Unsaturated Aluminum Alkyls. Stabilization and Reaction with Epoxides

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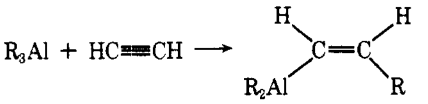
Reactions of various unsaturated aluminum alkyls with ethylene oxide and with propylene oxide were studied. When reaction with ethylene oxide is conducted in the presence of strongly basic ethers, the product is largely (85–95%) the expected cis alcohol. In the absence of a strong base, a relatively high percentage (30–37%) of an isomeric, substituted cyclopropanemethanol is obtained. Reaction of an unsaturated aluminum alkyl with propylene oxide affords predominantly a product resulting from alkenylation at the less substituted carbon atom. In addition to affecting the stereochemistry of reaction products, ethers in equimolar amounts also stabilize the unsaturated aluminum alkyls. If less than 1 molar equiv of ether is used, however, the decomposition of the unsaturated aluminum alkyl is accelerated.

Applications of aluminum alkyls to organic synthesis have received relatively little attention compared to investigations into their use as Ziegler–Natta catalysts.[1] Recently, however, there have been several reports on the use of unsaturated organoaluminum compounds in organic synthesis.[2–10] Because $R_2AlCH{=}CHR$ compounds are easily prepared by the method of Wilke and Müller[11] according to eq 1 and 2, these compounds are especially promising intermediates for the preparation of a variety of unsaturated organic compounds.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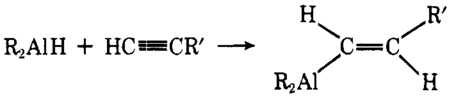
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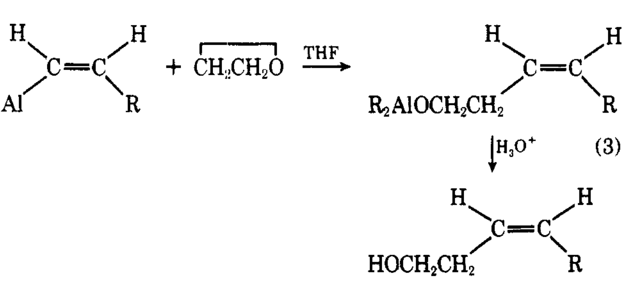
Two groups have recently reported the reaction of lithium *trans*-alkenyltrialkylaluminates with epoxides to give trans alkenols.[9,10] The organometallic substrates in these studies were prepared by reaction of lithium alkyls with products from reaction 2.

This paper reports the direct reaction of $R_2AlCH{=}CHR$ from eq 1 with epoxides to produce, after hydrolysis, predominantly cis-unsaturated alcohols. The effect of ethers on the stability of unsaturated organoaluminum compounds and on the course of reaction of $R_2AlCH{=}CHR$ with epoxides is also reported.

Results and Discussion

Unsaturated aluminum alkyls used in this study were prepared by reaction of trialkylaluminum compounds with acetylene as in eq 1. The resultant *cis*-dialkylalkenylaluminum compounds were used to synthesize predominantly cis alkenols via reaction with epoxides in the presence of tetrahydrofuran (THF), illustrated for the general case in eq 3 with ethylene oxide. The alkenylaluminum grouping reacts preferentially, a finding consistent with that of other investigations of unsaturated aluminum alkyls,[3,12] and the stereochemistry about the double bond is largely retained during reaction. Retention of the cis stereochemistry in the alkenyl grouping was demonstrated by spectroscopic data ($J_{ab} \simeq 6$ Hz for $CH_a{=}CH_b$ protons). In the case of *cis*-3-hexen-1-ol, identification was also confirmed by comparison with an authentic standard.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When reaction of $R_2AlCH{=}CHR$ with ethylene oxide is conducted in hydrocarbon or weakly basic solvents, a product is obtained that contains, in addition to the expected cis alkenol, a substantial amount of an isomeric, substituted cyclopropane alcohol. For the reaction of $Et_2AlCH{=}CHEt$ with ethylene oxide, spectroscopic data indicate that the isomeric by-product is 2-ethylcyclopropanemethanol, eq 4. The stereochemistry of the 2-ethylcyclopropanemethanol was not determined. Analysis by GC, however, showed the product to be one stereoisomer, indicating a stereospecific reaction for its formation.

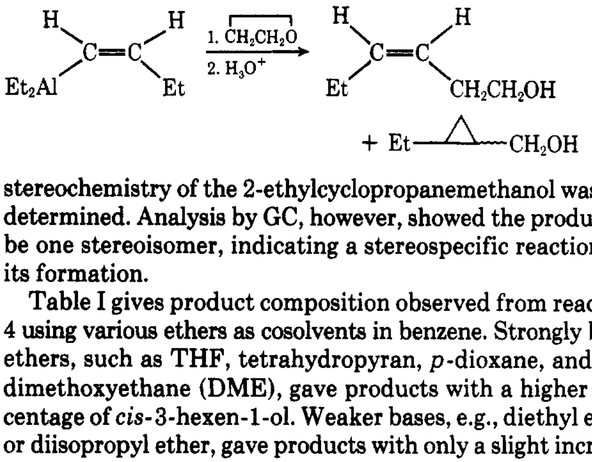
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Table I gives product composition observed from reaction 4 using various ethers as cosolvents in benzene. Strongly basic ethers, such as THF, tetrahydropyran, *p*-dioxane, and 1,2-dimethoxyethane (DME), gave products with a higher percentage of *cis*-3-hexen-1-ol. Weaker bases, e.g., diethyl ether or diisopropyl ether, gave products with only a slight increase in *cis*-3-hexen-1-ol content over that observed in a control run in which no base was used.

Triethylamine, pyridine, and 2,6-lutidine were also used in the study, but C_6 alcohols were not observed in the reaction products after hydrolysis. This indicates that the strongly basic amines form tight donor–acceptor complexes with the unsaturated aluminum alkyl that prevent reaction with ethylene oxide.

In the course of this study, it was discovered that $R_2AlCH{=}CHR$ compounds are not stable to long-term storage at ambient temperature. Instability is evidenced by an increase in viscosity and by a gradual decrease in 1-alkene content in the hydrolysis products. Decomposition is not accompanied by pressure buildup in the storage container and the aluminum content does not change.

The nature of the decomposition reaction is thought to be similar to the reaction proposed by Wilke and Schneider,[13] i.e., the $R_2AlCH{=}CHR$ is condensing with itself to form 1,1-dialuminum species, shown in eq 5 for R = Et. Wilke[14] states, however, that temperatures above 60 °C, and usually 80–90 °C, are necessary to effect this reaction. Our data indicate that this reaction is occurring to a significant extent, even at ambient temperatures. The formation of dialuminum

Table I. Effect of Ethers on Composition of Products from the Reaction of $Et_2AlCH=CHEt$ with Ethylene Oxide [a]

Ether	Product composition[b]	
	cis-3-Hexen-1-ol	ECPM[c]
None	68	32
Diethyl ether	77	23
Diisopropyl ether	77	23
Tetrahydrofuran	95	5
Tetrahydropyran	95	5
Dihydropyran	77	23
p-Dioxane	94	6
1,2-Dimethoxyethane	94	6
Furan	69	31

[a] Reaction conducted at ca. 0 °C in benzene using a 50% molar excess (based on $Et_2AlCH=CHEt$) of ether as cosolvent. [b] Normalized area percent by GC. Duplicate experiments in some cases showed composition values to be reliable to ±2 percentage points. [c] ECPM = 2-ethylcyclopropanemethanol.

species is consistent with the observed data: no change in aluminum content, increase in viscosity (expected for dialuminum species), a steady decrease in the 1-alkene content of the hydrolysis products, and no pressure buildup in the storage container. Further evidence was the observation of C_8 hydrocarbons in the hydrolysis products of aged samples of diethyl(butenyl)aluminum.

$$2Et_2AlCH=CHEt \rightarrow (Et_2Al)_2CHCH(Et)CH=CHEt \quad (5)$$

$R_2AlCH=CHR$ compounds can be stabilized for long-term storage by complex formation with at least an equimolar amount of an ether such as THF or diethyl ether. Figure 1 gives the results of experiments in which THF and diethyl ether complexes with freshly prepared $Et_2AlCH=CHEt$ were allowed to age along with control samples. Those samples with greater than 1 molar equiv of ether were more stable than control samples, based on 1-butene content in hydrolysis gas. Interestingly, less than 1 molar equiv of ether accelerates the decomposition rate over that of control samples.

Typical conditions and results from representative experiments on the reaction of $R_2AlCH=CHR$ with ethylene oxide are compiled in Table II. Optimum crude yields (distilled) of both isomeric products are 50–70% of theory. A viscous residue was obtained after distillation in every case. This material presumably results from oligomerization or polymerization of ethylene oxide catalyzed by the aluminum alkyl. This accounts, in part, for the low yields of desired products. In those experiments where THF (or DME) is used, *cis*-3-alken-1-ol of high purity (94–98%) is obtained upon redistillation.

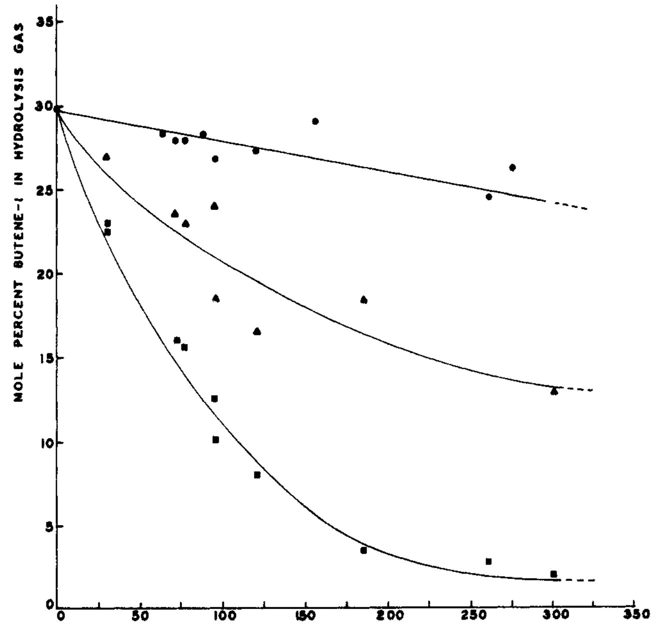

Figure 1. Stability of diethylbutenylaluminum in presence of various amounts of ethers: ▲, control samples of $Et_2AlCH=CHEt$; ●, $Et_2AlCH=CHEt$ with 1.5 molar equiv of an ether (THF or diethyl ether); ■, $Et_2AlCH=CHEt$ with 0.3–0.7 molar equiv of an ether (THF or diethyl ether).

In the reaction of $Et_2AlCH=CHEt$ with a large excess of ethylene oxide, a product with high *cis*-3-hexen-1-ol content is obtained, although in low yield. In this case, ethylene oxide seems to act both as reactant and strongly basic solvent, thereby fostering the formation of *cis*-3-hexen-1-ol. A significant amount of high-boiling by-product was observed in this experiment. Based on spectroscopic and analytical data, the compound has been tentatively identified as $EtCH=CH(CH_2)_2O(CH_2)_2OH$. This product presumably results from insertion of two ethylene oxide units between the butenylaluminum bond as in eq 6. Evidence for formation of

$$\begin{tikzcd}
Et_2AlCH{=}CHEt \arrow[r, "\overline{CH_2CH_2O}"] & Et_2AlO(CH_2)_2CH{=}CHEt \arrow[d, "\overline{CH_2CH_2O}"] \\
& Et_2AlO(CH_2)_2O(CH_2)_2CH{=}CHEt \arrow[d, "H_3O^+"] \\
& EtCH{=}CH(CH_2)_2O(CH_2)_2OH
\end{tikzcd} \quad (6)$$

Table II. Reaction of $R_2AlCH=CHR$ with Ethylene Oxide

Registry no.	Reactants: $R_2AlCH=CHR$ R	Reactants: $R_2AlCH=CHR$ Mol[c]	Reactants: Ethylene oxide, mol	Reaction temp, °C	Base[b] Compd	Base[b] Mol	Cosolvent Compd	Cosolvent Vol, mL	% yield[d]	Product composition[a]: $RCH=CHCH_2CH_2OH$	Product composition[a]: Cyclopropane isomer
56095-71-7	Et	7.01	7.91	27–32	None		Hexane	1400	70	67	33
	Et	2.52	3.06	5–15	DME	3.75	Benzene	1075	49	93	7
	Et	2.23	3.66	10–15	THF	3.66	Benzene	1500	53	93	7
	Et	1.25	8.98	9–15	None		Hexane	1000	18	94	6
56095-72-8	*n*-Bu	5.27	6.88	38–49	THF	7.35	None		61	92	8
56095-73-9	*i*-Bu	6.68	8.08	36–54	None		Hexane	208	63	63	37
56095-74-0	*n*-Hex	4.33	5.99	21–29	THF	6.91	None		53	95	5
62493-32-7	*n*-Oct	4.33	4.56	34	THF	4.84	None		48	95	5

[a] Normalized area percent by GC; once-distilled products typically contain 1–8% nonisomeric impurities. Redistillation affords *cis*-3-alken-1-ols of 94–98% purity in those experiments where THF (or DME) is cosolvent. [b] DME = 1,2-dimethoxyethane; THF = tetrahydrofuran. [c] Adjusted for purity of $R_2AlCH=CHR$. [d] Once-distilled crude yield of both isomers based on unsaturated aluminum alkyl. Nonadjusted yields are 5–10% lower.

products resulting from three or more ethylene oxide units inserting was also obtained, although the relative amount decreased as the molecular weight increased.

Reaction of $Et_2AlCH{=}CHEt$ with propylene oxide was also studied. There was no discernible reaction between propylene oxide and $Et_2AlCH{=}CHEt$ in the presence of THF. Consequently, it was necessary to conduct this reaction either with neat reactants or in hydrocarbon, which led to a diversity of products. Two reaction products are possible resulting from alkenylation at the nonequivalent ring carbon atoms as in eq 7. Other products resulting from rearrangement reactions similar to those observed earlier are also possible. The direction of ring opening is known to be dependent upon stoichiometry in reactions of this type.[15,16] With a $Et_2AlCH{=}CHEt$/propylene oxide ratio of 1.3, however, the predominant product is *cis*-4-hepten-2-ol, indicating alkenylation at the less substituted ring carbon. This finding was unusual in view of results obtained by previous workers,[15,16] who observed alkylation to occur at the more substituted carbon atom in reactions of R_3Al with propylene oxide using R_3Al:propylene oxide molar ratios of one or greater. The result is consistent, however, with the findings of Negishi, Baba, and King in their studies on the reaction of lithium *trans*-alkenyltrialkylaluminates with propylene oxide.[10]

$$Et_2AlCH{=}CHEt \xrightarrow[2.\ H_3O^+]{1.\ CH_3\overline{CHCH_2O}} CH_3CHOHCH_2CH{=}CHEt + HOCH_2CH(CH_3)CH{=}CHEt \quad (7)$$

Experimental Section

Reagents. Unsaturated aluminum alkyls were prepared by reaction of R_3Al compounds with acetylene according to the general procedure of Wilke and Müller.[11] The resultant $R_2AlCH{=}CHR$ compounds were typically 85–95% pure. Trialkylaluminum compounds are commercial products of Texas Alkyls and were used without further purification. Ethers, amines, and hydrocarbon solvents were reagent grade and dried over Linde 4A molecular sieves before use. Ethylene oxide (99.7% min) was obtained from Matheson Gas Products and propylene oxide from Eastman Kodak Co.

Instrumentation and Analytical Techniques. Organoaluminum compounds were analyzed for aluminum content by EDTA titration of the aqueous portion of hydrolyzed samples at pH 4.5 using dithizone indicator.[17] Gas chromatographic analysis of the hydrolysis products from organoaluminum compounds was achieved by the method of Watson, Mudry, and Philipp.[18]

Composition of alcohols was determined by GC using a 0.125 in. by 12 ft column packed with 10% Carbowax 20M on 60–80 mesh Chromosorb W, or the column described by Bedoukian.[19] Boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 recording infrared spectrophotometer. Proton magnetic resonance spectra were recorded on Varian A-60A or EM-360 NMR spectrometers. Elemental analyses were conducted at Galbraith Laboratories, Inc., Knoxville, Tenn. The mass spectrum of 2-ethylcyclopropanemethanol was run at the Hercules Research Center, Wilmington, Del.

Synthesis of Alcohols. The following examples illustrate procedures used in the synthesis of the various alcohols. All manipulations involving organometallic compounds were carried out in a nitrogen atmosphere.

A. Reaction of $Et_2AlCH{=}CHEt$ with Ethylene Oxide. To a 1-gal low-pressure autoclave were charged 1142 g of $Et_2AlCH{=}CHEt$ and 1.4 L of hexane. Ethylene oxide (348 g, 7.91 mol) was charged over a 6-h period into the vapor space while maintaining the reaction temperature at 27–32 °C. After addition was complete, the reaction mixture was heated to 49 °C for 1 h. A total of 2405 g of reaction mixture was recovered (98.9% material balance). The reaction product was hydrolyzed at 25–30 °C in two parts by slow addition to 10% sulfuric acid. The hydrocarbon layer was separated and washed with saturated sodium bicarbonate solution. The aqueous layer from the hydrolysis step was extracted with hexane and the extracts combined with the neutralized organic layer. Solvent was removed by distillation through a 3-ft column (Penn State packing) at atmospheric pressure. The pressure was reduced to 20 mmHg and material distilled until the vapor temperature reached 66 °C. A product fraction of 495 g was collected (bp 66.5–68.7 °C, 20 mmHg). Analysis of the product fraction showed 66% *cis*-3-hexen-1-ol, 33% 2-ethylcyclopropanemethanol, and the remainder lower boiling compounds. Yield of C_6 isomeric alcohols was 70%, adjusting for the 86.2% purity of $Et_2AlCH{=}CHEt$ starting material (nonadjusted yield, 61%).

B. Isolation and Characterization of 2-Ethylcyclopropanemethanol. The product from the preparation above was combined with a similar quantity from another experiment and the combined product subjected to vacuum distillation. The system used consisted of a 6-ft reflux column packed with Podbielniak no. 3013 stainless steel Heli-Pak and was equipped with a partial take-off head with variable reflux splitter. Light fractions rich in 2-ethylcyclopropanemethanol were collected, combined, and redistilled (bp 53.7–54.0 °C, 10 mmHg) to afford 97% pure 2-ethylcyclopropanemethanol: IR 3.03, 3.27, 3.35, 3.39, 3.44, 3.50, 6.85, 7.08, 7.27, 9.40, 9.67, 9.90 μ; NMR (Me_4Si external standard) δ 4.90 (s, 1, -OH), 3.29 (d, 2, $-CH_2O-$), 0.93 (m, 5, CH_3CH_2-), 0.25 (m, 4, ring protons); mass spectrum *m/e* 100 (M^+).

Anal. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08; O, 15.97. Found: C, 71.98; H, 12.08; O, 16.06.

C. Reaction of $Et_2AlCH{=}CHEt$ with Ethylene Oxide in the Presence of THF. The general procedure used in A was followed here except that benzene–THF cosolvent replaced hexane. Thus, to a solution consisting of 352 g (2.51 mol) of $Et_2AlCH{=}CHEt$, 264 g (3.66 mol) of THF, and 1.5 L of benzene was charged 131 g (2.97 mol) of ethylene oxide over a period of 3 h at 10–15 °C. The resultant mixture was hydrolyzed and worked up in the usual manner. Distillation of the organic layer afforded 118 g (53% adjusted yield, 47% nonadjusted yield) of product (bp 67.3–69.5 °C, 20 mmHg). Redistillation gave a product (bp 57.8–59.2 °C, 10 mmHg) which GC analysis revealed to be 96% *cis*-3-hexen-1-ol and <4% 2-ethylcyclopropanemethanol with the remainder primarily low-boiling contaminants. The main product was shown to be identical with an authentic sample of *cis*-3-hexen-1-ol from Norda Essential Oils. Product characterization: IR 2.99, 3.33, 3.38, 3.48, 4.24, 6.03, 6.85, 9.55, 9.77, 11.18, 11.58 μ; NMR (CCl_4, Me_4Si internal standard) δ 5.35 (m, 2, $-CH_a{=}CH_b-$, $J_{ab} \simeq 6$ Hz), 3.7 (s, 1, -OH), 3.53 (t, 2, $-CH_2O$), 2.2 (m, 4, protons α to double bond), 0.96 (t, 3, CH_3-).

Anal. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08; O, 15.97. Found: C, 71.89; H, 12.06; O, 16.20.

D. Reaction of $Et_2AlCH{=}CHEt$ with a Large Excess of Ethylene Oxide. Using the general procedure described in A, another reaction of ethylene oxide with $Et_2AlCH{=}CHEt$ was conducted, but here a large excess of ethylene oxide was employed, the mode of addition was reversed, and the reaction was conducted at about 0 °C. A poor yield (≃18%) of product was obtained. Analysis showed the product to be about 94:6 *cis*-3-hexen-1-ol:2-ethylcyclopropanemethanol.

A higher boiling fraction was isolated (bp 102–104 °C, 13 mmHg) and was tentatively identified to be primarily $EtCH{=}CH(CH_2)_2O(CH_2)_2OH$: IR 2.81, 3.33, 3.40, 4.15, 5.94, 6.75, 7.27, 7.58, 8.84, 9.3, 11.26 μ; NMR (CCl_4, Me_4Si internal standard) δ 5.5 (m, 2, $-CH_a{=}CH_b-$, $J_{ab} \simeq 6$ Hz), 3.4–3.6 (m, 6, methylene protons α to oxygen atoms), 2.65 (s, 1, -OH), 1.8–2.5 (m, 4, methylene protons α to double bond), 0.96 (t, 3, CH_3-).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18; O, 22.19. Found: C, 66.57; H, 11.29; O, 21.92.

E. Reaction of $Et_2AlCH{=}CHEt$ with Propylene Oxide. Following the usual procedure except that no solvent was employed, propylene oxide (10.93 mol) was slowly added to $Et_2AlCH{=}CHEt$ (8.70 mol) over the temperature range 30–60 °C. The reaction product was dissolved in about 300 g of hexane and hydrolyzed. Distillation afforded a 53% yield of product which GC analysis showed to be 65% *cis*-4-hepten-2-ol and 35% unidentified codistilling products, presumably C_7 isomeric alcohols. Redistillation (bp 45 °C, 6 mmHg) gave several fractions of 94–98% *cis*-4-hepten-2-ol: IR 3.01, 3.40, 6.04, 6.86, 7.27, 8.99, 10.34, 10.64, 11.25, 11.57, 11.87 μ; NMR (CCl_4, Me_4Si internal standard) δ 5.4 (m, 2, $-CH_a{=}CH_b-$, $J_{ab} \simeq 6$ Hz), 3.72 (m, 1, methine proton), 3.04 (s, 1, -OH), ca. 2 (m, 4, methylene protons), 1.13 (d, 3, methyl adjacent to -CHOH-), 0.96 (t, 3, methyl in ethyl group).

Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36; O, 14.01. Found: C, 73.72; H, 12.39; O, 14.07.

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Registry No.—Ethylene oxide, 75-21-8; 2-ethylcyclopropanemethanol, 62493-33-8; *cis*-3-hexen-1-ol, 928-96-1; EtCH=CH-

$(CH_2)_2O(CH_2)_2OH$, 62493-34-9; *cis*-4-hepten-2-ol, 34146-55-9; propylene oxide, 75-56-9.

References and Notes

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Synthesis of Bicyclo[*n*.2.0]alkanediols

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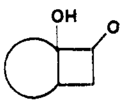
A general procedure for synthesis of bicyclo[*n*.2.0]alkane-1,*n*-diols is described. The synthesis involves thermal cycloaddition of dichloroketene to a cyclic alkene to generate the bicyclic skeleton (e.g., **6**), cine substitution with a carboxylate anion to give a bridgehead oxygen substituent (e.g., **12**), removal of the remaining halogen with chromous chloride, and reduction to give diol (e.g., **14**). The procedure allows for the synthesis of either cis or trans diols selectively.

The rearrangement reactions of fused-ring cyclobutanols have been the subject of considerable interest for several years.[1] Interest in the synthetic potential of rearrangement reactions of fused-ring cyclobutanols containing a bridgehead hydroxyl group led us to study general methods for the synthesis of such diols. This study resulted in the development of a convenient procedure for the synthesis of bicyclo[*n*.2.0]-alkanediols of the general structure **1**.[2] The demonstration by Paukstelis and Kao[3] that rearrangement of the monotosylate **2** leads to the novel, highly strained *trans*-bicyclo[4.1.0]heptan-2-one (**3**) serves as one example of the synthetic utility of this class of compounds.[4]



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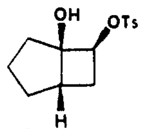

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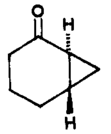

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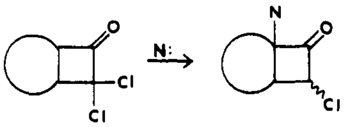
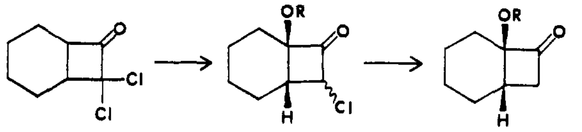


4 **5**

The synthetic method we have developed involves the addition of dichloroketene to a simple cycloalkene[5] with the bridgehead substituent being introduced by cine substitution on the resultant dichlorocyclobutanone (**4** → **5**).[6,7] The dichloroketene adducts used as starting materials were prepared by the method of Brady.[5b,8] Thus generation of dichloroketene by dehalogenation of trichloroacetyl bromide with zinc in the presence of cyclohexene gave the known adduct **6** in 70% yield. In a similar manner, reaction with cyclopentene gave adduct **7** in 49% yield.

Cine substitution on chloro ketone **6** proceeded readily upon treatment with a variety of nucleophiles. Reaction with 1 equiv of sodium methoxide in refluxing methanol gave chloromethoxy ketone **8** in good yield. However, extensive chromatography was necessary to remove numerous by-products apparently resulting from attack at the cyclobutanone carbonyl.[6] Adduct **6** gave a quantitative yield of ester **10** upon treatment with triethylammonium mesitoate in acetone.[7] Likewise chloro keto ester **12** was prepared in quantitative yield with triethylammonium acetate. Chromous chloride reduction of chloro ketones **8**, **10**, and **12** gave the corresponding keto esters in good yield. Keto acetate **13** was used for further conversions since cleavage of the mesitoate ester with lithium aluminum hydride was not successful. For synthetic purposes, the chloro keto ester **12** was not isolated. The acetone solution of **12** obtained after removal of triethylammonium chloride by filtration was treated directly with chromous chloride to give keto acetate **13** in a 70% overall yield from adduct **6**.



6

8, R = CH_3
10, R = 2,4,6-Me_3PhCO
12, R = CH_3CO

9, R = CH_3
11, R = 2,4,6-Me_3PhCO
13, R = CH_3CO

Keto acetate **13** could be converted to diol by a variety of procedures (see Scheme I). All procedures for direct reduction of the keto group of **13** led to production of trans diol **14t** as the only significant product. Treatment of keto acetate **13** with excess lithium aluminum hydride gave a single crystalline diol (**14t**) in 65% yield. The trans relationship of the hydroxyls in diol **14t** has been confirmed by comparison with an authentic