reduction of the acetate with $LiAlH_4$.

Experimental Section

General Methods. Melting points were determined on a hot-stage apparatus; they are uncorrected. Proton magnetic resonance spectra were recorded on a Varian HR-220 MHz instrument. Optical rotations were recorded on a Perkin-Elmer 241MC polarimeter. Preparative and analytical TLC work were performed on plates coated with silica gel F-254.

Racemic samples of the alcohols and acetates used in these studies were prepared by literature methods; their physical properties, melting points, and NMR and mass spectra were in accord with the proposed structures and with published data.

Microbial Hydrolyses. The substrate (0.5 mL, ~400 mg) was added as a liquid or as a solution in ~1 mL of THF to a 1-L Erlenmeyer flask containing 250 mL of medium (potato dextrose) which had previously been inoculated with a liquid culture of *Rhizopus nigricans* (ATCC 6227b) and grown for 6 days as described.[2] The flask was shaken overnight (16 h) or, if the hydrolysis was rapid, until approximately 30–50% of the substrate had been hydrolyzed. The hydrolyses were monitored by TLC and ^1H NMR. The medium and mycelium were extracted three times with ethyl acetate, and the extract was concentrated. An estimate of the yield of the crude extract is given in Table I. The percent hydrolysis was determined from an NMR measurement of the ratio of alcohol to acetate in the crude extract. The acetates and alcohols were then separated either by column or thick-layer chromatography, and their specific rotations are given in Table I.

Absolute Stereochemistry of 17B. A sample of **17B** ($[\alpha]^{25}_D$ +15.2° (*c* 3.16, $CHCl_3$)) was acetylated to yield **17A**, $[\alpha]^{25}_D$ −41.5° (*c* 1.30, $CHCl_3$). The acetate was reduced with excess $LiAlH_4$ in THF to yield 1(*S*)-tetralol, $[\alpha]^{25}_D$ + 4.9°, ee 18% (lit.[8] +26.8°).

Conclusion

The present study and an earlier one demonstrate the ability of *R. nigricans* to hydrolyze enantioselectively a variety of cyclic and acyclic acetates to yield chiral alcohols of a predictable configuration. The method appears superior to the use of elution order from a chiral HPLC column to assign the configuration of a previously unknown alcohol. Assignments based on data from the hydrolyses are as reliable as those obtained by using Horeau's method and appear to require fewer assumptions about the effect of distant substituents on the course of the reaction. These enantioselective hydrolyses can also be used to prepare chiral alcohols, of either configuration, in quantities suitable for preparative chemistry.

Registry No. (±)-**1A**, 708-44-1; **1B**, 697-64-3; (±)-**2A**, 79465-04-6; **2B**, 23357-45-1; (±)-**3A**, 79416-46-9; **3B**, 79416-49-2; (±)-**4A**, 88270-66-0; **4B**, 88230-06-2; (±)-**5A**, 79465-03-5; **5B**, 79465-08-0; (±)-**6A**, 79465-02-4; **6B**, 79416-48-1; (±)-**7A**, 79465-01-3; **7B**, 27564-15-4; (±)-**8A**, 88229-97-4; **8B**, 57089-39-1; (±)-**9A**, 88270-67-1; **9B**, 88270-73-9; (±)-**10A**, 88270-68-2; **10B**, 79465-06-8; (±)-**11A**, 88270-69-3; **11B**, 67528-23-8; (±)-**12A**, 88270-70-6; **12B**, 57018-62-9; (±)-**13A**, 88229-98-5; **13B**, 88270-74-0; (±)-**14A**, 88270-71-7; **14B**, 71214-80-7; (±)-**15A**, 88229-99-6; **15B**, 65941-81-3; (±)-**16A**, 88230-00-6; **16B**, 57496-61-4; (±)-**17A**, 88230-01-7; **17B**, 84194-94-5; (±)-**18A**, 79465-00-2; **18B**, 79465-07-9; (±)-**19A**, 88270-72-8; **19B**, 84275-49-0; (±)-**20A**, 88230-02-8; **20B**, 57495-92-8; **21B**, 64440-29-5; (±)-**21C**, 88230-03-9; (±)-**22A**, 79416-44-7; **22B**, 1072-86-2; (±)-**23A**, 88230-04-0; **23B**, 88270-75-1; (±)-**24A**, 50539-19-0; **24B**, 19043-03-9; (±)-**25A**, 50539-18-9; **25B**, 19043-02-8; (±)-**26A**, 88230-05-1; **26B**, 39947-47-2.

Halogenated Epoxides. 6.[1] Reactions of Selected Chlorooxiranes with Sodium Methoxide: About the Question of Acetylenic and Allenic Epoxides as Intermediates

Karl Griesbaum,* Giu Oan Lie,[2] and Helmut Keul

Engler-Bunte-Institut, Bereich Petrochemie, Universität Karlsruhe (TH), D-7500 Karlsruhe, Germany

Received February 25, 1983

Reactions of sodium methoxide with five chlorooxiranes (**1**, **3**, **11**, **18**, and **19**) and with the corresponding isomeric chlorocarbonyl compounds have been examined. In two cases the chlorooxirane and the corresponding chlorocarbonyl compound afforded the same products, however, in different yields. In the other cases the chlorooxiranes and the corresponding chlorocarbonyl compounds gave different products. It is concluded that chlorocarbonyl compounds are not formed to a large extent as intermediates. In the reactions of two chlorooxiranes (**18** and **19**) with sodium methoxide, acetylenic and allenic epoxides may be invoked as transient intermediates.

Introduction

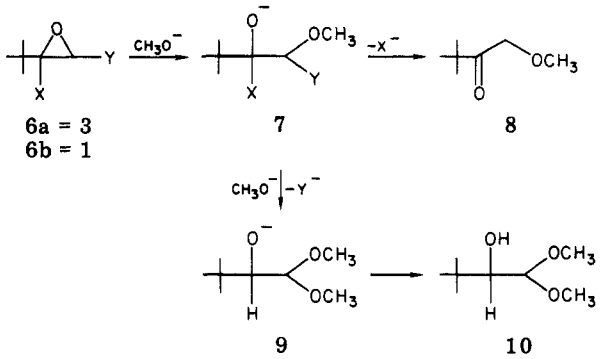
Reactions of 2-halooxiranes with nucleophiles such as amines,[3-5] organolithium compounds,[4,6,7] thiolates,[5] and alcoholates[4,5] have been reported by several groups. In most cases such reactions afforded the same products as those obtained from the respective nucleophiles with the α-halocarbonyl compounds, which are isomeric with the 2-halooxiranes used. However, starting from the α-halooxiranes the selectivities were usually higher, particularly in such cases where the isomeric α-halocarbonyl compounds can undergo a Favorskii reaction. It was, therefore, proposed[5] that the reactions of 2-halooxiranes with nucleophiles may proceed via their own routes rather than via isomerization to α-halocarbonyl compounds.

A considerable part of our research on halogenated epoxides is connected with their potential as precursors for acetylenic or allenic epoxides.[8,9] In line with this, it was of interest to us whether such species may be intermediates

(1) Previous paper in this series: Spraul, M.; Griesbaum, K. *Chem. Ber.* **1983**, *116*, 2641.
(2) Present address: Korea Research Institute of Chemical Technology, P.O. Box 9, Daedeogdanji, Korea.
(3) Hassner, A.; Catsoulacos, P. *J. Org. Chem.* **1967**, *32*, 549.
(4) Köbrich, G.; Werner, W.; Grosser, J. *Chem. Ber.* **1973**, *106*, 2620.
(5) Gasteiger, J.; Herzig, Ch. *Angew. Chem.* **1981**, *93*, 933.
(6) Nouri-Bimorghi, R. *Bull. Soc. Chim. Fr.* **1971**, 2971.
(7) Kirrmann, A.; Nouri-Bimorghi, R. *Bull. Soc. Chim. Fr.* **1972**, 2328.
(8) Spraul, M. Dissertation, Universität Karlsruhe, 1982.
(9) For leading references concerning this problem, see: Maier, G.; Reisenauer, H. P.; Sayrac, T. *Chem. Ber.*, in press and literature cited therein.

0022-3263/84/1949-0679$01.50/0

Scheme I [a]



6a = 3
6b = 1

7 8

9 10

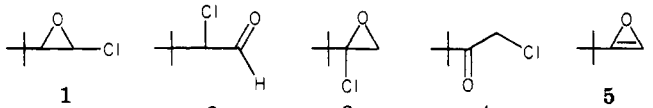
[a] a; X = Cl; Y = H. b; X = H; Y = Cl.

in dehydrochlorination reactions of chlorooxiranes and may, thus, provide one of several conceivable paths for reactions of chlorooxiranes with bases.

Results and Discussion

All reactions have been carried out with sodium methoxide in dry methanol, starting at temperatures well below 0 °C, and allowing a post-reaction period at room temperature. The course of the reaction was in each case followed by GLC analysis until complete conversion was reached.

In the first phase of the investigation, we have selected the monochlorooxiranes 1 and 3 for the following reasons.

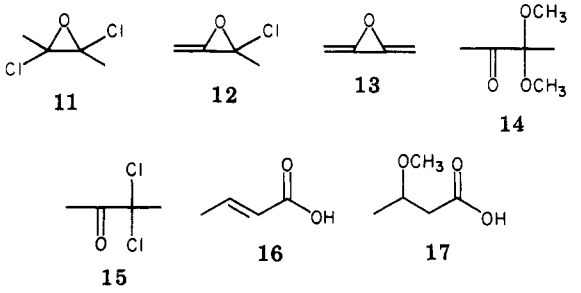


1 2 3 4 5

If the reactions would proceed by initial dehydrochlorination, 1 and 3 should provide the same oxirene intermediate, viz., 5, and hence also the same product(s). If, on the other hand, the reactions would proceed by initial isomerization, one would anticipate the α-chlorocarbonyl compounds 2 and 4, respectively. Since they are not apt to undergo Favorskii reactions, the results should not be obscured by this side aspect, and one should, therefore, expect virtually identical results from 1 and 2 and from 3 and 4, respectively.

Reaction of 1 with sodium methoxide was very slow below 0 °C. At room temperature it afforded in ca. 90% yield product 10 (Scheme I). Reaction of the isomeric aldehyde 2 under the same conditions produced 10, also, albeit only in 72% yield. A priori, this result could suggest that 1 reacts in a considerable part by initial isomerization to 2 and only to a lesser degree by alternate routes to form 10. However, in view of the results obtained with 3, the intermediacy of any significant portion of isomer 2 may be doubtful. Reaction of 3 with sodium methoxide under the same conditions as above afforded in ca. 88% yield 8, whereas the isomeric α-chloro ketone 4 gave a mixture consisting of at least four unidentified compounds and containing little if any product 8. This result shows that the intermediacy of 4 and hence the isomerization of 3 to 4 does not play any markable role in the reaction of 3 with sodium methoxide. We feel that the sequences 3 → 7a → 8 and 1 → 7b → 9b → 10 (Scheme I) represent the most likely reaction paths. In any event, since 1 and 3 gave rise to entirely different products in their eactions with sodium methoxide, oxirene 5 is not a common intermediate, i.e., at least one of the isomeric chlorooxiranes 1 and 3 does not react by initial dehydrohalogenation. In fact, there is no evidence that points to an oxirene intermediate in the reaction of either 1 or 3.

As a second type of substrate we have selected the dichlorooxirane 11, which could conceivable react via the allenic epoxides 12 and/or 13. Reaction of 11 with sodium



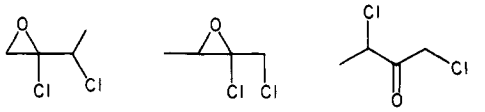
11 12 13 14

15 16 17

methoxide was again slow below 0 °C. At room temperature it afforded 14 in ca. 54% yield. Under similar conditions, reaction of the isomeric dichloro ketone 15, on the other hand, gave only 20% of 14, along with 16 (4%) and 17 (17%). This indicates again that the reaction of the chlorooxirane, viz., 11, occurs only to a minor part, if at all, by initial isomerization to 15 and to a major part by alternate routes. On the other hand, there was no experimental evidence for initial dehydrochlorination of 11, i.e., for the intermediacy of either 12 or 13.

The conversion of 15 into 14 may also proceed via different routes, viz., either by direct substitution of chlorine by methoxy groups or by a sequence similar to that of Scheme I. The other products obtained from 15, viz., 16 and 17, can be readily rationalized by a Favorskii reaction. The fact that 16 and 17 had not been detected in the reaction of 11 with sodium methoxide adds further evidence to the contention that 11 does not react via the isomer 15 to any appreciable extent.

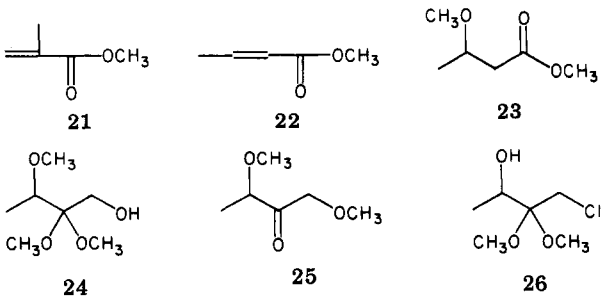
As a third type of substrates we have selected the dichlorooxiranes 18 and 19. Isomerization of either 18 or



18 19 20

19 produces the same dichloro ketone 20.[10] Consequently, a reaction path by initial isomerization should provide the same product(s) from 18 and from 19. This pair of substrates was, therefore, well suited to test the existence and the extent of such a route.

Reaction of the dichloro ketone 20 with sodium methoxide was fast even at −50 °C. GLC analysis of the crude product showed compound 21 (13%), *cis*- and *trans*-22 (52%), and 23 (13%) as the major components. Together



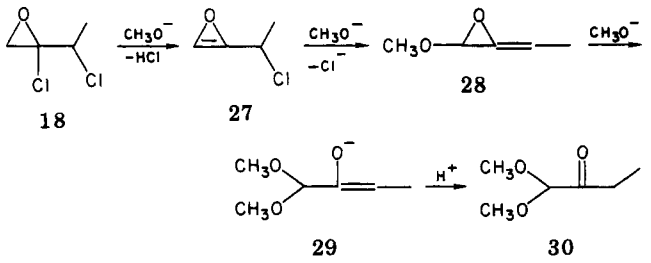
21 22 23

24 25 26

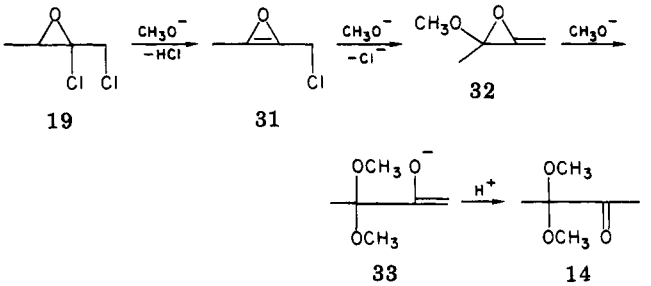
these components comprised 78% of the total peak area. Their formation is readily rationalized by a Favorskii reaction of 20 and subsequent reactions of the primary products with sodium methoxide. Minor products were

(10) Griesbaum, K.; Lie, G. O.; Raupp, E. *Chem. Ber.* **1981**, *114*, 3273.

Scheme II



Scheme III



compounds **24** (ca. 1%), **25** (ca. 1%), and **26** (ca. 3%) as well as **30** (16%) and **14** (ca. 1%). The formation of **24–26** can be explained by initial attack of the methoxide ion at the carbonyl group of **20** and subsequent reactions of the primary intermediate with sodium methoxide. Obviously, the formation of **25** could also be due to direct replacement of chlorine by methoxide in **20**.

Reactions of **18** and of **19** with sodium methoxide were also fast at −50 °C. GLC analyses of the crude products showed in each case one major product, viz., **30** (86%) starting from **18** and **14** (>90%) starting from **19**. These results show conclusively that the reactions of the dichloro epoxides **18** and **19** with sodium methoxide did not proceed to any considerable extent via the common dichloroketone **20** but that the dichloro epoxides reacted by their own individual reaction paths. Conceivable rationalizations for the formation of the reaction products **30** and **14** are depicted in Schemes II and III, respectively. They each involve three different, sequential reactions of methoxide ion, viz., a dehydrochlorination step to form acetylenic epoxide intermediates (**27** and **31**, respectively), an addition–displacement step to form allenic epoxide intermediates (**28** and **32**, respectively) and an addition–ring-opening step to give enolate intermediates (**29** and **33**, respectively). The latter, in turn, afford the stable end products **30** and **14**, respectively. Since we cannot provide any experimental evidence for the formulated acetylenic and allenic intermediates and in view of the negative experimental and unfavorable theoretical results concerning the stability of such species, we are aware that it is only a working hypothesis if we invoke the transient formation of such intermediates. Nevertheless, Schemes II and III probably offer the most straightforward explanations for the modes of formation of **30** and of **14**, respectively.

The results of the foregoing described investigations bear also on the ecological aspects of chlorooxirane chemistry. The experiments have shown that both mono- and dichlorooxiranes can be effectively converted into nonchlorinated products, which are probably less harmful and more amenable to biodegradation.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Bruker WP 60, GC/MS and mass spectra on a Hewlett-Packard 5985 B or on a Varian MAT 111, and IR spectra on a Beckman IR 4260 or on a Beckman Acculab 1 instrument. GLC analyses were carried out on a Varian Aerograph 1400 or on a Shimadzu GC 6A; preparative GLC separations were run on a Perkin Elmer F 21 instrument. Solutions of sodium methoxide were freshly prepared by reaction of sodium with methanol. The methanol used was always freshly dried.

Reaction of 2-*tert*-Butyl-3-chlorooxirane (1) with Sodium Methoxide. Methanol (20 mL) was cooled to −78 °C. Then 6.7 g (50 mmol) of a mixture of *cis*- and *trans*-**1**[11] and a solution of 3.2 g (59 mmol) of sodium methoxide in 12 mL of methanol was added dropwise with stirring. The mixture was allowed to reach room temperature, a second portion of 3.2 g (59 mmol) of sodium methoxide in 12 mL of methanol was added, and stirring was continued for 6 days. Finally, 45 mL of water was added and the mixture was continuously extracted with dichloromethane. The extract was dried over sodium sulfate, filtered, and the filtrate distilled through a 25-cm Vigreux column to remove the solvent. The residue was distilled in vacuum to yield 6.7 g (83%) of **10**.

1,1-Dimethoxy-3,3-dimethyl-2-butanol (10): colorless liquid; bp 70 °C (35 torr); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.95 (s, 9 H), 2.46 (d, J = 4.40 Hz, 1 H), 3.29 (dd, J = 4.40 and 4.58 Hz, 1 H), 3.39 (s, 3 H), 3.45 (s, 3 H), 4.31 (d, J = 4.58 Hz, 1 H); IR (film) 3500 cm^{-1} (OH); MS, m/e (relative intensity) 75 (100) $(CH(OCH_3)_2)^+$, 57 (29) $(C_4H_9)^+$.

Anal. Calcd for $C_8H_{18}O_3$: C, 59.23; H, 11.18. Found: C, 59.15; H, 11.00.

Reaction of 2-Chloro-3,3-dimethylbutanal (2) with Sodium Methoxide. Reaction of 12.2 g (91 mmol) of **2** in 20 mL of methanol with 6.2 g (115 mmol) of sodium methoxide in 50 mL of methanol was carried out as described above for **1** to yield 10.8 g (72%) of **10**.

Reaction of 2-*tert*-Butyl-2-chlorooxirane (3) with Sodium Methoxide. Reaction of 6.7 g (50 mmol) of **3**[12] in 20 mL of methanol with 3.2 g (59 mmol) of sodium methoxide in 12 mL of methanol was carried out as described above for **1** to yield 5.7 g (88%) of **8**.

1-Methoxy-3,3-dimethyl-2-butanone (8): colorless liquid; bp 52 °C (10 torr); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.17 (s, 9 H), 3.42 (s, 3 H), 4.29 (s, 2 H); IR (film) 1720 cm^{-1} (C=O); MS, m/e (relative intensity) 130 (4) M^+, 85 (12) $(C_4H_9CO^+$, 57 (100) $(C_4H_9)^+$, 45 (31) $(CH_2COCH_3)^+$.

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.56; H, 10.76.

Reaction of 1-Chloro-3,3-dimethyl-2-butanone (4) with Sodium Methoxide. Reaction of 5.7 g (42 mmol) of **4** in 15 mL of methanol with 2.8 g (52 mmol) of sodium methoxide in 10 mL of methanol was carried out as described above for **1**. Distillation of the residue after removal of dichloromethane gave 5.1 g of a colorless liquid; bp 52–62 °C (10 torr). GLC analysis (glass column 0.3 × 300 cm, 5% nitrile silicon oil on Chromosorb G; 60–160 °C at 4 °C/min) showed four major peaks, none of which corresponded to that of **8**.

Reaction of *trans*-2,3-Dichloro-2,3-dimethyloxirane (11) with Sodium Methoxide. Methanol (40 mL) was cooled to −78 °C. To this were added 14.0 g (0.1 mol) of **11**[13] and a solution of 11.9 g (0.22 mol) of sodium methoxide in 64 mL of methanol dropwise with stirring, and the mixture was allowed to reach room temperature. After 9 days a second portion of 5.9 g (0.11 mol) of sodium methoxide in 32 mL of methanol was added and stirring was continued for 39 days. Finally the reaction product was admixed with an equal amount of water, continuously extracted with dichloromethane, and the extract worked up as described above for the reaction of **1**. The residue after removal of dichloromethane was distilled, and the distillate (9.2 g) boiling up to a bath temperature of 100 °C and a pressure of 0.01 torr was collected. GLC analysis of this distillate (conditions as above) showed the peaks of **11** (4%, t_R 5.1 min), **14** (77%, t_R 11.4 min), and eight unidentified peaks. From the above data, the yield of **14** was calculated to be 54%.

(11) Duhamel, P.; Duhamel, L.; Gralak, J. *Bull. Soc. Chim. Fr.* **1970**, 3641.
(12) Griesbaum, K.; Keul, H.; Kibar, R.; Pfeffer, B.; Spraul, M. *Chem. Ber.* **1981**, *114*, 1858.
(13) Griesbaum, K.; Kibar, R.; Pfeffer, B. *Liebigs Ann. Chem.* **1975**, 214.

Compound 14 was independently synthesized by a published procedure[14] to aid its identification in the above mixture by means of GLC, GC/MS, and ^{1}H NMR analyses: ^{1}H NMR (CCl_4, Me_4Si) δ 1.27 (s, 3 H), 2.10 (s, 3 H), 3.18 (s, 6 H); MS, *m/e* (relative intensity) 101 (49) $(M - CH_3O)^+$, 89 (64) $(M - CH_3CO)^+$, 43 (100) $(CH_3CO)^+$, 32 (32) $(CH_3O)^+$.

The aqueous phase of the above-mentioned extraction was acidified with hydrochloric acid and again submitted to a continuous extraction with dichloromethane. The extract was dried over sodium sulfate and filtered; the filtrate was concentrated by vacuum distillation. The residue that remained (0.7 g) was a dark, resinous mass.

Reaction of 3,3-Dichloro-2-butanone (15) with Sodium Methoxide. Reaction of 24.5 g (175 mmol) of **15** in 40 mL of methanol with 21.6 g (400 mmol) of sodium methoxide in 100 mL of methanol was carried out and worked up as described above for **11**. Distillation of the extract obtained from the crude product gave 5.3 g of distillate and 6.4 g of a resinous residue. GLC analysis of the distillate (conditions as above) showed the peaks of **14** (90%) and of 12 additional, unidentified components. From the above data the yield of **14** was calculated to be 20%.

Distillation of the extract obtained from the acidified aqueous phase afforded 5.4 g of a distillate and 3.3 g of a resinous residue. GLC analysis of the distillate (conditions as above) showed the peaks of **16** (11%, t_R 7.9 min), **17** (67%, t_R 15.3 min), and of three unidentified components. From the above data the following yields have been calculated: 4% for **16**, and 17% for **17**. Compounds **16** and **17** have been isolated by preparative GLC (glass column 0.8 × 100 cm, 5% nitrile silicon oil on Chromosorb G; 60–160 °C at 4 °C/min) and identified by their ^{1}H NMR spectra ($CDCl_3$, Me_4Si). **16**: δ 1.93 (m, 3 H), 5.67 (m, 1 H), 6.27 (m, 1 H). **17**: δ 1.17 (d, J = 7.0 Hz, 3 H), 2.47–3.03 (m, 1 H), 3.33 (s, 3 H), 3.40–3.60 (m, 2 H).

Reaction of 1,3-Dichloro-2-butanone (20) with Sodium Methoxide. To 5 mL of methanol were added 1.1 g (8 mmol) of **20**[10] and 1.4 g (26 mmol) of sodium methoxide in 10 mL of methanol dropwise with stirring at −50 °C. The mixture was allowed to reach room temperature and was kept stirring for 3 h. GLC analysis of the crude product (column 0.3 × 500 cm, 5% Carbowax 20 on Chromosorb G; 60–160 °C at 2 °C/min) showed the peaks of **21** (13%), *cis*-**22** (36%), *trans*-**22** (16%), **23** (13%), **24** (1%), **25** (1%), **26** (3%), **30** (16%), and **14** (1%).[15]

Reaction of 2-Chloro-2-(1-chloroethyl)oxirane (18) with Sodium Methoxide. As described for **20**, a mixture of 500 mg (3.5 mmol) of **18**[10] in 3 mL of methanol and 540 mg (10 mmol) of sodium methoxide in 5 mL of methanol was allowed to react. GLC analysis (conditions as in the case of **20**) showed the peaks of *trans*-**22** (3%), **23** (11%), and **30** (86%).[15]

Reaction of 2-Chloro-2-(chloromethyl)-3-methyloxirane (19) with Sodium Methoxide. As described for **20**, a mixture of 1.5 g (11 mmol) of (*Z*/*E*)-**19**[10] in 5 mL of methanol and 2.7 g (50 mmol) of sodium methoxide in 20 mL of methanol was allowed to react. GLC analysis (conditions as in the case of **20**) showed the peaks of **14** (ca. 90%) and of **24**.[15]

Isolation and Identification of Products from the Reaction of 18–20 with Sodium Methoxide. Isolation of Products. The above-described reactions of **18–20** have been repeated, and the combined crude products added to water and extracted with dichloromethane. The extract was dried over sodium sulfate, and filtered, and the dichloromethane was removed by distillation at normal pressure. The residue (11.0 g) was distilled through a 10-cm packed column at 23–24 torr by gradually raising the bath temperature and collecting the distillates in cooled receivers. The following fractions were obtained: fraction 1, bp 25 °C, bath temperature 20–100 °C, receiver temperature −78 °C, 1.7 g; fraction 2, boiling point and bath temperature the same, receiver temperature −20 °C, 1.6 g; fraction 3, bp 25–55 °C, bath temperature 100–110 °C, receiver at room temperature, 4.1 g. The remaining liquid residue amounted to 3.0 g. From the above fractions the following compounds have been isolated by preparative GLC (column 0.8 × 500 cm, 5% Carbowax 20 M on Chromosorb G; 60–160 °C at 2 °C/min): *cis*-**22** and *trans*-**22** from fraction 1; **21**, **23**, and **25** from fraction 2, **14** and **30** from fraction 3, and **24** and **26** from the distillation residue.

Identification of Products. Compounds **21**, *cis*-**22**, and *trans*-**22** have been identified by comparison of their ^{1}H NMR, IR, and mass spectra with those of purchased samples. Compound **14** has been available from an independent synthesis and from the reaction of **11** with sodium methoxide, as described above. Compound **23** has been identified by comparison of its IR and ^{1}H NMR data with those published previously[16] and with those of an independently prepared sample.[17]

2,2,3-Trimethoxy-1-butanol (24): colorless liquid; ^{1}H NMR (CCl_4, Me_4Si) δ 1.15 (d, J = 7.0 Hz, 3 H), 2.72 (br, 1 H), 3.18 (s, 3 H), 3.28 (s, 3 H), 3.40 (s, 3 H); IR (film) 3500 cm^{-1} (OH); MS, *m/e* (relative intensity) 149 (6) $(M - OCH_3)^+$, 105 (100) $(M - CH_3CHOCH_3)^+$, 73 (34) $(C(OCH_3)_2)^+$, 59 (60) $(CH_3CHOCH_3)^+$, 45 (32) $(CH_2OCH_3)^+$, 31 (16) $(CH_3O)^+$.

Anal. Calcd for $C_7H_{16}O_4$: C, 51.20; H, 9.82. Found: C, 50.97; H, 9.80.

1,3-Dimethoxy-2-butanone (25): colorless liquid; ^{1}H NMR (CCl_4, Me_4Si) δ 1.25 (d, J = 7.0 Hz, 3 H), 3.33 (s, 3 H), 3.77 (q, J = 7.0 Hz, 1 H), 4.10 (s, 2 H); IR (film) 1740 cm^{-1} (C=O); MS, *m/e* (relative intensity) 132 (4) M^+, 59 (100) $(CH_3CHOCH_3)^+$, 45 (18) $(CH_2OCH_3)^+$, 31 (32) $(CH_3O)^+$.

Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.31; H, 9.00.

4-Chloro-3,3-dimethoxy-2-butanol (26): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.26 (d, J = 6.8 Hz, 3 H), 2.31 (br, 1 H), 3.35 (s, 3 H), 3.40 (s, 3 H), AB system with δ_A 3.42, δ_B 3.70, J_{AB} = 16.0 Hz (2 H), 3.11 (q, J = 6.8 Hz, 1 H); IR (film) 3470 cm^{-1} (OH); MS, *m/e* (relative intensity) 170, 168 (6, 3) M^+, 139, 137 (13, 39) $(M - CH_3O)^+$, 125, 123 (35, 100) $(M - CH_3CHOH)^+$, 121, 119 (4, 20) $(M - CH_3O - H_2O)^+$, 45 (58) $(CH_3CHOH)^+$, 43 (100) $(COCH_3)^+$, 31 (39) $(CH_3O)^+$; substance had a purity of ca. 90% by GLC.

1,1-Dimethoxy-2-butanone (30): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.07 (t, J = 7.0 Hz, 3 H), 2.60 (q, J = 7.0 Hz, 2 H), 3.41 (s, 6 H), 4.50 (s, 1 H), IR (film) 1730 cm^{-1} (C=O); MS, *m/e* (relative intensity) 101 (15) $(M - CH_3O)^+$, 75 (100) $(M - COCH_2CH_3)^+$, 57 (25) $(COCH_2CH_3)^+$, 43 (52) $(COCH_3)^+$, 31 (56) $(CH_3O)^+$. The above data were identical with those of a sample of **30** that was prepared by a published procedure.[18]

Registry No. *cis*-**1**, 78932-21-5; *trans*-**1**, 27521-50-2; **2**, 13422-65-6; **3**, 76955-39-0; **4**, 13547-70-1; **8**, 39195-77-2; **10**, 87938-47-4; **11**, 55949-61-6; **14**, 21983-72-2; **15**, 2648-57-9; **16**, 107-93-7; **17**, 10024-70-1; **18**, 51107-31-4; (*Z*)-**19**, 80212-73-3; (*E*)-**19**, 80212-74-4; **20**, 16714-77-5; **23**, 3136-17-2; **24**, 87938-48-5; **25**, 87938-49-6; **26**, 87938-50-9; **30**, 6342-57-0; $CH_3O^-Na^+$, 124-41-4.

(14) Brande, E. A.; Timmons, C. J. *J. Chem. Soc.* **1953**, 3131.
(15) The products were identified by coinjection with authentic samples and by comparison of the GC/MS data with the MS data of authentic samples.
(16) Fissekis, J. D.; Sweet, F. *J. Org. Chem.* **1973**, *38*, 1963.
(17) Doering, W. v. E.; Young, R. W. *J. Am. Chem. Soc.* **1952**, *74*, 2997.
(18) Royal, E. E.; Robinson, A. G. *J. Am. Chem. Soc.* **1956**, *78*, 4161.