (**8c**): bp 115–116 °C (150 mm); 83% yield; ^1H NMR (CCl_4) δ 0.3 (s, 9 H), 1.85 (d, 3 H), 4.05 (s, 2 H), 6.0 (q, 1 H). Anal. ($C_7H_{15}ClSi$) C, H. 3-Chloro-1-*p*-tolyl-2-(trimethylsilyl)-1-propene (**8i**): bp 80–81 °C (0.25 mm); 77% yield; ^1H NMR (CCl_4) δ 0.2 (s, 9 H), 2.2 (s, 3 H), 4.2 (s, 2 H), 6.7 (s, 1 H), 6.8–7.2 (m, 4 H). Anal. ($C_{13}H_{19}ClSi$) C, H. 3-Chloro-3-*p*-tolyl-2-(trimethylsilyl)-1-propene (**7i**): rearranged to **8i** on attempted distillation; ^1H NMR (CCl_4) δ 0.1 (s, 9 H), 2.4 (s, 3 H), 5.7 (m, 2 H), 6.2 (m, 1 H), 7.1 (s, 4 H).

1-Substituted-3-chloro-2-(trimethylsilyl)propylene 1,2-Oxide (9). The title epoxides **9a–f,h,i** were conveniently obtained from the epoxidation of 1-substituted-3-chloro-2-(trimethylsilyl)-1-propenes **8a–f,h,i** with an excess (10–20%) of either peracetic acid or *m*-chloroperbenzoic acid (*m*-CPBA) in methylene chloride. Following is a typical experimental procedure.

To a solution of 10 mmol of olefin **8** in 15 mL of CH_2Cl_2 was added slowly a mixture of 2.2 g of 40% peracetic acid in acetic acid and 0.17 g of sodium acetate over a period of 15–30 min. The resulting mixture was heated under reflux at 45 °C for 1 day. The mixture was washed twice with 15 mL of water, and the acidic mixture was neutralized with 5% aqueous Na_2CO_3 solution. After drying with anhydrous $MgSO_4$, the reaction mixture was reduced in volume in vacuo and was fractionally distilled at reduced pressure to give the desired epoxide **9** in 80% yield (Table I).

Comparable yield of the epoxide was also obtained with *m*-CPBA (10% excess) as the epoxidating agent. The procedure was essentially the same as above, except that the reaction was carried out at room temperature and the excess *m*-CPBA after the reaction was destroyed by washing the reaction mixture with 5% aqueous Na_2SO_3 solution.

Table I summarizes the physical data of the epoxides obtained as described above.

3-Chloro-3-substituted-2-(trimethylsityl)propylene 1,2-Oxides (9g,j). The chloro epoxides **9g** and **9j** were synthesized as follows. To a solution of 20 mmol of alcohol **6g** or **6j** in 30 mL of CH_2Cl_2 at room temperature was added in small portions 22 mmol of *m*-CPBA. The mixture was stirred for 2–4 h. The *m*-chlorobenzoic acid was filtered off, and the filtrate was washed with 5% aqueous Na_2SO_3 solution until the excess of *m*-CPBA was destroyed. The acidic mixture was neutralized with 5% aqueous Na_2CO_3 solution and dried with anhydrous $MgSO_4$. Fractional distillation of the dried reaction mixture at reduced pressure gave the epoxy alcohol in good yield.

To a well-stirred solution of 10 mmol of epoxy alcohol in 5 mL of dried pyridine and 5 mL of CCl_4 at room temperature was added dropwise a solution of 1.5 g of $SOCl_2$ in 4 mL of CCl_4. The mixture was stirred overnight. Petroleum ether was added to the reaction mixture, and the precipitated pyridinium chloride was filtered off. Removal of the solvent from the mixture afforded a viscous oil which was found to be the desired chloro epoxide **9g** or **9j** by ^1H NMR spectroscopy. Attempted distillation of **9g** or **9j** at low pressure led to its decomposition. The physical data of **9g** and **9j** are summarized in Table I.

1-*tert*-Butylallene Oxide. A. A mixture of 0.44 g (2 mmol) of the epoxide **9a** and 0.35 g of CsF in 6 mL of acetonitrile was stirred at room temperature. After 1 day, it was observed by ^1H NMR spectroscopy that the precursor epoxide was consumed to give a mixture of polymeric compounds. The mixture exhibited IR carbonyl absorptions at ~1710 cm^{-1} and ^1H NMR signals at 1.1 ppm (*tert*-butyl) and multiplets around 2.1 ppm.

B. The same reaction (0.44 g of **9a**/0.35 g of CsF) was conducted in diglyme (6 mL) with a slow stream of dried nitrogen bubbling into the reaction mixture so that any volatile products would be carried over into a cold trap at −78 °C. After 1 day, a colorless liquid was collected in the cold trap. Purification by reduced pressure bulb-to-bulb distillation (15 mm) twice at room temperature into another cold trap afforded a reasonably pure compound which was identified to be 1-*tert*-butylallene oxide in over 55% yield. It showed the following spectroscopic properties: MS *m/e* (intensity) 112 (3); ^1H NMR (CCl_4) δ 1.0 (s, 1 H), 3.25 (s, 1 H), 4.15 (AB, J = 4 Hz, 2 H); IR (CCl_4) 2960, 1815, 1780, 1220, cm^{-1}; ^{13}C NMR ($CDCl_3$) 25.94, 31.89, 68.01, 70.32, 144.32 ppm.

Reactions of 1-*tert*-Butylallene Oxide. 1-*tert*-Butylallene oxide (**5a**) was found to be stable in dilute CCl_4, $CHCl_3$, and CH_2Cl_2 solutions at room temperature for about 1.5 h, but polymerization was observed after 3 h. No sign of isomerization to *tert*-butylcyclopropanone could be detected spectroscopically either on heating or on treatment with BF_3. In either case, polymers were obtained. The polymers showed nonstrained IR carbonyl absorptions at ~1710 cm^{-1} and ^1H NMR signals at 1.1 ppm (*tert*-butyl) and around 2.1 (m) ppm.

1-*tert*-Butylallene oxide (**5a**) underwent rapid addition reaction with protic nucleophiles such as water, thiol, or acetic acid. Thus, when an excess of nucleophile was added to a solution of 1-*tert*-butylallene oxide in CCl_4, addition product was detected immediately by ^1H NMR spectroscopy; the isolated yield of the addition product was generally good (70%). Their physical properties are summarized in Table II.

Reaction of Epoxide 9 (b–j) with Fluoride Ion. The epoxide **9** (**b–j**) was treated with fluoride ion in polar aprotic solvents. Following is a description on our studies.

The epoxide **9** (**b–j**, 1 mmol) was stirred with CsF (0.18 g) in acetonitrile (4 mL) at room temperature for 2–3 days. Cleavage of the trimethylsilyl–carbon bond in the epoxide was observed by ^1H NMR spectroscopy. With the higher boiling epoxide, ^1H NMR analysis of the crude reaction mixture showed complete consumption of the epoxide and the formation of 3-chloro-2-ketone **11**. The chloro ketones from **9e,f** were purified by TLC chromatography (silica gel/CCl_4). 3-Chloro-4-methyl-2-pentanone from **9d** was distilled from the solvent-free reaction mixture at low pressure. The low-boiling 3-chloro-2-butanone from the epoxide **9c** was isolated by the following procedure.

The reaction was conducted in a higher boiling polar aprotic solvent such as triglyme for 3 days. Water (3 drops) was added to the well-

stirred reaction mixture, followed by drying with anhydrous $MgSO_4$. The volatile products in the mixture were distilled at reduced pressure (11 mm) at room temperature into a cold trap at −78 °C. The colorless liquid collected was purified by bulb-to-bulb distillation into another cold trap, and was found to be 3-chloro-2-butanone.

Reactions of Allene Oxides with Protic Nucleophiles. Allene oxides were generated from the epoxide precursors in the presence of threefold excess of protic nucleophiles. The products of the reactions were isolated by silica gel TLC chromatography. Following is an illustrative procedure.

The epoxide (1 mmol of **9b–j**) was stirred with s slight excess of CsF (0.18 g) in acetonitrile in the presence of a protic nucleophile (3 mmol of ROH, RSH, or RR'NH) at room temperature. After 2 days, the reaction mixture was filtered to remove the cesium salt, and the filtrate was rid of solvent. ^1H NMR analysis of the crude mixture revealed the formation of the addition product. The product was conveniently purified by TLC chromatography in 60–70% isolated yield. Their physical properties are summarized in Table II.

3'-(Chloromethyl)-3'-(trimethylsilyl)spiro[adamantane-2,-2'-oxirane]. The title epoxide **9k** was obtained from 2-[α-(trimethylsilyl)vinyl]-2-adamantanol (**6k**) by the following transformations.

The alcohol **6k** was first obtained from the reaction of α-lithiated vinyltrimethylsilane with adamantanone at −78 °C in 74% yield according to the published procedure.[17] The compound **6k** was recrystallized from acetone–water to give colorless solid: mp 84–85 °C; IR (CCl_4) 3450 cm^{-1}; ^1H NMR (CCl_4) δ 0.15 (s, 9 H), 1.3–2.3 (br, 14 H), 2.4 (br, 1 H), 5.7 (AB, 2 H).

Treatment of **6k** with thionyl chloride in ether led to its complete disappearance within 1 h. ^1H NMR analysis of the reaction mixture showed the formation of one major compound tentatively assigned to be 2-(β-chloroethylidene)adamantane: ^1H NMR (CCl_4) δ 1.5–2.1 (br, 12 H), 2.3 (br, 1 H), 2.8 (br, 1 H), 3.9 (d, 2 H), 5.2 (t, 1 H). The formation of this compound was thought to be due to acid-promoted desilylation. The reaction was, therefore, carried out in the presence of a base such as pyridine as follows. To a solution of 10 mmol of the alcohol **6k** and 2 mL of pyridine in 15 mL of ether was added dropwise a solution of 1.5 g (12.6 mmol) of thionyl chloride in 3 mL of ether. The mixture was stirred at room temperature for 3 h. The reaction mixture was washed with water, dried ($MgSO_4$), and concentrated to give the desired chloride **8k** in satisfactory purity as a viscous liquid. Its ^1H NMR (CCl_4) showed: 0.1 (s, 9 H), 1.6–2.2 (br, 12 H), 2.6 (br, 1 H), 3.2 (br, 1 H), 4.0 (s, 2 H).

The crude chloride **8k** was subjected to epoxidation with *m*-CPBA as before. It was observed that the reaction was highly exothermic and **8k** was virtually consumed in 1 h. On workup there was obtained a compound assigned to be 2-adamantyl chloromethyl ketone by spectroscopy. Its IR showed absorptions at 1710 cm^{-1}; its ^1H NMR ($CDCl_3$) showed δ 1.3–2.6 (br, 14 H), 2.85 (br, 1 H), 4.2 (s, 2 H).

The formation of the ketone was thought to be due to the acidic conditions employed during epoxidation. Accordingly, the reaction was conducted in the presence of an excess of sodium bicarbonate.

A quantity of 5.5 mmol of *m*-CPBA was added in small portions to a well-stirred mixture of 5 mmol of **8k** and 1 g of Na_2CO_3 in 20 mL of CH_2Cl_2 at room temperature. After the addition, the mixture was kept well stirred for another 3 h. Excess Na_2CO_3 and sodium *m*-chlorobenzoate were filtered off. The filtrate was then worked up as before. The crude epoxide **9k** was purified by silica gel chromatography (CCl_4–CH_2Cl_2, 15:1), and recrystallized from methanol–water to give colorless solid: mp 43–46 °C; 70% yield; ^1H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 1.4–2.2 (br, 14 H), 3.55 (AB, 2 H). Anal. ($C_{15}H_{25}ClOSi$) C, H.

Generation of 3'-Methylenespiro[adamantane-2,2'-oxirane]. The epoxide **9k** was treated with CsF in acetonitrile at room temperature. It was found that <50% of **9k** was consumed in 1 day. The more reactive Et_4NF was therefore used in place of CsF.

Treatment of **9k** (1 mmol) with Et_4NF (1.1 mmol) in acetonitrile (4 mL) and methanol (3 mmol) at room temperature for 1 day led to complete consumption of **9k.** The product was isolated from the reaction mixture by silica gel TLC (ethyl acetate–hexane, 1:19) and was identified to be methyl 2-(2-methyladamantane)carboxylate (**20;** 91%). Its structure is consistent with spectroscopic data: IR ($CHCl_3$) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (s, 3 H), 1.3–2.3 (br, 14 H), 3.6 (s, 3 H); MS *m/e* 208. When the above reaction was quenched with water ~0.5 h after the reaction, about 60% of the starting epoxide **9k** was recovered; the ester **20** was obtained in over 90% yield based on the consumed epoxide **9k.**

When the epoxide **9k** (1 mmol) was stirred with Et_4NF (1.1 mmol) in acetonitrile in the presence of ethanethiol (3 mmol) at room temperature for 1 day, the product isolated from the reaction mixture (silica gel TLC, hexane–ethyl acetate, 17:3) was the cyclopropanone hemithioketal **21** (mp 41–48 °C). The structure of the hemithioketal **21** was established by spectroscopic means. Its mass spectrum showed a weak molecular ion at *m/e* 238. Its ^1H NMR (CCl_4) showed δ 0.75 (AB, 2 H), indicative of the cyclopropane structure, 1.3 (t, 3 H), 1.3–2.2 (br, 14 H), 2.75 (q, 2 H), 3.05 (br, 1 H); its IR showed a strong hydroxy absorption at 3300 cm^{-1}.

The hemithioketal was thermodynamically unstable; it gradually decomposed at room temperature to the corresponding thioester **22** (mp 87–89 °C, recrystallized from methanol–water); the isomerization was complete in ~10 days. The isomerization was accelerated by heating at a temperature above 50 °C or by treating with a catalytic amount of Et_4NF in acetonitrile. The structure of the thio ester **22** was assigned on the basis of its spectroscopic data: IR 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 3 H), 1.3 (t, 3 H), 1.5–2.3 (br, 14 H), 2.65 (q, 2 H); MS *m/e* 238.

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