10321-71-8; 3-[(carboxymethyl)thio]-4-methylpentanoic acid, 75782-70-6; 4,5-dihydro-5-(1-methylethyl)-3(2*H*)-thiophenone, 75782-71-7; 4,5-dihydro-5-(1-methylethyl)-3(2*H*)-thiophenone oxime, 75782-72-8; 3-amino-5-(1-methylethyl)thiophene HCl, 75782-73-9; 1,4-dibromobutane, 110-52-1; 4,4-dimethyl-2-pentenoic acid, 6945-35-3; 3-[(carboxymethyl)thio]-4,4-dimethylpentanoic acid, 75782-74-0; 4,5-dihydro-5-(1,1-dimethylethyl)-3(2*H*)-thiophenone, 75782-75-1; 4,5-dihydro-5-(1,1-dimethylethyl)-3(2*H*)-thiophenone oxime, 75782-76-2; 3-amino-5-(1,1-dimethylethyl)thiophene HCl, 75782-77-3; 3-(2-methoxyphenyl)propenoic acid, 6099-03-2; 3-[(carboxymethyl)-thio]-3-(2-methoxyphenyl)propanoic acid, 75782-78-4; 4,5-dihydro-5-(2-methoxyphenyl)-3(2*H*)-thiophenone, 75782-79-5; 2,3-dihydro-2-(2-methoxyphenyl)-4-(1-pyrrolidinyl)thiophene, 75790-45-3; 3-(1-pyrrolidinyl)benzo[*b*]thiophene, 40311-37-3; 4,5-dihydro-5-phenyl-3-(2*H*)-thiophenone, 36748-19-3; 4,5-dihydro-5-phenyl-3(2*H*)-thiophenone oxime, 75782-80-8; 3-amino-5-phenylthiophene, 75782-81-9; 1,4-dibromobutane-*1,1,4,4-d*$_4$, 36684-45-4; phenyl isocyanate, 103-71-9; dicyanoacetylene, 1071-98-3; methyl propiolate, 922-67-8; morpholine, 110-91-8; DMAD, 762-42-5.

**Supplementary Material Available:** X-ray structure, fractional atomic coordinates, mean square amplitudes of thermal vibration, bond distances, and bond angles of **6e** (6 pages). Ordering information is given on any current masthead page.

# Effect of an Alkynyl Group on the Regio- and Stereochemistry of the Ring Opening of 1,2-Epoxides. Ring-Opening Reactions of 1-Ethynyl-1,2-epoxycyclohexane

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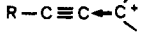
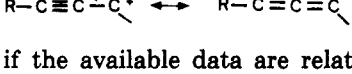
The regio- and stereochemistry of the ring-opening reactions of 1-ethynyl-1,2-epoxycyclohexane (**1**) under acidic conditions have been examined. The reactions were almost completely regiospecific, giving mainly products arising from attack by the nucleophile on the tertiary carbon. The stereoselectivity was not completely anti, affording mixtures of syn and anti addition products, which vary markedly with the reaction conditions (a maximum of 65% syn addition was observed in the reaction of **1** with $CCl_3COOH$ in $CH_2Cl_2$). The results were rationalized through a mechanism analogous to that previously admitted for aryloxiranes, which implies intermediate structures with a discrete carbocationic character and shows that the ethynyl group has a discrete capability of stabilizing an adjacent carbenium ion. Comparison of the relative percentages of syn opening observed in the reactions of **1** with the corresponding ones obtained in the reactions of the analogous phenyl-substituted (**9**) and methyl-substituted (**10**) epoxides seems to indicate that the stabilizing effect of an ethynyl group is lower than that of a phenyl but, contrary to expectations, higher than that of a methyl.

It is well-known that the ring opening of aliphatic and cycloaliphatic oxiranes under acidic conditions occurs with almost complete inversion of configuration.[1,2] However, when substituents as double bonds or aromatic systems are directly linked to the epoxide ring, the steric course of the ring-opening reactions is not entirely anti.[1,3] The stereoselectivity of these reactions is highly variable, depending to a large extent on the structure of the epoxide and on the reaction conditions in general. It can range from an excess of anti ring opening to complete syn stereoselectivity. As with the reactions of 1-aryl-substituted 1,2-epoxides, it has been found that there is strict relationship between the capability of the aromatic system to stabilize the carbocationic center at the time of the breaking of the benzylic C–O bond of the protonated oxirane and the percentage of syn opening.[1b,c]

The effect of an alkynyl group in stabilizing an adjacent carbenium ion should result from the sum of two conflicting effects: its electron withdrawing effect (expression 1) and its mesomeric electron releasing effect (expression 2).[4]



(1)



(2)

Even if the available data are relatively scarce, the solvolysis rates for tertiary halides (2-substituted 2-propyl halides)[4] reflect the capability of an ethynyl group to stabilize an adjacent carbocation is much lower not only than that of an ethenyl or phenyl group but also than that of an alkyl group.[4] The same order could be also derived from the $\sigma_p^+$ values of the same groups[5,6] (see Table I). The $\sigma_m$ substituent constant for the ethynyl group,[5] 0.205,

Table I. Selected Substituent Constants

| substituent | $\sigma_p^+$ | $\sigma_m^+$ | $\sigma_m$ |
|---|---|---|---|
| $C_2H_5$ | −0.265[a] | −0.064[a] | −0.07[c] |
| $C_6H_5$ | −0.179[a] | 0.109[a] | 0.06[c] |
| HC≡C | 0.179[b] | 0.330[b] | 0.205[b] |

[a] Reference 6. [b] Reference 5. [c] Reference 7.

(1) Buchanan, J. G.; Sable, H. Z. in "Selective Organic Transformations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1972; Vol. 1, p 1.
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(3) (a) Battistini, C.; Crotti, P.; Ferretti, M.; Macchia F. *J. Org. Chem.* **1977**, *42*, 4067. (b) Battistini, C.; Balsamo, A.; Berti, G.; Crotti, P.; Macchia, B.; Macchia, F. *J. Chem. Soc., Chem. Commun.* **1974**, 712. (c) Balsamo, A., Crotti, P.; Macchia, B.; Macchia, F. *Tetrahedron* **1973**, *29*, 199 and references therein cited.
(4) Richey, H. G., Jr.; Richey, J. M. In "Carbenium Ions"; Olah, G. A., Schleyer, P. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2, p 931.
(5) Landgrebe, J. A.; Rynbrandt, R. H. *J. Org. Chem.* **1966**, *31*, 2585.
(6) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.
(7) McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420.

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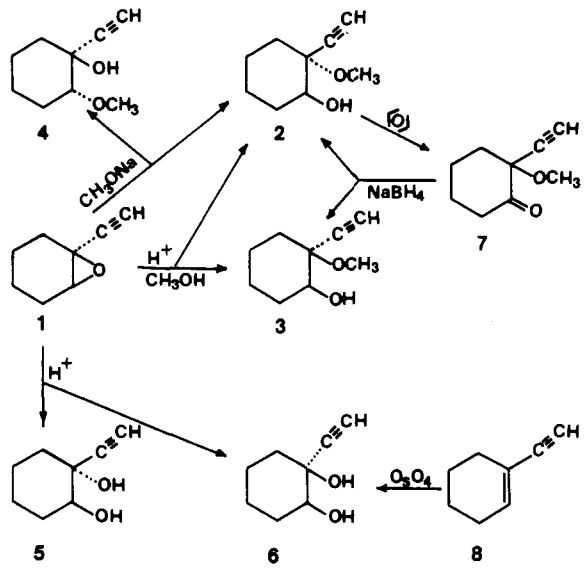
Scheme I



indicates a marked electron-withdrawing effect.[4,5] On the other hand, on the assumption that $\sigma_p^+ - \sigma_m^+$ can be used as a crude measure of direct resonance effects of a substituent,[5] the negative value of $\sigma_p^+ - \sigma_m^+$ for the ethynyl group, −0.16, is a reflection of the presence of a substantial electron-donating resonance effect (expression 2).[4,5] Furthermore, the large increase of solvolysis rates of 2-ethynyl-2-propyl halides accompanying the introduction of a methyl group on the terminal ethynylic carbon confirms a considerable contribution of the tautomeric electron-releasing effect (expression 2) in stabilizing the alkynyl carbocation.

In order to obtain information on the effect of an alkynyl group on the regio- and stereochemistry of the ring opening of 1,2-epoxides, we decided to undertake an examination of some reactions of 1-ethynyl-1,2-epoxycyclohexane (1).

## Results

The reaction of 1 with sodium methoxide in methanol yielded a mixture of trans ethers 2 and 4 in a ratio of 25/75 (Scheme I), from which the secondary ether 4 can be isolated pure after preparative TLC. Under different conditions the acid-catalyzed methanolysis of 1 is not completely stereorandom. Mixtures consisting of the trans tertiary ether 2 accompanied by small amounts of the cis epimer 3 and of the regioisomer 4 (~1–2%) (see Table II) are formed. From the reaction mixture in methanol, pure 2 was separated by preparative TLC. Hydroxy ether 2 was converted by oxidation into the keto ether 7, which on reduction with $NaBH_4$ yielded a 59/41 mixture of 2 and 3, from which the latter can be obtained pure by preparative TLC.

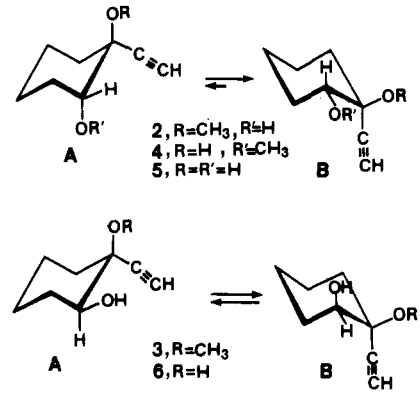
The acid hydrolysis of 1 leads to a mixture of the two diols *cis*-6 and *trans*-5 in which the latter markedly predominates (see Table II). Cis diol 6 can be obtained pure through catalytic $OsO_4$ dihydroxylation[8] of the enyne 8. When the ring opening of 1 is effected with acetic acid in the presence of a catalytic amount of *p*-toluenesulfonic acid, and with trichloroacetic acid in nonprotic solvents, one obtains, after saponification of the monoesters, mixtures containing marked amounts of the syn addition product (the cis diol 6). Under the latter reaction conditions the amount of syn addition products changes noticeably with the type of the nonprotic solvent (see Table II; from 10% to 65% on passing from cyclohexane to $CH_2Cl_2$). An analogous solvent–stereoselectivity dependence has been observed in the ring opening of aryl-substituted oxiranes.[3c] The addition of salt ($LiClO_4$) only slightly modifies the stereoselectivity of these reactions (slight increase of syn-addition products).

Table II. Stereoselectivity of the Ring-Opening Reactions of Epoxide 1 under Acid Conditions

| solvent | acid | % syn adduct | % anti adduct |
|---|---|---|---|
| MeOH | $H_2SO_4$ | 1.0[c] | 99.0[d] |
| MeOH-$LiClO_4$[a] | TsOH | 0.5[c] | 99.5[d] |
| MeOH-$CH_2Cl_2$[b] | TsOH | 2.5[c] | 97.5[d] |
| $H_2O$ | $H_2SO_4$ | 2.0[e] | 98.0[f] |
| cyclohexane | $CCl_3COOH$ | 11.0[e,g] | 89.0[f,g] |
| $CCl_4$ | $CCl_3COOH$ | 16.5[e,g] | 83.5[f,g] |
| benzene | $CCl_3COOH$ | 42.0[e,g] | 58.0[f,g] |
| $CHCl_3$ | $CCl_3COOH$ | 44.5[e,g] | 55.5[f,g] |
| $CH_2Cl_2$ | $CCl_3COOH$ | 65.0[e,g] | 35.0[f,g] |
| $CH_3COOH$ | TsOH | 24.5[e,g] | 75.5[f,g] |
| $CH_3COOH$-$LiClO_4$[a] | TsOH | 26.0[e,g] | 74.0[f,g] |

[a] 0.5 M solution in $LiClO_4$. [b] Molar ratio of epoxide/acid/MeOH of 1:0.1:6. [c] Cis hydroxy ether 3. [d] Trans hydroxy ether 2 accompanied by small amounts (1–2%) of the regioisomer 4. [e] Trans diol 5. [f] Cis diol 6. [g] After saponification of the crude reaction mixture.

Scheme II



Compounds 2 and 3 have not been previously described whereas compound 4 has been obtained,[9] but not isolated and characterized. The diols 5 and 6 were prepared previously[10,11] by different methods. The structures and configurations of hydroxy ethers 2–4 have been deduced and those of the diols 6 and 7 confirmed by NMR spectroscopy and by IR studies in the 3000–3600-$cm^{-1}$ range. These data also give interesting information on the conformational equlibria of 2–6. It can be derived that in trans compounds 2, 4, and 5 conformation B (ethynyl group axial) is markedly favored (see Scheme II): one can observe the presence of a strong band due to an OH···O interaction in the IR spectra in dilute $CCl_4$[12–16] and very high values of the half-bandwidth of the signal of the methynyl pro-

(8) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.

(9) Battioni, J.-P.; Chadkiewicz, W. *Bull. Soc. Chim. Fr.* **1977**, 320.
(10) Preuss, R.; Willig, G. *Arzneim.-Forsch.* **1963**, *13*, 155.
(11) Murata, T. *Chem. Pharm. Bull.* **1961**, *9*, 167.
(12) Tichi, M. *Adv. Org. Chem.* **1965**, *5*, 115.
(13) Macchia, B.; Macchia, F.; Monti, L. *Gazz. Chim. Ital.* **1970**, *100*, 35.
(14) Battistini, C.; Crotti, P.; Macchia, F. *Gazz. Chim. Ital.* **1977**, *107*, 153.
(15) Berti, G.; Macchia, B.; Macchia, F. *Tetrahedron* **1968**, *24*, 1755; **1972**, *28*, 1299.
(16) Battistini, C.; Crotti, P.; Damiani, D.; Macchia, F. *J. Org. Chem.* **1979**, *44*, 1643.

Scheme III

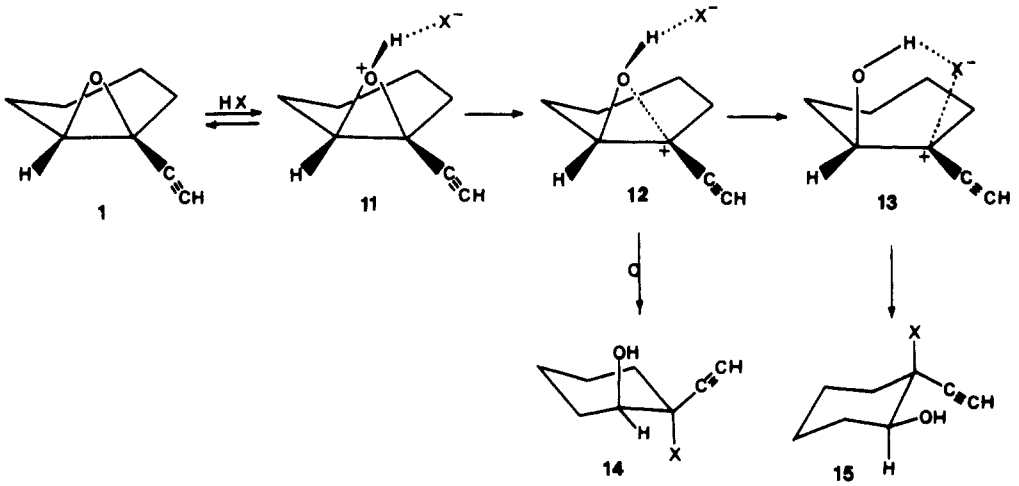
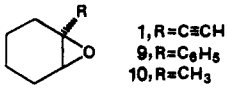



Table III. Stereoselectivity of the Trichloroacetolysis and of the Hydrolysis of Epoxides 1, 9, and 10




| epoxide | acid | solvent | % syn adduct | % anti adduct |
|---|---|---|---|---|
| 1, R = C≡CH | $CCl_3COOH$ | benzene | 42 | 58 |
| 9, R = $C_6H_5$ [a] | $CCl_3COOH$ | benzene | 100 | <0.2 |
| 10, R = $CH_3$ [b] | $CCl_3COOH$ | benzene | 6 | 94 |
| 1, R = C≡CH | $H_2SO_4$ | $H_2O$ | 2 | 98 |
| 9, R = $C_6H_5$ [c] | $H_2SO_4$ | $H_2O$ | 63 | 37 |
| 10, R = $CH_3$ [d] | $H_2SO_4$ | $H_2O$ | <0.2 | 100 |

[a] Reference 19. [b] Reference 2. [c] Reference 3b. [d] Unpublished results.

ton[15-17] $\beta$ to the ethynyl group in the NMR. On the other hand, the values of the half-bandwidth of the methynyl proton in cis compounds **3** and **6** are intermediate between those of an axial proton and those of an equatorial one[15-17] and are consistent with an equilibrium between the conformers A and B. These results seem to be ascribed to the very low conformational *A* value for the ethynyl group.[18]

## Discussion

The most interesting feature in the reactions of epoxide **1** is the significant lack of complete anti stereoselectivity in the ring opening and the high variability of the syn/anti ratio with the reactions conditions. Futhermore, some interesting points arise from a comparison of the reactions of **1** with the corresponding ones of the analogous phenyl- and methyl-substituted epoxides **9** and **10**, respectively (see Table III). The percentages of syn addition observed for the reactions of **1** are much lower than those obtained in the reactions of the phenyl-substituted oxirane **9** but significantly higher than those observed in the reactions of the methyl-substituted epoxide **10**.

The regioselectivity and the lack of complete anti stereoselectivity in the reactions of **1** suggest the intervention in the ring opening of intermediate structures with a discrete carbocationic character. Even if tentative, a mechanism it may be suggested, in order to rationalize the stereochemical results (see Scheme III; no conformational implication is given to formulas), which is analogous to that admitted for aryloxiranes.[3a,b,16,20] According to this mechanism, the protonated oxirane **11** can lead to an intramolecular intimate ion/dipole pair (**12**) which on attack of the nucleophile from the backside affords the anti products (**14**). On the other hand, an internal rearrangement of **12** with further loosening of the dipole (OH) from the carbocation $\alpha$ to the ethynyl group leads to a nucleophile separated ion/dipole pair (**13**), which collapses to afford the syn adduct (**15**). The higher percentages of syn products observed in the reactions of **1** in nonprotic solvents are in agreement with analogous results obtained with aryloxiranes.[3c,19] The strong solvent–stereoselectivity dependence observed in the trichloroacetolysis of **1** in nonprotic solvents can be ascribed, as in the case of aryloxiranes,[3c] to a backside nucleophilic solvation which should stabilize the more carbocation-like intermediate **13** and therefore favor the attack of the nucleophile from the syn side. This effect should roughly increase with the polarity of the solvent.[3c] Somewhat surprisingly, the addition of salt causes only a small increase of the syn stereoselectivity. On the basis of the result obtained with aryloxiranes, a larger effect could have been expected.[3a]

Finally, let us assume that, in general, as it has been shown previously for the ring opening of aryloxiranes,[1b,c] the percentages of syn opening is linked directly to the stability of the carbocation **13**. The results obtained show that the ethynyl group, notwithstanding its marked electron-withdrawing inductive effect (expression 1), has a discrete capability of stabilizing an adjacent carbocation, and this should be ascribed to the ability of this group to supply electrons to the cationic center through resonance (expression 2). Furthermore, the data in Table III seem to indicate that, contrary to the expectations, the stabilizing effect of an ethynyl group is lower than that of a phenyl group but higher than that of a methyl group.

## Experimental Section

Melting points were determined on a Kofler apparatus and are uncorrected. IR spectra for comparison between compounds were taken on paraffin oil mulls on a Perkin-Elmer Infracord Model 137, and those for the detemination of OH stretching bands were taken with a Perkin-Elmer Model 257 double-beam grating spectrophotometer in dried ($P_2O_5$) $CCl_4$, and the indene band at 3110 $cm^{-1}$ was used as calibration standard; a quartz cell of 2-cm optical length was employed, and the concentration of the solution was $5 \times 10^{-3}$ M or lower to prevent intermolecular association.

(17) Jackman, L. M.; Sternhell, S. "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; p 288.
(18) Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.
(19) Berti, G.; Bottari, F.; Macchia B.; Macchia F. *Tetrahedron* **1965**, *21*, 3277.
(20) Battistini, C.; Crotti, P.; Macchia F. *Tetrahedron Lett.* **1975**, 2091.

NMR spectra were determined on ~10% $CDCl_3$ solutions with a JEOL C 60 HL spectrometer using $Me_4Si$ as an internal standard. In the cases of compounds **2** and **3** the NMR spectra were also measured with an XL-100 A spectrometer. GLC analyses of the mixtures of diols **5** and **6** were run on a Perkin-Elmer apparatus Model F 11 with a flame-ionization detector and glass columns (1.5 m × 2.5 mm) packed with 3% neopentylglycol succinate on 80–100-mesh silanized Chromosorb W (column 100 °C, evaporator and detector 180 °C; nitrogen flow rate 40 mL/min); the order of increasing retention times was **6** < **5**. GLC analyses of mixtures of hydroxy ethers **2–4** were performed on a Carlo Erba Fractovap GV apparatus with a flame-ionization detector with glass columns (1.5 m × 2.5 mm) packed with 10% Carbowax 20M on 80–100-mesh silanized Chromosorb W (column 115 °C, evaporator and detector 210 °C; nitrogen flow rate 30 mL/min); the order of increasing retention times was **3** < **2** < **4**. Preparative TLC was performed on 2-mm-layer silica gel plates (Merck $F_{254}$) containing a fluorescent indicator; the TLC plates were visualized first by UV light (254 nm) and then by spraying with 1 N $K_2Cr_2O_7$ in 40% aqueous sulfuric acid followed by gentle heating. All comparisons between compounds were made on the basis of IR and NMR spectra and GLC. Magnesium sulfate was always used as drying agent. Evaporations were done in vacuo (rotating evaporator). Cyclohexane, $CCl_4$, $CHCl_3$, and $CH_2Cl_2$ were refluxed on $P_2O_5$ and rectified. Benzene was washed with concentrated sulfuric acid, kept at reflux over sodium, and distilled.

**1-Ethynylcyclohexene (8)** was prepared as previously described:[21] bp 57–58 °C (40 mm) [lit.[21] bp 71–72 °C (60 mm)].

**1-Ethynylcyclohexene Oxide (1).** A solution of **8** (25.7 g, 0.243 mol) in $CHCl_3$ (70 mL) was treated dropwise (with stirring) with a 0.435 M solution of peroxybenzoic acid[23] in $CHCl_3$ (560 mL, 0.243 mol), while the temperature was kept at 0 °C. The resulting solution was left 48 h at 0 °C and then washed (water, 10% aqueous $Na_2CO_3$, water), dried, and evaporated to yield crude **1** (28.5 g) as an oil. The oil was distilled in the presence of powdered KOH [bp 72–73 °C (28 mm)] to give **1** (23.2 g) slightly impure for carbonylic products (IR), which crystallized spontaneously. Recrystallization from petroleum ether (bp 30–50 °C) at −5 °C yielded pure **1**: 22.3 g; mp 41.5–42 °C [lit.[21] oil, bp 70–72 °C (15 mm)].

**Reaction of 1 with Sodium Methoxide in Methanol.** A solution of sodium methoxide (13.4 g) in anhydrous methanol (120 mL) was added to a solution of **1** (1.0 g) in anhydrous methanol (20 mL), and the resulting mixture was maintained at gentle reflux for 24 h, diluted with water, and extracted with ether. Evaporation of the washed (water) ether extracts yielded a residue (1.1 g) mainly consisting of the ethers **2** and **4** in a ratio of 25:75. When the mixture was subjected to preparative TLC (an 8:2 mixture of petroleum ether and ether was used as the eluent; elution was repeated eight times), extraction of the lower band yielded **4** still contaminated with **2** (GLC).

Further TLC of impure **4** under the same conditions gave pure **1-ethynyl-*trans*-2-methoxy-*r*-1-cyclohexanol (4)**: 0.120 g; oil; IR ($CCl_4$) $\nu$ 3605 (weak band, OH···C≡C, interaction between the hydroxyl and the triple bond bonded on the same carbon atom), 3580 $cm^{-1}$ (OH···O); NMR $\delta$ 3.05 (m, 1, $W_{1/2}$ = 18 Hz, $CHOCH_3$).

**2-Ethynyl-*trans*-2-methoxy-*r*-1-cyclohexanol (2).** A solution of **1** (2.0 g) in 0.2 N $H_2SO_4$ (200 mL) was stirred at room temperature for 30 min, quenched with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$, and extracted with ether. Evaporation of the washed ($H_2O$) and dried ether extracts yielded a residue (2.25 g) mainly consisting of **2** accompanied by small amounts of **3** and **4** (see Table II). This residue was chromatographed through a 1.8 × 52 cm column of silica gel by elution in succession with petroleum ether (1200 mL), 98:2 petroleum ether–ether (1600 mL), and 96:4 petroleum ether–ether (3000 mL). Elution with 96:4 petroleum ether–ether (2000 mL) yielded pure **3**: 0.60 g; oil; IR ($CCl_4$) $\nu$ 3595 (OH···O) $cm^{-1}$; NMR $\delta$ 3.45 (m, 1, $W_{1/2}$ > 16 Hz, the signal is partially overlapped with the one of the methyl group, CHOH). Anal. Calcd for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 70.16; H, 9.42.

**2-Ethynyl-2-methoxycyclohexanone (7).** A solution of **2** (0.560 g, 3.63 mmol) in acetone (70 mL) was treated dropwise with Jones reagent[22] (2.0 mL). After 30 min at room temperature the mixture was diluted with water and extracted with ether. Evaporation of the washed ($H_2O$, saturated aqueous $NaHCO_3$, and $H_2O$) and dried ether extracts gave an oily residue (0.490 g) of crude **7** which was purified by preparative TLC (a 9:1 mixture of petroleum ether and ether was used as the eluent; elution was repeated four times). Extraction of the band with the highest $R_f$ yielded pure **7**: 0.360 g; IR $\lambda$ 5.88 $\mu$m (C=O); NMR $\delta$ 3.51 (s, 1, $OCH_3$), 2.82 (s, 1, C≡CH), 2.66 (m, 2, $CH_2CO$). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.94. Found: C, 70.83; H, 8.07.

**Reduction of 7 with $NaBH_4$.** A solution of **7** (0.360 g, 2.36 mmol) in 95% ethanol (38 mL) was treated with $NaBH_4$ (0.40 g, 10.56 mmol) and stirred at room temperature for 3 h. The reaction mixture was acidified with 2 N $H_2SO_4$, diluted with water, and extracted with ether. Evaporation of the washed (saturated aqueous $NaHCO_3$ and $H_2O$) ether extracts gave a residue (0.320 g) consisting of a 59:41 mixture of **2** and **3** (GLC), which was subjected to preparative TLC (a 75:25 mixture of petroleum ether and ether was used as the eluent; elution was repeated four times). Extraction of the two main bands (the faster moving band contained **3**) gave **2** (0.070 g) and **2-ethynyl-*cis*-2-methoxy-*r*-1-cyclohexanol (3)**: 0.070 g; oil; IR ($CCl_4$) $\nu$ 3605 (weak band, OH···C≡C, interaction between the hydroxyl and the triple bond bonded on the same carbon atom), 3580 (OH···O) $cm^{-1}$. NMR $\delta$ 3.87 (m, 1, $W_{1/2}$ = 10.9 Hz, CHOH). Anal. Calcd for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 69.80; H, 9.38.

**1-Ethynyl-*r*-1-*t*-2-cyclohexane-1,2-diol (5). Method A.** A suspension of **1** (2.00 g) in 0.2 N aqueous $H_2SO_4$ was stirred at room temperature for 3.5 h, treated with solid $NaHCO_3$ and NaCl, and extracted thoroughly with ether. Evaporation of the washed ($H_2O$) ether extracts yielded a residue (2.10 g) which was crystallized from petroleum ether (bp 60–80 °C) to give pure **5**: 1.51 g; mp 76.5–77.5 °C (lit.[11] mp 73.5–74.5 °C); IR ($CCl_4$) $\nu$ 3605 (weak band, OH···C≡C, interaction between the hydroxyl and the triple bond bonded on the same carbon atom), 3576 (OH···O) $cm^{-1}$; NMR $\delta$ 3.50 (m, 1, $W_{1/2}$ = 17.3 Hz, CHOH).

**Method B.** Epoxide **1** (0.200 g) was treated with stirring with 2 N aqueous KOH (20 mL) and then heated at 100 °C for 1 h. After being cooled, the reaction mixture was extracted with ether, and the dried extracts were evaporated to dryness. The solid residue (0.160 g) was crystallized from petroleum ether (bp 60–80 °C) to yield **5**: 0.090 g; mp 76.0–76.5 °C.

**1-Ethynyl-*r*-1-*c*-2-cyclohexane-1,2-diol (6).** A mixture of *N*-Methylmorpholine *N*-oxide monohydrate[8] (3.03 g, 22.4 mmol), water (9.4 mL), acetone (2 mL), and osmium tetraoxide (0.020 g) in *tert*-butyl alcohol (2.0 mL) was treated with **8** (2.00 g, 18.9 mmol) in acetone (4 mL). The resulting mixture was maintained at room temperature with a water bath for 1 h and then stirred overnight at room temperature under nitrogen. After this time, the reaction mixture was added to a slurry of $NaHSO_3$ (0.20 g), magnesium silicate (2.30 g), and water (25 mL), and then the magnesium silicate was filtered. The filtrate was acidified (pH 2) with 1 N $H_2SO_4$, saturated with NaCl, and thoroughly extracted with ether. The ether extracts were washed with a small amount of NaCl-saturated water, dried, and evaporated to yield a residue (1.30 g), which was purified thorugh a silica gel column. Elution with 8:2 petroleum ether–ether yielded a crystalline product (1.30 g) consisting of **6**. Recrystallization from petroleum ether (bp 40–70 °C) gave pure **6**: 0.40 g; mp 68.5-69 °C; IR ($CCl_4$) $\nu$ 3605 (weak band, OH···C≡C, interaction between the hydroxyl and the triple bond bonded on the same carbon atom), 3586 (OH···C≡C, interaction between the hydroxyl and the triple bond bonded on vicinal carbon atoms), 3568 (OH···O) $cm^{-1}$; NMR $\delta$ 3.78 (m, 1, $W_{1/2}$ = 13.0 Hz, CHOH). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.62. Found: C, 68.72; H, 8.43. Compound **6** was previously prepared by oxidation with $KMnO_4$, but it was described to be unstable and oily.[11]

**Acid-Catalyzed Reactions of 1 in Water, Methanol, and Acetic Acid.** A suspension (water) or a solution (methanol and acetic acid) of the epoxide (0.100 g, 0.81 mmol) in a 0.2 N solution of the acid ($H_2SO_4$ for the reactions in water, and *p*-toluensulfonic acid monohydrate for the reactions in methanol and acetic acid)

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in the solvent (10 mL) was stirred at 25 °C for 60 min (reaction in water), 20 min (reaction in methanol), or 30 min (reaction in acetic acid), quenched with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$ (in the case of the reaction in acetic acid the mixture was previously diluted with water), and thoroughly extracted with ether. Evaporation of the washed (NaCl-saturated $H_2O$) ether extracts yielded mixtures consisting of diols **5** and **6** (reaction in water), hydroxy ethers **2–4** (reaction in methanol), or monoacetates (reaction in acetic acid) which were analyzed by GLC (see Table II), except for the reaction carried out in acetic acid. The crude product obtained from the reaction in acetic acid was analyzed by GLC after saponification of the monoacetates to the corresponding diols **5** and **6** as described later for the reactions of **1** with trichloroacetic acid. The reaction of **1** in methanol and that in acetic acid were also performed in the presence of anhydrous $LiClO_4$ (1.0 M) to give the results reported in Table II.

The solvolysis addition products of these reactions were completely stable under the reaction conditions used.

**Reactions of Epoxide 1 with Trichloroacetic Acid in Several Solvents.** The reactions were carried out in anhydrous benzene, cyclohexane, $CCl_4$, $CHCl_3$, and $CH_2Cl_2$ in the following way. A solution of **1** (0.100 g, 0.81 mmol) in the solvent (9 mL) at 25 °C was treated with a 1 M solution of trichloroacetic acid in the same solvent (1.0 mL), stirred 1 h at the same temperature, washed with saturated aqueous $NaHCO_3$ and water, and evaporated to dryness. The residue obtained, consisting mainly of mixtures of monotrichloroacetates was hydrolyzed in the following way. The crude product was dissolved in freshly distilled THF (8 mL), treated with 1 M KOH in ethanol (2.5 mL), and then left 5 h at room temperature. The reaction mixture was diluted with water, saturated with NaCl and extracted four times with ether. Evaporation of the washed (NaCl-saturated $H_2O$) and dried ether extracts yielded a mixture of **5** and **6** which was analyzed by GLC (see Table II). Reaction of **1** in each solvent carried out under the same conditions, but being stopped after a longer reaction time of contact with the acid, yielded the same product composition within experimental error. Experiments were carried out in order to verify if the diols **5** and **6** are stable under the saponification conditions, and if the method of saponification used does not alter the stereoselectivity of the reactions.

**Reaction of 1 with Methanol in Methylene Dichloride in the Presence of *p*-Toluenesulfonic Acid.** To the epoxide **1** (0.100 g, 0.81 mmol) was added a solution of *p*-toluenesulfonic acid monohydrate and methanol in a molar ratio (expoxide/acid/methanol) of 1:0.1:6 in anhydrous $CH_2Cl_2$ (10 mL) at 25 °C. The resulting mixture was stirred for 1 h at the same temperature and then treated with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$. Evaporation of the washed ($H_2O$) organic solvent gave a residue, which was analyzed by GLC.

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# Aromatic Substitution. 46. Methyl (Ethyl) Thio(Dithio)carboxylation of Aromatics with *S*-Methyl (*S*-Ethyl) Thiocarboxonium and Dithiocarboxonium Fluoroantimonates[1a]

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*S*-Methyl(*S*-ethyl)thio(dithio)carboxinium ions were prepared by reacting methyl (ethyl) fluoride–antimony pentafluoride with carbonyl sulfide (carbon disulfide) and studied with $^1H$ and $^{13}C$ NMR spectroscopy. The ions were subsequently used in the novel carboxylation reaction of arenes to *S*-methyl (*S*-ethyl) thio(dithio)benzoates. The method was also found to be adaptable to the carboxylation of polystyrene to poly(styrenecarboxylic acid) without degradation of the polymer backbone.

Aromatic carboxylic acids can be synthesized by Friedel–Crafts reactions using phosgene, oxalyl chloride, or carbamoyl chlorides and hydrolyzing (deaminating) the intermediate carboxylic acid derivatives.[2] Arenethiocarboxylic esters can be prepared[3,4] by reacting aromatic hydrocarbons with alkyl chlorothioformates in the presence of $AlCl_3$ or other Friedel–Crafts catalysts (eq 1). The dithiocarboxylic acids of pyrroles have been prepared by Friedel–Crafts reaction with carbon disulfide and $AlCl_3$.[5-7]

$$ArH + ClC(O)SR \xrightarrow{AlCl_3} ArC(O)SR + HCl \quad (1)$$

In these methods generally a 2-mol excess of the strong Lewis acid catalyst is needed, and significant side reactions take place, including alkylations. Yields are modest and applicability is limited.

We now report an efficient and mild method for the preparation of methyl and ethyl thio(dithio)benzoates by electrophilic substitution of aromatic hydrocarbons with *S*-methyl(*S*-ethyl)thiocarboxonium and -dithiocarboxonium fluoroantimonates, readily prepared by methylating (ethylating) carbonyl sulfide and carbon disulfide,

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