Reactions of 1-Halo-2-methyl-3-alkoxy- and 3-alkylaminopropenes with Potassium *t*-Butoxide in Tetrahydrofuran[1]

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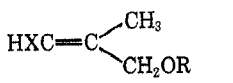
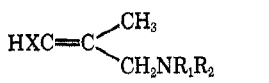
Several *cis*- and *trans*-1-halo-2-methyl-3-alkoxypropenes (**1a–1f**) and 1-halo-2-methyl-3-alkylaminopropenes (**2a–2c**) were prepared and treated with potassium *t*-butoxide (KO-*t*-Bu) in boiling tetrahydrofuran (THF). The principal products obtained from the methyl, ethyl, and isopropyl ethers (**1a–1e**) were the corresponding 2,5-dihydrofuran (**3**), 2-methyl-3-*t*-butoxy-3-alkoxypropene (**5**), and 2-*t*-butoxymethyl-3-alkoxypropene (**6**). The *t*-butyl ether **1f** gave 1-methylene-2-*t*-butoxycyclopropane (**7**) as the only cyclic product, together with the corresponding acetal **5d**, diether **6d**, and two isomeric vinyl ethers. Geometrical assignments were made to **1a–1f** and **2a–2c** on the basis of their nmr spectra; in all cases, the higher boiling isomer was assigned the *trans* configuration. The *cis* isomers of **1a–1f** consistently gave more cyclic product and acetal, but less diether, than the *trans* isomers. Second-order rate constants for formation of **3**, **5**, and **6** from *trans*-1-chloro-2-methyl-3-isopropoxypropene (**1a**) and *cis*- and *trans*-1-chloro-2-methyl-3-isopropoxypropene (**1d**) were determined. Each of the 3-alkylaminopropenes **2a–2c** gave the corresponding 3-pyrroline (**4**) and 2-*t*-butoxymethyl-3-alkylaminopropene (**19**). 1-Methylamino-2-butyne and 2-methyl-2-propenal methylimine were also identified as products from 1-bromo-2-methyl-3-methylaminopropene (**2a**). The *cis* isomers of **2a–2c** gave greater yields of **4** and lesser yields of **19** than the *trans* isomers.

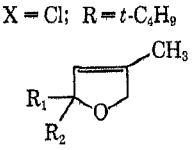
In 1963, Tanabe and Walsh[2] reported that the reaction of isocrotyl chloride with potassium *t*-butoxide (KO-*t*-Bu) in a 4:1 (by volume) mixture of tetrahydrofuran (THF) and cyclohexene gave a modest yield of 7-isopropylidenenorcarane, and they proposed that this product was formed by a mechanism involving 2,2-dimethylethylidene carbene. This suggested to us that similar treatment of compounds such as **1** might give alkylidene carbenes or carbenoids that would undergo intramolecular insertion into carbon–hydrogen bonds.[3]



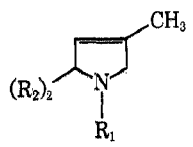
1a, X = Cl; R = CH_3
b, X = Br; R = CH_3
c, X = Cl; R = C_2H_5
d, X = Cl; R = *i*-C_3H_7
e, X = Br; R = *i*-C_3H_7
f, X = Cl; R = *t*-C_4H_9



2a, X = Br; R_1 = H; R_2 = CH_3
b, X = Cl; R_1 = H; R_2 = *i*-C_3H_7
c, X = Cl; R_1 = R_2 = CH_3



3a, R_1 = R_2 = H
b, R_1 = H; R_2 = CH_3
c, R_1 = R_2 = CH_3



4a, R_1 = R_2 = H
b, R_1 = H; R_2 = CH_3
c, R_1 = CH_3; R_2 = H

Preliminary experiments with the bromo amine **2a** revealed that reaction with KO-*t*-Bu in THF converted it into a complex mixture of amines from which 3-methyl-3-pyrroline (**4a**) could be isolated, and subsequent experiments with the chloro ether **1a** showed that it gave the corresponding heterocycle, 3-methyl-2,5-dihydrofuran (**3a**), together with several other products. Further, samples enriched in the lower boiling isomer of **1a** or **2a** gave significantly greater yields of the heterocyclic product.

In order to assess the value of 2,2-disubstituted 1-haloethylenes as precursors of cyclic systems, we examined the reactions of *cis* and *trans* isomers of **1a–1f** and **2a–2c** with KO-*t*-Bu in THF.

Isocrotyl bromide was converted by the action of N-bromosuccinimide into a 2.4:1 mixture of the higher and lower boiling isomers of 1,3-dibromo-2-methylpropene. Similarly, isocrotyl chloride gave a 2.1:1 mixture of the 1-chloro-2-methyl-3-bromopropenes, with the higher boiling isomer again predominating. The mixtures of dihalides were not separated but converted directly into mixtures of *cis* and *trans* ethers or alkylamines by treatment with alkoxide in alcohol or with excess amine. Except for **1f**, which was obtained in 53% yield, yields ranged from 77 to 90%, and the product from every reaction consisted of 70 ± 3% of the higher boiling isomer.

Stereochemical assignments to the dihalides, ethers, and alkylamines were made on the basis of their nmr spectra. From consideration of nmr data for propene and substituted propenes,[4] it seems reasonable to expect than an aminomethyl, halomethyl, or hydroxymethyl group will deshield, and that the methyl group will shield a *cis*-C_1 proton in compounds of the type HXC=$C(CH_3)CH_2Z$. Further, it can also be expected that the C_1 halogen will exert a greater deshielding effect on the methylene protons of the *cis* isomer. For every pair of *cis*- and *trans*-1-halo-2-methyl-3-alkoxypropenes (**1a–1f**), 1-halo-2-methyl-3-alkylaminopropenes, and 1,3-dihalo-2-methylpropenes, the signal of the C_1 proton of the lower boiling isomer is more shielded than that of the higher boiling isomer by 0.09–0.33 ppm, whereas the signal which is due to its C_3 proton is less shielded by 0.10–0.28 ppm. These data are completely consistent with assignment of the *trans* configuration to all of the higher boiling isomers. Interestingly, the *trans* isomers of 1,3-dibromopropene,[5,6] 1,3-dichloropropene,[7]

(1) Taken from the Ph.D. Thesis of R. A. Walsh, University of California, Davis, 1969. Supported by Grants GM 10606 and CA 10740 from the National Institutes of Health, Public Health Service.

(2) M. Tanabe and R. A. Walsh, *J. Amer. Chem. Soc.*, **85**, 3522 (1963).

(3) K. L. Erickson and J. Wolinski [*ibid.*, **87**, 1142 (1965)] have described such a reaction. They found that heating 1-bromo-2-ethyl-1-hexene with sublimed KO-*t*-Bu gave a *ca.* 30% yield of 1-ethyl-3-methylcyclopentene, as well as other products, including 3-octyne.

(4) M. Y. De Wolf and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **13**, 344 (1964), and references 1–13 cited therein.

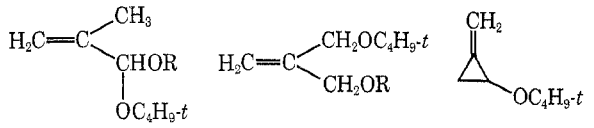
(5) L. F. Hatch and K. E. Harwell, *J. Amer. Chem. Soc.*, **75**, 6002 (1953).

(6) A. T. Bottini, B. J. King, and J. M. Lucas, *J. Org. Chem.*, **27**, 3688 (1962).

(7) L. F. Hatch and R. H. Perry, *J. Amer. Chem. Soc.*, **71**, 3262 (1949).

1-bromo-3-*n*-butylaminopropene,[6] 1-bromo-3-hydroxypropene,[5] and 1-chloro-3-hydroxypropene[7] are also the higher boiling isomers. It should also be pointed out that no correlation between the geometry of these compounds and their refractive index or the chemical shift of their C_2-methyl protons is apparent.

The major products isolated from reactions of the ethers **1a–1e** with a slight excess (<12%) of KO-*t*-Bu in THF were the corresponding 2,5-dihydrofuran (**3**), 3-*t*-butoxy-3-alkoxypropene (**5**), and 2-*t*-butoxymethyl-3-alkoxypropene (**6**). The only cyclic product obtained from similar treatment of 1-chloro-2-methyl-3-*t*-butoxypropene (**1f**) was 1-methylene-2-*t*-butoxycyclopropane (**7**); the corresponding acetal (**5d**) and diether (**6d**) were also obtained. Minor products were observed in all product mixtures, and it was estimated that these accounted for 5–10% of the starting materials. Without taking into account the tarry distillation residues, which were 10–15% of the weight of the starting ethers, material balances from these reactions ranged from 60 to 80%.



5 **6** **7**

a, R = CH_3; b, R = C_2H_5; c, R = *i*-C_3H_7; d, R = *t*-C_4H_9

Yields of **3** (or **7**), **5**, and **6** from samples enriched in the *cis* and *trans* isomers of **1a–1f** are summarized in Table I. All of the reactions studied were examined by glpc at various degrees of completion; no isomerization of the starting ethers under the reaction conditions was detected. Note that the *cis* isomers consistently gave more cyclic product and acetal, but less diether, than the *trans* isomers. It should also be noted that yields obtained using 30:70 mixtures of the *cis* and *trans* halo ethers were entirely consistent with those obtained from the enriched samples.

TABLE I

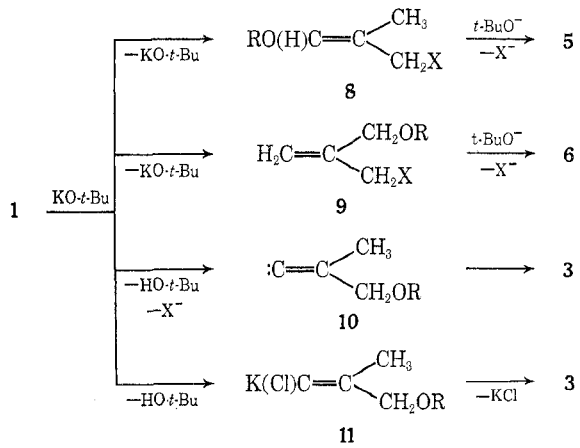
YIELDS FROM REACTIONS OF 1-HALO-2-METHYL-3-ALKOXYPROPENES (**1a–1f**) WITH KO-*t*-Bu IN THF

Reactant (purity, %[a])	Yield,[b] % 3	5	6
cis-**1a** (86)	16	15	19
trans-**1a** (96)	9	8	36
cis-**1b** (84)	30	8	23
trans-**1b** (95)	8	3	52
cis-**1c** (82)	23	26	14
trans-**1c** (94)	18	18	32
cis-**1d** (95)	33	32	18
trans-**1d** (99)	25	15	38
cis-**1e** (93)	36	7	17
trans-**1e** (97)	29	2	33
cis-**1f** (86)	10[c]	8	13
trans-**1f** (99)	5[c]	3	31

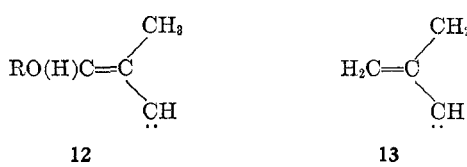
[a] The single contaminant was the isomeric halo ether. [b] Yields from the chloro ethers were corrected for recovered starting material, which amounted to 4–12%. [c] **7**.

Formation of the acetal **5** is most readily explained as occurring by prototropic rearrangement of the starting ether to the corresponding 1-alkoxy-2-methyl-3-halopropene (**8**), followed by SN2′ attack of *t*-butoxide. Similarly, rearrangement of the starting ether to the corresponding 2-alkoxymethyl-3-halopropene (**9**), followed by SN2 and/or SN2′ attack of *t*-butoxide, will lead to the diether **6**. The dependence of yields of **5** and **6** on the stereochemistry of the starting ether shows that the preferred, but not exclusive, direction of prototropic rearrangement is to the carbon of **1** that is *cis* to the halogen.[8] Formation of a 2,5-dihydrofuran (**3**) can be explained on the basis of the intermediacy of a free alkylidene carbene (**10**), which inserts into an α-C–H bond of the alkoxyl group, or an organometallic alkylidene carbenoid (**11**), from which potassium chloride is displaced by the same C–H bond.[11] These pathways are summarized in Scheme I.

SCHEME I



Alternative mechanisms for formation of **3** involving α-dehydrohalogenation of **8** and **9** are not consistent with the results. The intermediate from **8** (**12**) would give a 2,3-dihydrofuran, a vinyl ether that would be stable with respect to **3**.[12] The intermediate from **9** (**13**) would give a 3-methylenetetrahydrofuran; although it is conceivable that this product would rearrange to **3** under the reaction conditions, yield data for **3** and **6** show that the same intermediate, specifically **9**, is not involved in the formation of more than a fraction of these products. Mechanisms for formation of



12 **13**

3 involving abstraction of an α hydrogen of the alkoxyl group of **1**, *e.g.*, an addition–elimination reaction, also seem unlikely. This is because *cis*- and *trans*-1-ethoxy-4-*t*-butylcyclohexane undergo negligible exchange of

(8) Prototropic rearrangements of *allyl* to *propenyl* ethers occur with a high degree (*ca.* 99%) of stereoselectivity.[9] Similar rearrangements of amines[9c] and thioethers[10] occur with markedly less stereoselectivity. In all those rearrangements of allyl compounds, the *cis*-propenyl compound is the major product.

(9) (a) T. J. Prosser, *J. Amer. Chem. Soc.*, **83**, 1701 (1961); (b) C. C. Price and W. H. Snyder, *i bid.*, **83**, 1773 (1961); (c) *Tetrahedron Lett.*, 69 (1962); (d) C. D. Broaddus, *J. Amer. Chem. Soc.*, **87**, 3706 (1965).

(10) C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

(11) See G. Kobrich, *Angew. Chem. Intern. Ed. Engl.*, **4**, 49 (1967).

(12) Treatment of a 60:40 mixture of **2** and 2,3-dihydrofuran with 1.1 equiv of KO-*t*-Bu in dimethyl sulfoxide at 60° for 6 hr destroyed 60% of the 2,5 isomer and less than 5% of the 2,3 isomer.[13]

(13) F. P. Corson, Ph.D. Thesis, University of California, Davis, 1967.

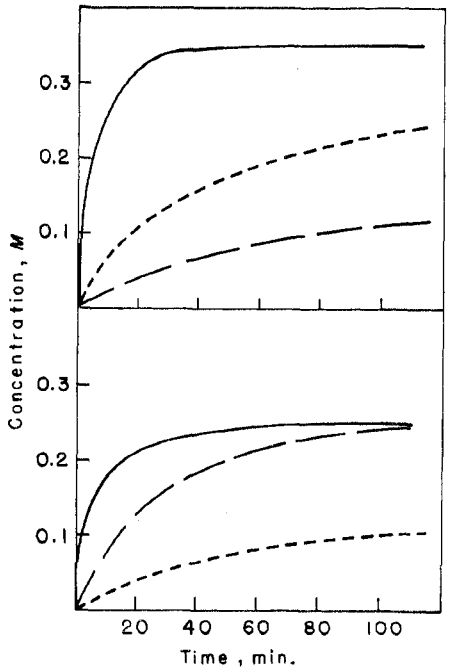


Figure 1.—Rates of formation of 2,2,4-trimethyl-2,5-dihydrofuran (———), 2-methyl-3-*t*-butoxy-3-isopropoxypropene (– – – –), and 2-*t*-butoxymethyl-3-isopropoxypropene (— — —) from reactions of *cis*- (upper) and *trans*-1-chloro-2-methyl-3-isopropoxypropene (lower) with potassium *t*-butoxide in tetrahydrofuran.

α hydrogens when treated with 1.5 equiv of KO-*t*-Bu in tritiated dimethyl sulfoxide at 100° for 6 hr.[13]

A carbene or carbenoid from **1f** (**10** or **11**, R = *t*-C_4H_9) is a likely intermediate in the formation of **7**. Cyclization involving a C_3–H bond would give 1-methyl-3-*t*-butoxycyclopropene, which would be expected to rearrange to the less strained **7** under the reaction conditions.[14] Our failure to find *t*-butoxymethylenecyclopropane, which would arise by cyclization involving a C–H bond of the methyl group at C_2 followed by *exo* migration of the double bond, indicates that either this product is unstable under the reaction conditions or that the carbene or carbenoid from **1f** shows a marked degree of selectivity toward the two types of C–H bonds.

In order to obtain a more detailed picture of these reactions, we determined the rates of reaction of *cis*- and *trans*-1-chloro-2-methyl-3-isopropoxypropene (**1d**) and *trans*-1-chloro-2-methyl-3-methoxypropene (**1a**) with equimolar amounts of KO-*t*-Bu in boiling THF. The rates of appearance of the three major products from the reactions of *cis*- and *trans*-**1d** are presented graphically in Figure 1. The striking feature of these reactions is the rapid decrease in the rate of formation of the cyclic product. By the time half of the starting ether was consumed, the rate of formation of the cyclic product is virtually nil. This can be explained in terms of the effect of *t*-butyl alcohol on the basicity of KO-*t*-Bu. For each mole of 2,5-dihydrofuran formed, a mole of *t*-butyl alcohol is formed. *t*-Butyl alcohol forms a sparingly soluble 1:1 complex with KO-*t*-Bu,[15] and the effective basicity of the *t*-butoxide ion, particularly its ability to abstract a vinyl hydrogen, is substantially reduced.[16] It is apparent that this decrease in basicity does not affect to the same extent the rates of formation of the two allyl chlorides **8** and **9**, which are the precursors of the acetal **5** and the diether **6**.

These results suggested that improved yields of 2,5-dihydrofuran could be obtained by using a KO-*t*-Bu:**1** mole ratio of greater than 1.1:1. When this mole ratio was increased to 2:1 with *trans*-1-chloro-2-methyl-3-methoxypropene (**1a**), the yield of **3a** was increased from 9 to 24%, and the combined yields of **5a** and **6a** fell from 44 to 15%.[17a] Further, when *cis*-enriched 1-chloro-2-methyl-3-ethoxypropene (**1c**) was treated with a slurry prepared from equivalent amounts of KO-*t*-Bu and *t*-butyl alcohol, only 3% was converted into the dihydrofuran **3b**; the corrected yields (83% conversion of **1c**) of the acetal **5b** and diether **6b** were 33 and 14%.[17b]

Because of the rapid falloff in rates of reaction, the apparent second-order rate constants that we determined for *trans*-**1a** and *cis*- and *trans*-**1d**, which are summarized in Table II, were calculated using data obtained during the first 30–35% of the reactions. In these calculations, the rate constant for disappearance of **1** was taken as equal to the sum of the rate constants for formation of **3**, **5**, and **6**.

TABLE II

APPARENT SECOND-ORDER RATE CONSTANTS FOR REACTIONS OF 1-CHLORO-2-METHYL-3-ALKOXYPROPENES WITH KO-*t*-Bu IN BOILING THF

Reactant	k_3[a]	k_5[a]	k_6[a]
trans-**1a**	4.0	0.37	1.8
cis-**1d**	6.8	2.0	0.53
trans-**1d**	3.7	0.57	1.7

[a] $\times 10^4\ M^{-1}\ \text{sec}^{-1}$.

These data clarify several features of the reactions. The rate constants for formation of **5** and **6** from a given chloro ether differ by a factor of 4 to 5, the acetal being formed more rapidly from the *cis* isomer and less rapidly from the *trans* isomer. From this, the degree of stereoselectivity in prototropic rearrangements of the chloro ethers to **8** and **9** can be estimated as 80 ± 5%; *i.e.*, of the starting ether that undergoes prototropic rearrangement, 80 ± 5% rearranges by migration of the double bond to the carbon *cis* to halogen. Although the rate constant for formation of **3c** from *cis*-**1d** is almost twice that of the *trans* isomer, the sum of the rate constants for formation of the acetal and diether is nearly the same for the two halo ethers. Thus the greater yields of cyclic products from the *cis* isomers are due to faster rates of conversion of *cis*-**1** into **3** (or **7**) rather than slower rates of conversion into **5** and **6**. The greater rate of cyclization of the *cis* isomer appears to result from the lesser hindrance to attack by *t*-butoxide ion in the rate-limiting abstraction of the vinyl hydrogen. Interestingly, change of the alkoxyl group from methoxyl to

(14) See N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 3966 (1967).

(15) A. J. Speziale, K. W. Ratts, and D. E. Bissing, *Org. Syn.*, **45**, 35 (1965).

(16) See V. A. Bessenov, P. P. Alikhanov, E. N. Gur'yanova, A. P. Simonov, I. O. Shapiro, E. A. Yakovleva, and A. I. Shatenshtein, *J. Gen. Chem. USSR*, **37**, 96 (1967).

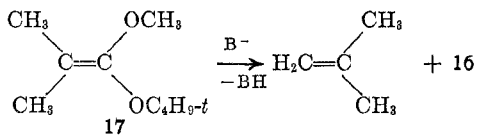
(17) (a) Part of the large decrease in yield of **5a** and **6a** is due to their instability, relative to **3a**, when treated with KO-*t*-Bu in THF. Treatment of a 1:0.27:1.25 mixture of **3c**, **5c**, and **6c** (total concentration, 0.57 *M*) with 0.79 *M* KO-*t*-Bu in boiling THF for 18 hr destroyed <5% of **3c**, 72% of **5c**, and 42% of **6c**. (b) Experiment carried out by Mr. K. A. Frost after submittal of this paper.

isopropoxyl has relatively little affect on the rates of all three processes. Finally, these data do not allow us to choose between the free carbene or organometallic carbenoid pathway for cyclization.

Although change of the alkoxyl group has no appreciable affect on the rates of reaction of the *trans* isomers of **1a** and **1d**, change of halogen has a large affect. The *cis* and *trans* isomers of 1-bromo-2-methyl-3-isopropoxypropene (**1e**) underwent reaction too rapidly to measure at the boiling temperature of THF. That terminal vinyl bromides react faster than chlorides is in agreement with the observation that α-halogen substituents facilitate carbanion formation in the order I $\cong$ Br > Cl > F.[18]

As mentioned earlier, it was estimated that minor products accounted for 5–10% of the starting materials. Except for minor products from **1a**, **1b**, and **1f**, which were examined in some detail, these estimates were based on the assumptions that each minor product had the same molecular weight and thermal conductivity as the major product that had most nearly the same retention time on the glpc column used for analysis.

Compounds **1a** and **1b** gave three minor products in combined yields of 4–10%, and they were identified as 2-methyl-3,3-dimethoxypropene (**14**), 2-methoxymethyl-3-methoxypropene (**15**), and methyl isobutyrate (**16**). Examination by glpc showed that **14**–**16** were not present in the starting materials. Formation of the acetal **14** and the diether **15** indicates that *t*-butoxide displaces methoxide from the starting halo ether and possibly one or more of the acyclic products, and that methoxide competes with *t*-butoxide in reactions of the allylic halides (**8** and **9**) formed by prototropic rearrangement of **1a** and **1b**. A plausible pathway by which the ester could be formed is prototropic rearrangement of **5a** to the mixed dimethylketene acetal **17**, followed by elimination of isobutylene.



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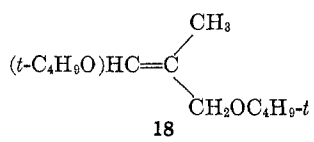
In addition to **5d**, **6d**, and **7**, *cis*- and *trans*-1-chloro-2-methyl-3-*t*-butoxypropene (**1f**) gave nearly equal amounts of two other products in combined yields of 8–9%. The retention times and nmr spectra of these products indicated that they were the *cis* and *trans* isomers of 1,3-di-*t*-butoxy-2-methylpropene (**18**).



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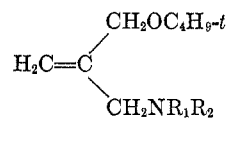
Each of the ethyl and isopropyl halo ethers (**1c**–**1e**) gave three unidentified products in combined yields of 4–9%. Of these, two appeared to be isomeric with the corresponding diether and acetal. The third minor product was probably isomeric with the corresponding 2,5-dihydrofuran; it was formed in greatest amount (3% yield) from **1c**.

(18) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 1406 (1957).

Treatment of each of the 1-halo-2-methyl-3-alkylaminopropenes (**2a**–**2c**) with KO-*t*-Bu in the same manner as the 1-halo-2-methyl-3-alkoxypropenes (**1a**–**1f**) gave the corresponding 3-pyrroline (**4**) and 2-*t*-butoxymethyl-3-alkylaminopropene (**19**). Note that **19** would be formed from **2** by a mechanism analogous to that proposed for formation of the diethers (**6a**–**6d**) from **1a**–**1f**. As might be expected from the behavior of **1a**–**1f**, samples enriched in the *cis* isomers of **2a**–**2c** gave higher yields of **4** and lower yields of **19** than those obtained from samples enriched in the *trans* isomers. These yield data are summarized in Table III.



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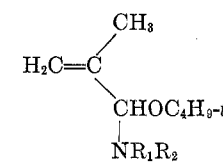

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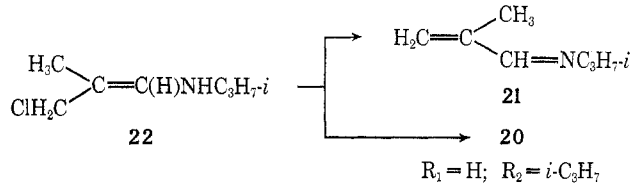
TABLE III

YIELDS FROM REACTIONS OF 1-HALO-2-METHYL-3-ALKYLAMINOPROPENES (**2a**–**2c**) WITH KO-*t*-Bu IN THF

Reactant (purity, %[a])	Yield,[b] % **4**	**19**
cis-**2a** (99)	18	5
trans-**2a** (94)	4	22
cis-**2b** (86)	14	3
trans-**2b** (92)	17	18
cis-**2c** (71)	36	6
trans-**2c** (83)	30	13

[a] The single contaminant was the geometric isomer. [b] Corrected for 8–18% recovered starting material.

No 2-methyl-3-*t*-butoxy-3-alkylaminopropene (**20**), which would correspond to the acetals (**5a**–**5d**) obtained from the halo ethers, was identified as a product from **2a**–**2c**. However, 2-methyl-2-propenal isopropylimine (**21**) was isolated in yields of 25 and 14%, respectively, from samples enriched in *cis*- and *trans*-1-chloro-2-methyl-3-isopropylaminopropene (**2b**). Again by analogy with the halo ethers, it seems likely that **2b** rearranges to the vinylamine **22**, and that **22** undergoes dehydrochlorination to **21** more rapidly that it undergoes SN2′ attack by *t*-butoxide.



22 **21** **20**

$R_1 = H$; $R_2 = i\text{-}C_3H_7$

Compounds **2a**–**2c** gave other products, but only two of these accounted for more than an estimated 2% of the starting amine.[19] At least 7% of both *cis*- and *trans*-**2b** were converted into an unidentified, thermally unstable product, which was probably isomeric with **4b** and **22**. *cis*-Enriched and *trans*-enriched 1-bromo-2-methyl-3-methylaminopropene (**2a**) gave 1-methyl-

(19) As with minor products from the halo ethers, estimates were based on the assumptions that each minor product had the same molecular weight and thermal conductivity as the major product that had most nearly the same retention time on the glpc column used for analysis. Each of the starting amines gave one to three additional products that were probably isomeric with **4**, and at least one that was probably isomeric with **19**.

TABLE IV

BOILING POINTS, REFRACTIVE INDICES, AND ELEMENTAL ANALYSES OF ENRICHED SAMPLES OF *cis*- AND *trans*-1-HALO-2-METHYL-3-ALKOXY- AND -3-ALKYLAMINOPROPENES

Compd	Purity, %	Bp, °C (mm)	$n^{23}D$	Calcd, % C	Calcd, % H	Found, % C	Found, % H
cis-1a	86	120–122	1.4390	49.75	7.55[a]	49.45	7.24
trans-1a	96	126–128	1.4412			49.55	7.53
cis-1b	84	134–136	1.4728	36.36	5.52[b]	36.17[c]	5.39[c]
trans-1b	95	146–148	1.4705				
cis-1c	82	140–142	1.4372	53.49	8.25[d]	53.44	8.26
trans-1c	94	145–147	1.4373			53.55	8.34
cis-1d	95	80–82 (90)	1.4355[e]	56.55	8.82[f]	56.73	8.69
trans-1d	99	85–86 (90)	1.4348[e]			56.70	8.69
cis-1e	93	90–92(65)	1.4586	43.52	6.79[g]	43.65[c]	6.78[c]
trans-1e	97	95–97 (65)	1.4587				
cis-1f	86	99–101 (88)	1.4370	59.07	9.29[h]	59.10[c]	9.25[c]
trans-1f	99	105–107 (88)	1.4390				
cis-2a	99	77–78.5 (41)	1.4931[i]	36.59	6.16	36.38[c]	5.92[c]
trans-2a	94	82.5–84 (41)	1.4957[i]				
cis-2b	86	96–98 (80)	1.4580[i]	42.56[j]	4.68[j]	42.53[k]	4.43[k]
trans-2b	92	99–101 (80)	1.4548[i]			42.59[l]	4.46[l]
cis-2c	71	139	1.4486[i]	53.89	9.06[m]	54.04	8.69
trans-2c	83	140	1.4486[i]			54.08	8.78

[a] Calcd: Cl, 29.44. Found: *cis*, 29.48; *trans*, 29.63. [b] Calcd: Br, 48.42. Found:[c] Br, 48.65. [c] Analysis of *ca.* 30% *cis*–70% *trans* mixture. [d] Calcd: Cl, 26.37. Found: *cis*, 26.09; *trans*, 26.34. [e] At 25°. [f] Calcd: Cl, 23.68. Found: *cis*, 23.61; *trans*, 23.73. [g] Calcd: Br, 41.40. Found:[c] 41.68. [h] Calcd: Cl, 21.80. Found:[c] Cl, 21.85. [i] At 22°. [j] Calculated for *p*-bromobenzenesulfonamide. [k] Analysis of *p*-bromobenzenesulfonamide, mp 97.5–98.5°. Calcd: N, 3.82. Found: N, 3.56. [l] Analysis of *p*-bromobenzenesulfonamide, mp 72.5–73.5°. Calcd: N, 3.82. Found: N, 3.55. [m] Calcd: Cl, 26.57. Found: *cis*, 26.62; *trans*, 26.65.

amino-2-butyne (**23**) in yields of 12 and 2%, respectively. Conversion of a 2,2-disubstituted 1-haloethylene into an acetylene by treatment with a strong base is not a novel reaction,[3] and it is noteworthy that such a rearrangement plays no more than a minor role in reactions of most of the 2,2-disubstituted 1-haloethylenes described here.

$H_3CC{\equiv}CCH_2NHCH_3$

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Experimental Section

Temperatures are uncorrected. Ir spectra were obtained with either a Beckman IR-8 or Perkin-Elmer 237B spectrophotometer; spectra of samples available in only microliter quantities were obtained using micro NaCl plates with the Beckman IR-8 fittted with a beam condenser. Nmr spectra were obtained of CCl_4 solutions with a Varian Associates A-60A spectrometer; resonance frequencies in nmr spectra were determined relative to 1–2% internal tetramethylsilane. Glpc chromatograms were obtained with an Aerograph Model A-700 of A-90-P3 or a Varian Model 90-P. Stationary phases and dimensions of columns used were: 20% SE 30, 12 ft × 0.25 in.; 30% SE 30, 10 ft × 0.25 in.; 20% XF 1150, 16 ft × 0.25 in.; 20% FFAP, 15 ft × 0.25 in. The packing for the last column was DMCS-treated Chromosorb P; the packing for the other columns was Chromosorb W. Microanalyses were performed at The Microanalytical Laboratory, University of California, Berkeley; Galbraith Laboratories, Inc., Knoxville, Tenn., and Chemalytics, Inc., Tempe, Ariz. Potassium *t*-butoxide (KO-*t*-Bu) was obtained from MSA Research Corp. Tetrahydrofuran (THF) was filtered through Woelm basic alumina, activity grade one, immediately prior to use. All of the vinyl halides used showed definite signs of decomposition, accompanied by evolution of hydrogen halide, within 24 hr of their purification. The rate of decomposition was reduced substantially by storage under nitrogen. Before any vinyl halide that gave evidence of decomposition was treated with KO-*t*-Bu, it was filtered through basic alumina and its purity was checked by examination of its nmr spectrum.

The 1,3-Dihalo-2-methylpropenes.—A procedure patterned after that described for the preparation of 4-bromo-2-heptene[20] was used to convert 193 g of isocrotyl bromide into 200 g (75%) of a 1:2.4 mixture of *cis*- and *trans*-1,3-dibromo-2-methylpropene: bp 85–90° (44 mm), $n^{23}D$ 1.5478; nmr for lower boiling (*cis*) isomer, δ 6.11 (m, 1, =CH), 4.09 (d, 2, J = 1.4 Hz, CH_2), and 1.93 (d, 3, J = 1.4 Hz, CH_3); for higher boiling (*trans*) isomer, 6.43 (m, 1, =CH), 3.99 (d, 2, J = 1.4 Hz, CH_2), and 1.93 (d, 3, J = 1.4 Hz, CH_3).

Anal. Calcd for $C_4H_6Br_2$: C, 22.45; H, 2.81. Found: C, 22.23; H, 2.73.

A similar procedure was used to convert 151 g of freshly distilled isocrotyl chloride, bp 67–68°, into 228 g (81%) of a 1:2.1 mixture of *cis*- and *trans*-1-chloro-2-methyl-3-bromopropene: bp 90–100° (90–100 mm); $n^{23}D$ 1.5142; nmr for lower boiling (*cis*) isomer, δ 5.96 (m, 1, =CH), 4.08 (d, 2, J = 1.4 Hz, CH_2), and 1.92 (d, 3, J = 1.4 Hz, CH_3); for higher boiling (*trans*) isomer, 6.29 (m, 1, =CH), 3.97 (d, 2, J = 1.4 Hz, CH_2), and 1.92 (d, 3, J = 1.4 Hz, CH_3).

Anal. Calcd for C_4H_6BrCl: C, 28.34; H, 3.54. Found: C, 28.35; H, 3.50.

Preparation of the 1-Halo-2-methyl-3-alkoxypropenes (1a–1f).—Except that KO-*t*-Bu, not sodium *t*-butoxide, was used to prepare **1f**, the following procedure, used for the preparation and isolation of *cis*- and *trans*-1-chloro-2-methyl-3-ethoxypropene (**1c**), is typical.

To a stirred solution prepared from 18.4 g of sodium and 700 ml of absolute ethanol under nitrogen was added dropwise, in 10 min, 120 g of 1-chloro-2-methyl-3-bromopropene. When the addition was complete, the mixture was heated cautiously to reflux, held there for 3 hr, cooled, and added to 800 ml of water. The aqueous solution was extracted with CCl_4 (four 120-ml portions), and the extracts were combined, washed with water (three 150-ml portions), and dried (K_2CO_3). Distillation gave an 84.2-g fraction, bp 75–82° (88 mm), that was a 1:2.2 mixture of *cis*- and *trans*-**1c**. This fraction was redistilled through a 60 × 0.8 cm spinning-band column, and three fractions, bp 140–144°, 144–145°, and 145–147°, were collected. The lowest boiling fraction was redistilled through the same column to give a 17.0-g fraction, bp 140–142°, which was an 82:18 mixture of *cis*- and *trans*-**1c**: The highest boiling fraction consisted of 94% *trans*- and 6% *cis*-**1c**: nmr for lower boiling (*cis*) isomer, δ 5.95 (m, 1, =CH), 4.09 (d, 2, J = 1.4 Hz, CH_2), 3.28 (s, 3, OCH_3), and 1.77 (d, 3, J = 1.4 Hz, CCH_3); for higher boiling (*trans*) isomer, 6.10 (m, 1, =CH), 3.81 (d, 2, J = 1.4 Hz, CH_2), 3.26 (s, 3, OCH_3), and 1.77 (d, 2, J = 1.4 Hz, CCH_3).

The boiling points, refractive indices, and elemental analyses of fractions enriched in the *cis* and *trans* isomers of **1a–1f** are included in Table IV.

(20) F. L. Greenwood, M. D. Kellert, and J. Sedlak, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 108.

Preparation of the 1-Halo-2-methyl-3-alkylaminopropenes (2a–2c).—The following procedure, used for preparation and isolation of *cis*- and *trans*-1-chloro-2-methyl-3-dimethylaminopropene (2c), is typical.

A 160-g sample of the 1:2.1 mixture of *cis*- and *trans*-1-chloro-2-methyl-3-bromopropene was added dropwise in 45 min to *ca.* 600 ml of stirred, refluxing dimethylamine. When the addition was complete, the mixture was allowed to reflux for 4 hr, and then most of the excess dimethylamine was removed by distillation through a 30 × 1.5 cm column packed with glass helices. The residue was cooled with an ice bath, and 60 g (1.5 mol) of NaOH was added in portions. Water (100 ml) was added carefully until all the solid material in the mixture dissolved, the aqueous layer was separated and extracted with ether (two 75-ml portions), and the extracts were combined with the organic layer. This was washed with water (40 ml) and saturated NaCl solution (two 75-ml portions), dried (KOH), and distilled to give a 108-g fraction, bp 138–141°. Several distillations through a 60-cm annular spinning-band column gave a 38.6-g fraction which was a 1:5 mixture of *cis*- and *trans*-2c. Only 8.9 g of predominantly (71%) *cis*-2c was obtained: nmr for lower boiling (*cis*) isomer, δ 6.00 (m, 1, =CH), 3.06 (d, 2, J = 1.4 Hz, CH_2), 2.19 (s, 6, NCH_3), and 1.80 (d, 3, J = 1.4 Hz, CCH_3); for higher boiling (*trans*) isomer, 6.10 (m, 1, =CH), 2.82 (d, 2, J = 1.4 Hz, CH_2), 2.15 (s, 6, NCH_3), and 1.80 (d, 3, J = 1.4 Hz, CCH_3).

The boiling points, refractive indices, and elemental analyses of fractions enriched in the *cis* and *trans* isomers of 2a–2c are included in Table IV.

Reactions of the 1-Halo-2-methyl-3-alkoxy- and -3-alkylaminopropenes with KO-*t*-Bu in THF.—The following procedure is typical. To a stirred mixture of 30.2 g (0.27 mol) of KO-*t*-Bu and 150 ml of THF under nitrogen was added 30.0 g (0.25 mol) of a 1:2.0 mixture of *cis*- and *trans*-1-chloro-2-methyl-3-methoxypropene (1a). The reaction mixture, which turned brown immediately, was heated at reflux for 16 hr, cooled, and added to 150 ml of cold 2 M K_2CO_3 solution. The organic phase was separated and the aqueous phase was extracted with 50 ml of ether. The organic solutions were combined, washed with saturated K_2CO_3 solution, dried (KOH), and distilled.

Reactions with 1-bromo-2-methyl-3-methylaminopropene (2a) were the most exothermic, and these reaction mixtures were filtered through Filter Aid before work-up.

Identification of Products.—Products obtained from 30:70 mixtures of *cis* and *trans* isomers were separated by a combination of fractional distillation and glpc, and these products were used for purposes of identification as well as estimating the relative thermal conductivities of the major products. Products from enriched samples of the *cis* and *trans* isomers were collected with a minimum of fractionation and analyzed by means of glpc and nmr spectroscopy.

Summarized below are spectral bands common to the various classes of compounds obtained from 1a–1f and 2a–2c, as well as pertinent data for individual compounds. The stationary phase of the glpc column used for purifying the compound is given in parentheses. Unless a compound was isolated in a relatively pure state (>97%) by distillation, its boiling point is not given.

3-Methyl-2,5-dihydrofurans (3a–3c) gave the following data: nmr δ 5.37–5.45 (m, 1, =CH), 4.42–4.45 (m, 2 or 4, CH_2O), and 1.69–1.74 (m, 3, $=CCH_3$); ir 1665–1670 cm^{-1} (C=C).

3-Methyl-2,5-dihydrofuran (3a) (SE 30) gave the following data: $n^{22}D$ 1.4369; lit.[21] bp 83–85°.

Anal. Calcd for C_5H_8O: C, 71.43; H, 9.52. Found: C, 71.16; H, 9.38.

2,4-Dimethyl-2,5-dihydrofuran (3b) (SE 30) gave the following data: nmr δ 4.65–5.12 (m, 1, C_2H) and 1.17 (d, 3, J = 6 Hz, C_2CH_3); $n^{23}D$ 1.4294.

Anal. Calcd for $C_6H_{10}O$: C, 73.39; H, 10.30. Found: C, 73.10; H, 10.38.

2,2,4-Trimethyl-2,5-dihydrofuran (3c) (XF 1150 and SE 30) gave the following data: nmr δ 1.22 (s, 6, C_2CH_3); $n^{24}D$ 1.4226.

Anal. Calcd for $C_7H_{12}O$: C, 74.93; H, 10.79. Found: C, 74.79; H, 10.55.

2-Methyl-3-*t*-butoxy-3-alkoxypropenes (5a–5d) gave the following data: nmr δ 4.71–5.15 (s or 3 multiplets, 3, $H_2C=CCH$), 1.67–1.72 (m, 3, C_2CH_3), and 1.20–1.26 (s, 9 or 18, t-C_4H_9); ir 910 and 1655–1660 cm^{-1} (C=C).

2-Methyl-3-*t*-butoxy-3-methoxypropene (5a) (SE 30 and FFAP) gave the following data: nmr δ 3.05 (s, 3, OCH_3); $n^{23}D$ 1.4106.

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.45. Found: C, 68.59; H, 11.47.

2-Methyl-3-*t*-butoxy-3-ethoxypropene (5b) (SE 30) gave the following data: nmr δ 3.39 (q, 2, J = 7.5 Hz, OCH_2CH_3) and 1.14 (t, 3, J = 7.5 Hz, OCH_2CH_3); $n^{23}D$ 1.4125.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.69; H, 11.73. Found: C, 69.53; H, 12.03.

2-Methyl-3-*t*-butoxy-3-isopropoxypropene (5c) (SE 30 and XF 1150) gave the following data: nmr δ 3.71 [septet, 1, J = 6 Hz, $OCH(CH_3)_2$] and 1.10 [d, 6, J = 6 Hz, $OCH(CH_3)_2$].

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.97; H, 11.83. Found: C, 70.77; H, 11.15.

2-*t*-Butoxymethyl-3-alkoxypropenes (6a–6d) gave the following data: nmr δ 5.01–5.17 (1 or 2 multiplets, 2, $=CH_2$), 3.83–3.99 (1 or 2 multiplets, 4, OCH_2), and 1.17–1.20 (s, 9 or 18, t-C_4H_9); ir 895–905 and 1660–1670 cm^{-1} (C=C).

2-*t*-Butoxymethyl-3-methoxypropene (6a) gave the following data: nmr δ 3.23 (s, 3, OCH_3); bp 101–102° (91 mm); $n^{22}D$ 1.4210.

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.45. Found: C, 68.43; H, 11.55.

2-*t*-Butoxymethyl-3-ethoxypropene (6b) gave the following data: nmr δ 3.49 (q, 2, J = 7 Hz, OCH_2CH_3) and 1.18 (t, 3, J = 7 Hz, OCH_2CH_3); bp 112° (90 mm); $n^{23}D$ 1.4220.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.69; H, 11.73. Found: C, 69.89; H, 11.79.

2-*t*-Buoxymethyl-3-isopropoxypropene (6c) gave the following data: nmr δ 3.56 [septet, 1, J = 6 Hz, $HC(CH_3)_2$] and 1.10 [d, 6, $C(CH_3)_2$]; bp 114–116° (63 mm); $n^{22}D$ 1.4210.

Anal. Calcd for $C_{11}H_{22}O$: C, 70.97; H, 11.83. Found: C, 70.69; H, 11.68.

2-*t*-Butoxymethyl-3-*t*-butoxypropene (6d) (SE 30 and XF 1150) was not obtained pure, and was analyzed as the major component of a mixture with *cis*- and *trans*-18.

Anal. Calcd for $C_{12}H_{24}O_2$: C, 70.52; H, 11.85. Found: C, 70.73; H, 12.05.

1-Methylene-2-*t*-butoxycyclopropane (7) (SE 30) gave the following data: nmr δ 5.67 (m, 1, =CH), 5.51 (m, 1, =CH), 3.69 (m, 1, OCH), 1.33 (m, 2, CH_2), and 1.23 (s, 9, t-C_4H_9); ir 1790 cm^{-1} (C=C); $n^{23}D$ 1.4314.

Anal. Calcd for $C_8H_{14}O$: C, 76.13; H, 11.18. Found: C, 75.77; H, 11.46.

2-Methyl-3,3-dimethoxypropene (14) (SE 30 and FFAP) gave the following data: nmr δ 4.48–5.05 (3 multiplets, 3, $H_2C=CCH$), 3.19 (s, 6, OCH_3), and 1.63 (m, 3, CCH_3); ir 900 and 1655 cm^{-1} (C=C).

2-Methoxymethyl-3-methoxypropene (15) (SE 30 and FFAP) gave the following data: nmr δ 5.08 (m, 2, $=CH_2$), 3.82 (m, 4, CH_2), and 1.73 (2, 6, OCH_3).

1,3-Di-*t*-butoxy-2-methylpropene (19) gave the following data: nmr for first isomer, δ 5.94 (m, 1, =CH), 3.89 (broadened 2, s, OCH_2), 1.56 (d, 3, J = 1.2 Hz, $=CCH_3$), and 1.22 (s, 18, t-C_4H_9); nmr for second isomer, 6.21 (m, 1, =CH), 3.68 (broadened s, 2, OCH_2), 1.56 (d, 3, J = 1.2 Hz, $=CCH_3$), and 1.21 (s, 18, t-C_4H_9); ir for both isomers, 1685 cm^{-1} (C=C). A mixture of both isomers and 6d was analyzed (see under 6d).

3-Pyrrolines (4a–4c) (SE 30) gave the following data: nmr δ 5.32–5.36 (m, 1, =CH) and 1.72–1.73 (m, 3, $=CCH_3$); ir 1660–1665 cm^{-1} (C=C).

3-Methyl-3-pyrroline (4a) gave the following data: nmr δ 3.65 (m, 4, NCH_2) and 1.4 (variable, s, 1, NH).

Anal. Calcd for C_5H_9N: C, 72.29; H, 10.85; N, 16.87. Found: C, 72.01; H, 10.83; N, 16.62.

2,2,4-Trimethyl-3-pyrroline (4b) gave the following data: nmr δ 3.61 (m, 2, NCH_2), 1.4 (variable, s, 1, NH), and 1.14 (s, 6, C_2CH_3); $n^{23}D$ 1.4441. Several attempts failed to give a satisfactory analysis, so a sample was converted into the *p*-bromobenzenesulfonamide, mp 96.5–97.0° (80% EtOH).

Anal. Calcd for $C_{13}H_{16}BrNO_2S$: C, 47.26; H, 4.88; N, 4.24. Found: C, 47.44; H, 4.83; N, 4.07.

1,3-Dimethyl-3-pyrroline (4c) gave the following data: nmr δ 3.33 (m, 4, NCH_2) and 2.39 (s, 3, NCH_3); $n^{23}D$ 1.4404.

Anal. Calcd for $C_6H_{11}N$: C, 74.15; H, 11.43; N, 14.42. Found: C, 73.77; H, 11.33; N, 14.47.

2-*t*-Butoxymethyl-3-alkylaminopropenes (19a–19c) (SE 30) gave the following data: nmr δ 3.85–3.96 (broadened 2, s, OCH_2) and 1.20–1.23 (s, 9, t-C_4H_9); ir 905–910 and 1650–1655 cm^{-1} (C=C).

(21) E. E. Schweizer and J. H. Liehr, *J. Org. Chem.*, 33, 583 (1968).

2-*t*-Butoxymethyl-3-methylaminopropene (19a) gave the following data: nmr δ 5.11 (broadened 2, 1, =CH), 5.00 (m, 1, =CH), 3.20 (broadened s, 2, NCH_2), and 2.40 (s, 3, NCH_3).

Anal. Calcd for $C_9H_{19}NO$: C, 68.72; H, 12.20; N, 8.91. Found: C, 68.55; H, 11.96; N, 9.17.

2-*t*-Butoxymethyl-3-isopropylaminopropene (19b) gave the following data: nmr δ 5.12 (m, 2, $=CH_2$), 3.27 (broadened s, 2, NCH_2), 2.83 [septet, 1, J = 6.5 Hz, $HC(CH_3)_2$], 1.02 [d, 6, J = 6.5 Hz, $C(CH_3)_2$], and 0.9 (variable, s, 1, NH), $n^{23}D$ 1.4343. This compound was not obtained analytically pure, and these values may not be characteristic.

2-*t*-Butoxymethyl-3-dimethylaminopropene (19c) gave the following data: nmr δ 5.18 (broadened s, 1, =CH), 5.00 (m, 1, =CH), 2.84 (broadened s, 2, NCH_2), and 2.15 (s, 6, NCH_3); $n^{23}D$ 1.4275.

Anal. Calcd for $C_{10}H_{21}NO$: C, 70.09; H, 12.38; N, 8.18. Found: C, 70.21; H, 12.17; N, 8.25.

2-Methyl-2-propenal isopropylimine (21) (SE 30) gave the following data: nmr δ 7.98 (s, 1, N=CH), 5.55 (m, 1, HC=), 3.39 [septet, 1, J = 6.5 Hz, $CH(CH_3)_2$], 1.92 (m, 3, $=CCH_3$), 1.17 [d, 6, J = 6.5 Hz, $CH(CH_3)_2$]; ir 1620 and 1640 cm^{-1} (C=N and C=C); $n^{23}D$ 1.4270.

Anal. Calcd for $C_7H_{13}N$: C, 75.61; H, 11.79; N, 12.60. Found: C, 75.86; H, 11.75; N, 12.41.

1-Methylamino-2-butyne (23) (SE 30) gave the following data: nmr δ 3.32 (q, 2, J = 2.4 Hz, NCH_2), 2.45 (s, 3, NCH_3), and 1.76 (t, 3, J = 2.4 Hz, CCH_3).

Rates of Reaction of *trans*-1-Chloro-2-methyl-3-methoxypropene (1a) and *cis*- and *trans*-1-Chloro-2-methyl-3-isopropoxypropene (1d) with KO-*t*-Bu in THF.—A 0.87 M solution of KO-*t*-Bu in THF under nitrogen, contained in a 100-ml round-bottom flask fitted with a side arm, was stirred with a magnetic stirrer and heated to boiling. Chloroether sufficient to give a 0.87 M solution was added by means of a syringe through the side arm, which was covered by a rubber septum, and the timer was started when one-half had been added (addition time of *ca.* 6 sec). At measured time intervals (five times in the first 13 min), 0.5-ml samples were withdrawn with the syringe. Each was immediately added to 0.2 ml of water and shaken thoroughly, and the aqueous layer was separated with a pipet. The organic layer was dried (K_2CO_3) and analyzed by glpc (30% SE 30). At 1.5–2 hr after each reaction was initiated, the combined yields of **3**, **5**, and **6**, as estimated by glpc and corrected for unreacted starting material, exceeded 94%. With data obtained in the first 30–35% of the reaction, the apparent second-order rate constant for the disappearance of starting material was determined by plotting the reciprocal of the concentration of starting material *vs.* time. Rate constants for formation of **3** (k_3), **5** (k_5), and **6** (k_6) were estimated by assuming that these products were formed by second-order processes and that the sum of the rate constants for their formation was equal to the rate constant for disappearance of the starting material. The rate constants are summarized in Table II.

Relative Stability of 2,2,4-Trimethyl-2,5-dihydrofuran (3c), 2-Methyl-3-*t*-butoxy-3-isopropoxypropene (5c), and 2-*t*-Butoxymethyl-3-isopropoxypropene (6c) in Boiling THF Containing KO-*t*-Bu.—To 17 ml of THF under nitrogen was added 1.5 g of a 28:15:57 wt % mixture of **3c**, **5c**, and **6c**. *o*-Xylene (0.2 g) was added as an internal reference, and then 1.5 g (13 mmol) of KO-*t*-Bu was added. The solution was heated to reflux, and after measured time intervals, 0.5-ml samples were withdrawn with a syringe from a side arm of the flask that was covered with a rubber septum. Each sample was immediately added to 0.5 ml of water, and the aqueous phase was separated with a pipet. The organic phase was dried (K_2CO_3) and analyzed by glpc (30% SE 30). After 18 hr, the area ratio of the bands which were due to **3c** and *o*-xylene was the same within the precision of the measurements (*ca.* 5%), but the area ratios of the bands which were due to **5c** and *o*-xylene and **6c** and *o*-xylene had decreased to 28 and 58% of their original value. After 42 hr, the band which was due to **6c** was replaced by two bands with nearly equal areas at slightly longer retention times. The band which was due to **5c** was replaced by another with a slightly longer retention time. The nmr spectrum of the solution possessed a band at δ 5.80, characteristic of C_1 protons of 1-alkoxyalkenes.

Registry No.—Potassium *t*-butoxide, 865-47-4; tetrahydrofuran, 109-99-9; *cis*-**1a**, 23240-29-1; *trans*-**1a**, 23240-30-4; *cis*-**1b**, 23240-31-5; *trans*-**1b**, 23240-32-6; *cis*-**1c**, 23240-33-7; *trans*-**1c**, 23240-34-8; *cis*-**1d**, 23240-35-9; *trans*-**1d**, 23240-36-0; *cis*-**1e**, 23240-37-1; *trans*-**1e**, 23240-38-2; *cis*-**1f**, 23240-39-3; *trans*-**1f**, 23240-40-6; **cis-2a**, 23240-41-7; *trans*-**2a**, 23240-42-8; *cis*-**2b**, 23240-43-9; *trans*-**2b**, 23240-44-0; *cis*-**2c**, 23240-45-1; *trans*-**2c**, 23240-46-2; **3a**, 1708-31-2; **3b**, 23240-48-4; **3c**, 23230-79-7; **4a**, 23230-80-0; **4b**, 23230-81-1; **4c**, 23230-82-2; **5a**, 23230-83-3; **5b**, 23230-84-4; **5c**, 23230-85-5; **6a**, 23230-86-6; **6b**, 23230-87-7; **6c**, 23230-88-8; **6d**, 23230-89-9; **7**, 23230-90-2; **14**, 23230-91-3; **15**, 23230-92-4; **18**, 23230-93-5; **19a**, 23230-94-6; **19b**, 23230-95-7; **19c**, 23230-96-8; **21**, 23230-97-9; **23**, 23230-98-0; **4b** (*p*-bromobenzenesulfonamide), 23230-99-1.

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