All non-hydrogen atoms were located on an E map based upon 256 data with the largest E values.[22] The structure was refined by using SHELX[23] with weights of $w = \sigma^{-2}(F)$. Hydrogen atoms were located on a difference electron density map. An analysis of the variance after refinement of the data revealed no systematic variation of $\sum w(|F_o| - |F_c|)^{11}$ with either sin θ or F. The scattering factors for C and O were from Cromer and Mann[24] and the scattering factors for H were from Stewart, Davidson, and Simpson.[25] Atomic parameters, bond angles, and observed and calculated structure factors are included in the supplementary material.

Acknowledgment. We thank Dr. P. R. Pednekar (University of Alberta) for kindly obtaining the high-resolution mass spectrum of 8. Financial support of our study by the United States Army Armament Research and Development Command, the Naval Air Systems Command, The Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee is gratefully acknowledged. The X-ray crystallographic structure determination of **3c** was supported in part by a grant from the DHHS, National Cancer Institute, CA17562 (to D.v.d.H.); we also thank the University of Oklahoma Computing Center for providing computing facilities and service in this connection.

Supplementary Material Available: A list of atomic parameters, bond angles, and observed and calculated structure factors for **3c** (11 pages). Ordering information is given on any current masthead page.

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Enantioselective Ester Hydrolyses Employing *Rhizopus nigricans*. A Method of Preparing and Assigning the Absolute Stereochemistry of Cyclic Alcohols

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The mold *Rhizopus nigricans* has been used to hydrolyze enantioselectively the acetates of several series of benzocycloalken-3-ols and 2-substituted cycloalkanols to yield chiral alcohols. The configurations of the alcohols formed were established. The absolute stereochemistries of 25 of the 26 alcohols obtained were found to conform to a generalization based on the effective sizes of substituents on the carbinol carbon. The relative sizes of substituents required for agreement were identical with those employed in Horeau's method of establishing the absolute stereochemistry of the same compounds. The use of these microbially mediated hydrolyses to assign the absolute stereochemistry of cyclic secondary alcohols is compared to Horeau's method and to the use of empirical relations between the absolute stereochemistry of an enantiomer and the order, relative to its antipode, in which it is eluted from a chiral (Pirkle) column.

Recently we have shown[2,3] that the mold *Rhizopus nigricans* could be used to hydrolyze a series of racemic 1-arylalkyl acetates to yield alcohols enriched in one enantiomer, while the recovered acetate is enriched in the antipode. The absolute stereochemistry of the alcohol formed could be predicted by using a rule which states that the enantiomer shown in Figure 1, where R_1 is larger than R_2, is the one more rapidly hydrolyzed. In the acyclic series the aromatic ring (carbocyclic or heterocyclic) is always R_1 and an alkyl group (including tert-butyl) R_2. In addition to providing a new method for assigning the configurations of 1-arylalkanols, these hydrolyses can also be used in the preparation of synthetically useful amounts of chiral alcohols. These findings prompted us to examine the ability of *R. nigricans* to hydrolyze acetates of cyclic carbinols and to determine whether the rule accounts for the absolute stereochemistry of the alcohols formed. Since we wanted to examine as many compounds as possible and since it was important to compare our results with published information, substrates were chosen which satisfy the following criteria: (1) the absolute stereochemistry of the alcohol should be known; (2) it should be possible to compare the relative sizes of the same substituents in two series of esters in order to determine whether the relative sizes established in one series could be used in another one; (3) some of the alcohols should have been studied previously by Horeau's method[4] to provide an independent estimate of the relative sizes of substituents on the carbinol carbon; (4) in order to establish the general utility of the method some of the substrates studied should be alicyclic acetates.

Results

In probing the ability of *R. nigricans* to hydrolyze acetates of cyclic alcohols to yield chiral carbinols of a pre-

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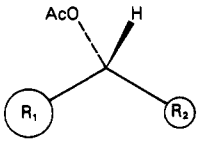
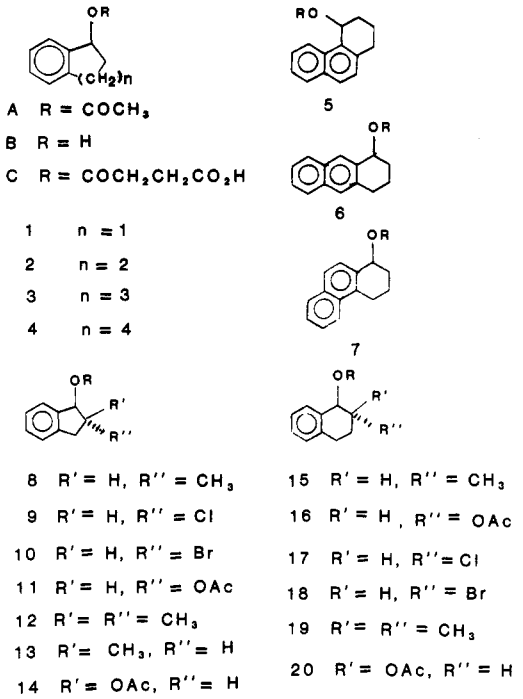


Figure 1. The enantiomer that is more rapidly hydrolyzed, where R_1 is effectively larger than R_2.

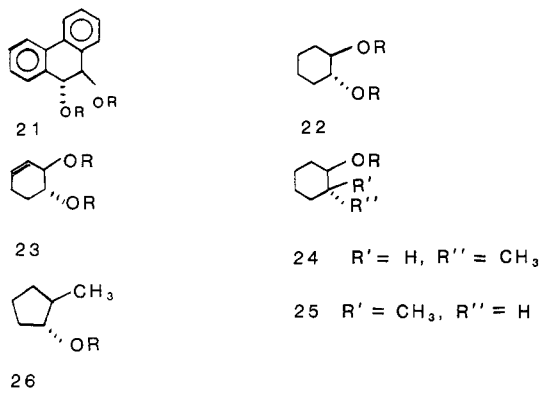
Chart I



dictable configuration, we first examined the effect of varying the size of the ring on the stereochemical course of the reaction. Preliminary experiments[3] established that the hydrolysis of **1A** and **2A** (Chart I) produced the corresponding *R* alcohols; this investigation has been extended to include the corresponding seven- and eight-membered analogues, **3B** and **4B**. Increasing the size of the benzocycloalkenol (compounds (**1B–4B**) does not affect the stereochemical course of these hydrolyses. The observed insensitivity of the configuration of the alcohols formed to these changes is consistent with expectations from the proposed rule, if it is assumed that the fused aromatic ring is the larger substituent, R_1.

While the number of substituents on the α-carbon of the alkyl group (R_2) in the acyclic esters did not affect the configurations of the carbinols formed,[2] it could not be assumed a priori that this would also be the case with cyclic acetates. We have therefore examined the effect of introducing cis and trans substituents on the carbon adjacent to the carbinol carbon in two series: 2-substituted 1-indanols and 2-substituted 1-tetralols, compounds **8A–14A** and **15A–20A**, respectively. The results given in Table I clearly indicate that the presence of a substituent on C-2 in 1-indanol and 1-tetralol alters the absolute stereochemistry at the resulting carbinol carbon. The configurations at C-1 of the 2-substituted compounds differ from that of the unsubstituted parents. In the case of the one exception, compound **13A**, the enantiomeric excess (ee) is small (6%). A comparison of the relative sizes of a *cis*- and *trans*-acetoxy can be made by examining the results for compounds **14A** and **11A** and for compounds **20A** and **16A**. A similar comparison can be made for a methyl substituent from compounds **8A** and **13A**. While the absolute stereochemistry of the carbinol formed at C-1 is the same in each of the six compounds, the ee of the trans-substituted compound in each comparison is larger than that of the cis.

Chart II



In order to establish the general utility of the method, we examined the hydrolyses of the alicyclic esters **22A–26A** (Chart II). The absence of aromatic functions and the high volatility of some of the compounds presented some technical difficulties. However, chiral alcohols with respectable ee's were obtained in most cases. Their absolute stereochemistry was also in accord with that expected from the rule and the assumption that a disubstituted carbon was larger than a monosubstituted one. These results suggest that *R. nigricans* can indeed hydrolyze a variety of cyclic esters as well as the previously described acyclic acetates to yield chiral alcohols; however, for alcohols such as **26B** and **13B**, which are obtained with low ee one should be extremely cautious in using these results to assign absolute stereochemistries.

While the rates for the hydrolyses of these compounds vary, only one compound, **21A**, was inert under the conditions employed. It is unclear whether the poor reactivity of **21A** is a consequence of its poor solubility and inability to enter the cell and reach the enzyme or because it is merely a poor substrate. We therefore chose to examine the hydrolysis of another ester of **21B**, in particular the succinate ester **21C**. This compound is less crystalline and more water soluble than **21A** and was hydrolyzed slowly by *R. nigricans* (~12% reaction in 48 h) to yield the diol **21B** (ee 8%). The absolute stereochemistry of the diol formed was that predicted by the rule.

Discussion

The absolute stereochemistries of the alcohols listed in Table I, except **13B** (see discussion below), are accounted for by the rule[3] if it is assumed that a fused aromatic ring is intermediate in size between a methylene group and a substituted methylene. In alicyclic esters where saturated carbons flank the carbinol carbon, a substituted methylene is effectively larger than an unsubstituted one. Earlier study of the hydrolyses of 1-arylalkyl acetates by *R. nigricans* showed[2] that the comparative sizes of aryl and alkyl groups were identical in Horeau's method and in these hydrolyses. Horeau[4] has reported that the absolute stereochemistry of **1A** and **2A** was accounted for by his method if it is assumed that the aromatic system is effectively larger than a methylene group. Brooks and Ketaly[5] have subjected samples of **3B** and **4B** to their microscale version of Horeau's method;[6] their results also account for the absolute stereochemistry of these com-

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Table I

racemic acetate	% recovd crude	% hydrolysis	predicted config	abs stereochem of alcohol formed (ee)	specific rotation, deg: acetate	specific rotation, deg: alcohol	ref to stereochem
1	95	53	1*R*	1*R* (59)	−48.4 (*c* 5.25, EtOH)	−13.8 (*c* 5.4, $CHCl_3$)	3, 15
2	64	27	1*R*	1*R* (71)	−15.2 (*c* 1.73, EtOH)	−16.0 (*c* 0.7, $CHCl_3$)	8
3	51	56	1*R*	1*R* (88)	−41.7 (*c* 1.40, $CHCl_3$)	+25.5 (*c* 3.93, $CHCl_3$)	12
4	41	58	1*R*	1*R* (71)	−33.0 (*c* 1.40, $CHCl_3$)	+25.0 (*c* 2.25, $CHCl_3$)	12
5	49	26	4*R*	4*R* (26)	−2.9 (*c* 0.55, $CHCl_3$)	+5.0 (*c* 0.38, acetone)	8
6	55	11	1*R*	1*R* (43)	−3.8 (*c* 1.93, $CHCl_3$)	−59.6 (*c* 0.51, $CHCl_3$)	8
7	37	35	1*R*	1*R* (54)	−24.3 (*c* 0.51, $CHCl_3$)	+39.1 (*c* 0.37, acetone)	8
8	57	44	1*S*,2*R*	1*S*,2*R* (38)	+25.1 (*c* 1.90, $CHCl_3$)	−3.8 (*c* 0.46, $CHCl_3$)	13
9	30	68	1*R*,2*R*	1*R*,2*R* (56)	+15.1 (*c* 0.97, $CHCl_3$)	−22.9 (*c* 3.89, $CHCl_3$)	23
10	64	32	1*R*,2*R*	1*R*,2*R* (98)	+12.5 (*c* 2.23, EtOH)	−28.5 (*c* 1.20, EtOH)	14
11		40	1*R*,2*R*	1*R*,2*R* (78)	+21.4 (*c* 1.10, $CHCl_3$)	−8.3 (*c* 0.805, EtOH)	14, 15
12	33	39	1*S*	1*S* (77)	+34.4 (*c* 1.04, $CHCl_3$)	+16.5 (*c* 0.66, $CHCl_3$)	13
13	71	57	1*S*,2*S*	1*R*,2*R* (6)	−7.47 (*c* 3.48, $CHCl_3$)	−1.83 (*c* 3.98, $CHCl_3$)	13
14	100	31[a]	1*R*,2*S*	1*R*,2*S* (12)	−22.7 (*c* 4.40, $CHCl_3$)	−6.1 (*c* 0.63, $CHCl_3$)	14, 15
15	65	42	1*S*,2*R*	1*S*,2*R* (22)	+8.25 (*c* 3.15, $CHCl_3$)	+20 (*c* 2.0, $CHCl_3$)	13
16		50	1*R*,2*R*	1*R*,2*R* (77)	+39.1 (*c* 5.06, $CHCl_3$)	+84.7 (*c* 0.89, $CHCl_3$)	19
17	83	19	1*R*,2*R*	1*R*,2*R* (18)	+7.9 (*c* 4.43, $CHCl_3$)	+15.2 (*c* 3.16, $CHCl_3$)	17
18		55	1*R*,2*R*	1*R*,2*R* (56[c])	+4.0 (*c* 4.86, $CHCl_3$)	+23.3 (*c* 0.41, $CHCl_3$)	17
19	48	55	1*S*	1*S*[b]	+57.6 (*c* 1.25, $CHCl_3$)	+24.8 (*c* 1.5, $CHCl_3$)	13, 16
20	39	65	1*R*,2*S*	1*R*,2*S* (20)	+120 (*c* 0.00, $CHCl_3$)	−7.5 (*c* 0.0, $CHCl_3$)	18
21		12	9*R*,10*R*	9*R*,10*R* (8)	−4.5 (*c* 0.22, $CHCl_3$)[d]	+10.9 (*c* 0.22, $CHCl_3$)	19
22	70	33	1*R*,2*R*	1*R*,2*R* (89)	+12.4 (*c* 1.20, $CHCl_3$)	−36.9 (*c* 1.4, H_2O)	20
23			1*R*,2*R*	1*R*,2*R* (95)		−72.4 (*c* 0.73, H_2O)	20
24		54	1*R*,2*R*	1*R*,2*R* (49)	+15.5	−4.2 (*c* 2.54, $CHCl_3$)	21
25		46	1*R*,2*S*	1*R*,2*S* (95)	+28.2 (*c* 2.01, $CHCl_3$)	−8.3 (*c* 2.12, $CHCl_3$)	21
26		85	1*R*,2*R*	1*R*,2*R* (2.4)	+27.3 (*c* 1.77, $CHCl_3$)	−1.1 (*c* 4.27, MeOH)	22

[a] Complete hydrolysis and an additional 14% of half-hydrolyzed material. [b] Specific rotation larger than reported in the literature. [c] Based on conversion to oxide. [d] Disuccinate.

pounds if the aromatic ring is the largest substituent. Thus, the relative sizes of substituents derived from Horeau's method and our enzymatic hydrolyses are identical (see Table I).

Several samples[4,7,8] have been reported in which it is necessary to reverse the usual sizes of a methylene and a fused aromatic ring in Horeau's method in order to reconcile the deduced and independently established absolute stereochemistries of the alcohol. The acetate of one such compound, **5B**, was hydrolyzed with *R. nigricans* and data on the alcohol formed in concert with the usual assumptions as to the relative sizes of a fused aromatic ring and a methylene group account for the known absolute stereochemistry of the compound. No changes in the usual sizes of aromatic rings and aliphatic substituents are required to interpret the hydrolysis results for **5A**. The studies on **8A** to **21A** were undertaken to examine the effect of substituents on the effective size of the adjacent saturated carbon; the results are given in Table I. The presence of a cis or trans substituent adjacent to the carbinol carbon *alters* the stereochemical course of the hydrolysis, so that it is necessary to assume that a vicinal substituted carbon is effectively larger than the fused aromatic system in each case except **13A**. There appear to be quantitative differences in the ee for cis and trans isomers, i.e., the ee's of the trans compounds are consistently larger than those of the corresponding cis compounds. These observations are consistent with the idea that if the relative sizes of the

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substituents on the carbinol carbon differ greatly, the enzyme easily differentiates between the two substituents, and the ee is large. As the relative sizes of the two substituents become similar, the enzyme is less able to distinguish between the substituents and the ee decreases. This interpretation implies that trans substituents on C-2 make the methine group effectively larger than the corresponding cis isomers. The effects associated with cis and trans substituents (compounds **12B** and **19B**) appear additive; i.e., the alcohols obtained have very large ee's as would be expected from the above analysis.

While the behavior of **13A** could not have been predicted from previous results, it appears that the presence of a small cis substituent at C-2 of 1-indanyl acetate makes the relative sizes of the fused aromatic ring and the group at C-2 almost equal. This would account for the small ee observed for the alcohol. The analysis of the stereochemical course of these hydrolyses based on the relative sizes of substituents should *only* be considered as a first approximation. Too little is known about the importance of other factors for an attempt to rationalize the result for **13A**. It is advisable, however, to be wary of assigning a configuration to an alcohol formed with a small ee.

Although we have few results with alicyclic esters (compounds **22B–26B**) in comparison with the aromatic examples, it is apparent that the former are readily hydrolyzed and the configurations of the resulting alcohols are consistent with expectations based on the above rule and the relative sizes of substituents on the carbinol carbon. Further study of alicyclic esters is planned in order to establish the scope and limitations of this method of assigning the configuration of a secondary alcohol.

Lutche et al. have examined the behavior of compounds **12B**, **15B**, and **19B** and other 2-substituted 1-indanols in Horeau's method.[9] In each case the investigators postulate that the substituted methylene group is effectively larger than the fused aromatic ring in order to reconcile their results with the known absolute stereochemistries of the compounds. Thus, the relative sizes of substituents are again identical in the two methods.

In addition to comparing our hydrolyses procedure to Horeau's method, it was also of some interest to compare our method with some recent reports on the use of a chiral HPLC column to accomplish the same task. Pirkle et al.[10] have recently prepared a chiral HPLC column and have demonstrated its ability to resolve a variety of 1-arylalkanols. They also suggested a chiral recognition mechanism to account for the absolute stereochemistry of the enantiomer preferentially retained by the column. Their results implied that the absolute stereochemistry of a new 1-arylalkanol could be assigned from the order in which enantiomers are eluted. We have investigated this suggestion[11] and found that the absolute stereochemistry about the carbinol carbon for the enantiomer preferentially retained on the column differed in the acyclic and cyclic carbinols. In addition, the relation between elution order and absolute stereochemistry was not constant for all acyclic or cyclic carbinols. The order for a series of 2-substituted 1-indanols and 1-tetralols differs from that of benzocyclohepten-3-ol and benzocycloocten-3-ol.[12] The alcohols can be grouped to provide a constant relationship between elution order and absolute stereochemistry about the hydroxyl-bearing carbon within each group. It is therefore useful to compare the information needed to assign the absolute stereochemistry of compounds **1A–26A** by the two methods. In using data on elution order to assign absolute stereochemistry, it is essential to place the compound in its proper subgroup. The number of groups and their characteristics may be incomplete; in contrast, the configuration of the alcohol formed in the microbially mediated hydrolyses depends predominantly, if not exclusively, on the relative sizes of substituents flanking the carbinol carbon. The relative sizes of substituents are simple and constant in this method. In examining the chromatographic behavior of a variety of substituted 1-indanols, 1-tetralols, and other benzocycloalkenols on a chiral Pirkle HPLC column, we found that a significant number of compounds were not resolved, so that it was impossible to assign stereochemistry. In contrast, the use of *R. nigricans* permitted the partial resolution of 25 out of 26 compounds examined. While some of the observed ee's were low, the data were generally sufficient to enable the investigator to make tentatve assignments of configuration. So far, the configuration of only one compound, **13B**, would be incorrectly assigned from data on the hydrolysis of the acetate and the usual assumptions of the relative sizes of a fused aromatic ring and a substituted methylene group. It should be noted that while the configuration of **26B** is correctly predicted, the ee of the alcohol is also very small. The enzyme appears to have limited ability to distinguish between enantiomers of a substituted cyclopentyl acetate. The chiral HPLC column was designed specifically to separate compounds that contain aromatic groups, while the microbial hydrolyses work as readily with alicyclic esters as they do with aromatic ones. The use of *R. nigricans* therefore appears to offer a more reliable, consistent, and general method of assigning the configuration of secondary alcohols than does the use of chiral HPLC.

Synthetic Implications

Two methods of preparing strongly enriched samples of either enantiomer were described in an earlier study.[2] The first of these used a chemical method for inverting the configuration about the carbinol carbon;[8] the second one involved carrying the partial hydrolyses further to completion and then utilizing the recovered ester. The observation that the configuration at the carbinol carbon of a cycloalkenol is controlled by the presence or absence of substituents at a vicinal carbon offers a third method of preparing a specific enantiomer: for preparation of the *R* enantiomers of **1B–4B** the unsubstituted parent ester would be used as a substrate. If the *S* enantiomer is needed, the *trans*-2-bromo derivative would be used as a substrate, and the resulting alcohol would be reacetylated. The halogen and acetyl group are then easily removed by

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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

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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

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