Experimental Section

Preparations of Tropinone 1-Oxide. Method A. A solution of tropinone (1.4 g, 0.01 mol), H_2O_2 (1.5 mL 30% aqueous solution) in acetone (50 mL) was kept at 25 °C for 48 h. The solution was dried with K_2CO_3 and concentrated in vacuo, and a solid precipitated (1.3 g, 89%) upon addition of CCl_4. It was found to be a mixture of **1** and **2** (9:1). Crystallization from acetone–petroleum ether gave pure **1**: mp 100 °C; NMR ($CDCl_3$) δ 2–2.5 (m, 6 H), 3.42 (s, 3 H), 3.5–4.0 (m, 4 H); IR (Nujol) 1710 cm^{-1}; picrate, mp 210 °C; IR (KBr) no carbonyl abssorption band. Anal. Calcd for $C_{14}H_{16}N_4O_9$; C, 43.76; H, 4.20; N, 14.58. Found: C, 43.96; H, 4.32; N, 14.66.

By use of thick layer chromatography (Neutral Alumina) with chloroform–methanol (9:1) **2** was obtained: mp 100 °C (acetone–petroleum ether); NMR δ ($CDCl_3$) 1.9–2.5 (m, 6 H), 2.5–3.0 (m 2 H), 3.65 (s, 3 H), 3.6–4.1 (2 H); IR (Nujol) 1720 cm^{-1}; picrate, mp 214 °C; IR (KBr) 1740 cm^{-1}.

Method B. The procedure of Kashman et al.[3] wtih 1.08 g of 2,6-cycloheptadienone was followed. The reaction mixture was filtered and pcric acid (ethanol) was added; 2.6 g (77%) of a mixture of the picrates of **1** and **2** (40:60) was obtained.

Method C. A solution of tropinone (1.4 g) and *m*-chloroperbenzoic acid (3.0 g) in CH_2Cl_2 (50 mL) was kept at 25 °C for 72 h. Addition of picric acid (ethanol) gave a solid (3.59 g, 93%) which was found to be a mixture of the picrates of **1** and **2** (40:60).

Equilibration Experiments. The picrate of **2** (0.5 g) in acetone (20 mL) was loaded on a column of basic alumina (III). A chloroform methanol mixture (9:1) eluted the free amine oxide. The solution was concentrated at room temperature to a volume of 20 mL. A saturated solution of picric acid in $CHCl_3$ was added. There was obtaineg 0.45 g (90%) of a mixture of the picrates of **1** and **2** in a ratio of 9:1, respectively (NMR).

The same procedure was followed by using the mixture of the picrates obtained by method C. The distribution of the amine oxides was identical with that of the previous experiment.

Registry No. **1**, 54807-25-9; **1** picrate, 54807-27-1; **2**, 54807-26-0; **2** picrate, 54807-28-2.

Reaction of Dimethyl Acetylenedicarboxylate with 2-Ethyl-3-phenyl-2*H*-5,6-dihydro-1,2-oxazine

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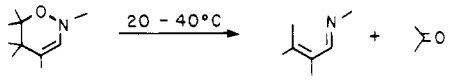
Received June 1, 1981

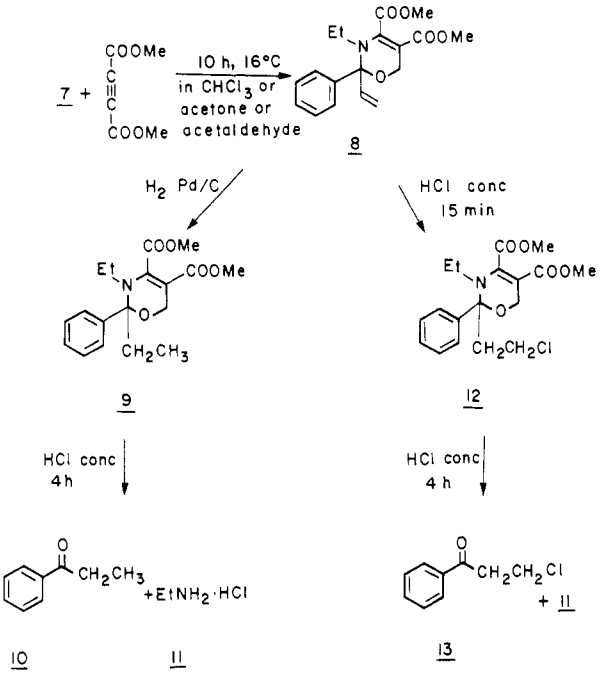
2-Alkyl-2*H*-5,6-dihydro-1,2-oxazine derivatives **1** have been shown by Eschenmoser to undergo a clean cleavage to α,β-unsaturated imines **2** and aldehydes or ketones **3**.[1]



1 **2** **3**

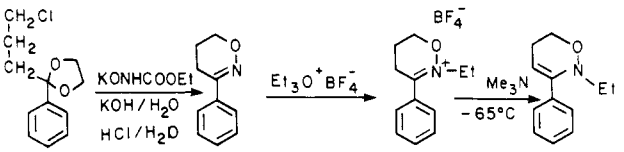
The basis for the ease of this clean decomposition is not completely clear, with repulsion between the higher nuclear charges and/or nonbonded electron pairs considered as responsible.[1] Although this process found use in the synthesis of medium-ring lactones[2] and pyridine derivatives,[3] little work has been published on other reactions of this system.[4]

Scheme I



As part of our research on the synthetic uses of 1,2-oxazines, we examined the reaction of 2-ethyl-3-phenyl-5,6-dihydro-1,2-2*H*,4*H*-oxazine (**7**) with dimethyl acetylenedicarboxylate (DMAD).

The starting cyclic oxime ether **5** was obtained from 2-(3-chloropropyl)-2-phenyl-1,3-dioxolane (**4**), in analogy



4 **5** **6** **7**

to the preparation of 3-methyl-4*H*-5,6-dihydro-1,2-oxazine described by Brandman and Conley.[5] N-Ethylation with $Et_3O^+BF_4^-$ in CH_2Cl_2 gave the oxoimminium salt **6** in 87% yield. Reaction of **6** with 1 equiv Me_3N in $CHCl_3$ for 1 min at −65 °C gave a quantitative yield of **7** isolated as an oily liquid.

A mixture of **7** and DMAD in chloroform, acetone, or acetaldehyde solutions after 10 h at 16 °C gives, after workup and separation, an adduct in 50–75% yield. Analytical data are consistent with a 1:1 adduct ($C_{18}H_{21}NO_5$), and the spectral data indicate structure **8** (Scheme I). The ^1H NMR spectrum shows a vinylic ABX proton system indicating a monosubstituted ethylene moiety. The ^{13}C NMR spectrum is also in good accord with the structure **8**.

The following degradation reactions prove structure **8**. Hydrogenation with 1 equiv of H_2 affords **9**. Acid hydrolysis of **9** for 4 h affords 1-phenyl-1-propanone (**10**) and $EtNH_3^+Cl^-$ (**11**). Similarly, acid hydrolysis of **8** gave **11** and the β-chloro ketone **12**. The final proof for the structure of **8** was given by X-ray crystallography. The overall molecular structure is shown in Figure 1; detailed geometry data are given in Table I (supplementary material). The overall shape of the 2,3,5,6-tetrahydro-1,3-

(1) Gygax, P.; Das-Gupta, T. K.; Eschenmoser, A. *Helv. Chim. Acta* **1972**, *55*, 2205.
(2) Shalom, E.; Zenou, J.-L.; Shatzmiller, S. *J. Org. Chem.* **1977**, *42*, 4213.
(3) Faragher, R.; Gilchrist, T. L. *J. Chem Soc., Chem. Commun.* **1977**, 252.
(4) Ahmed, G.; Ahmed, A.; Hickmott, P. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2383.
(5) Brandman, H. A.; Conley, R. T. *J. Org. Chem.* **1973**, *38*, 2236.

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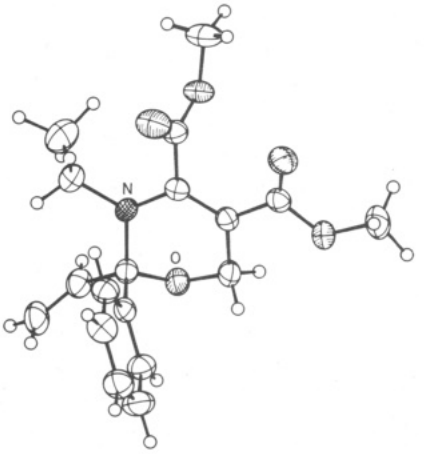


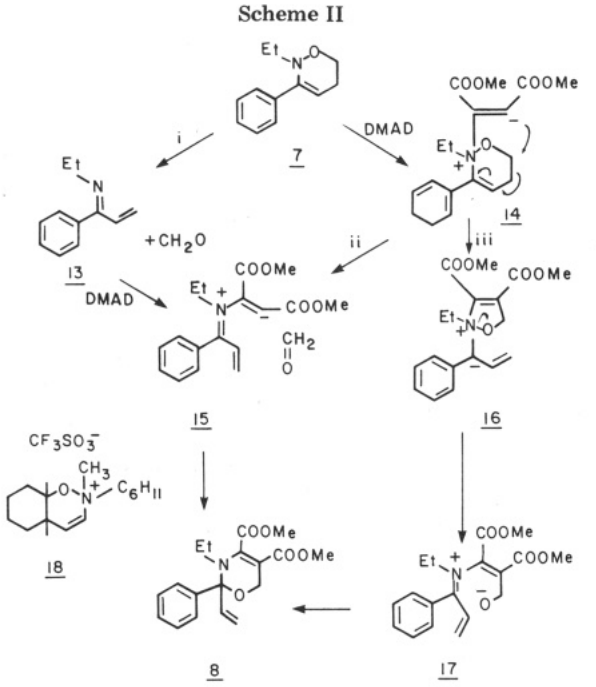
Figure 1. Overall molecular structure of compound 8.

oxazine system is envelope-like, where the 0 atom deviates by about 0.5 Å from the mean plane defined by the remaining atoms. The enamine part is almost fully conjugated to the β-carbomethoxy group. This is reflected in a coplanar arrangement of the two fragments and the distribution of bond distances along the vinylogeous urethan moiety. The second carbomethoxy group forms a torsion angle of 72° with the plane of the conjugated system and is characterized by usual geometry. Crystal forces appear to have little influence on the molecular geometry, as all intermolecular distances are greater than or approximately equal to the sums of the van der Waals radii.

There are three ways to account for the formation of **8** (Scheme II): (i) decomposition to the α,β-unsaturated imine **13** and formaldehyde, followed by a stepwise recombination of the components via the dipolar intermediate **15**; (ii) decomposition of the dipolar intermediate **14** to **15** and formaldehyde and recombination to **8**; (iii) rearrangement of **14** to the isomeric dipolar intermediate **16**, N–O cleavage to form **17** and ring closure to **8**. Paths i and ii involving recombination with CH_2O are excluded for the following reasons. (a) There is no incorporation of acetone or acetaldehyde in the reaction products when these are used as reaction solvents. (b) When DMAD was added to the mixture obtained by thermal decomposition of **7**, no reaction with DMAD to form **8** was observed. It is also unlikely that **15** is formed from **14** since Eschenmoser and Gygax found that the ammonium ion 3-cyclohexyl-1,6-dimethyl-2-oxa-3-azoniabicyclo[4.4.0]decane (**18**) is thermally stable.[6] We believe, therefore, that iii, involving **14** and its rearrangement to **16** may account for the formation of **8**.

The reaction of enamines with DMAD is a known synthetic method used to effect ring enlargements.[7] It is usually assumed that the introduction of a Michael acceptor at the nitrogen atom of an enamine can be neglected because this reaction is reversible. However, our results suggest that the formation of **14** may lead to an alternative reaction route involving the isomeric dipolar intermediates **16** and **17**, ending in the formation of **8**. The presence of the N–O bond in **7** accounts for the unusual reaction, changing the nature of the enamine so that reaction at the nitrogen is preferred. The formation of **17** by N–O cleavage in **16** precedes the cyclization to **8**.

Scheme II



Experimental Section[8]

3-Phenyl-4*H*-5,6-dihydro-1,2-oxazine (5) was prepared from 58 g (0.26 mol) of 2-(3-chloropropyl)-2-phenyl-1,3-dioxalane (**4**) and 27 g (0.31 mol) of ethyl *N*-hydroxycarbamate according to the procedure described by Brandmann and Conley:[5] 30% overall yield; mp 70 °C; IR (KBr) 3050, 2980, 1680, 1600 cm^{-1}; UV (CH_3CN) λ_{max} 246 nm (ε 8100); ^1H NMR ($CDCl_3$) δ 2.05 (m, 2 H), 2.42 (t, J = 7 Hz, 2 H), 3.80 (t, J = 6 Hz, 2 H), 7.10 (m, 3 H), 7.40 (m, 2 H). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.79; H, 6.57; N, 8.68.

2-Ethyl-3-phenyl-4*H*-5,6-dihydro-1,2-oxazinium Tetrafluoroborate (6). $Et_3O^+BF_4^-$ (2 g, 9.95 mmol) and 2.23 g (10 mmol) of **5** were dissolved in dry methylene chloride and left at room temperature for 30 min. The solvent was evaporated, and the residue was recrystallized from a CH_2Cl_2/Et_2O mixture to give **6**: 2.279 g (83% yield); mp 90–92 °C IR (KBr) 3050, 2980, 2360, 1640, 1600, 1450, 1100 cm^{-1}; UV (CH_3CN) λ_{max} 213 (ε 4480); ^1H NMR ($CDCl_3$) δ 1.45 (t, J = 8 Hz, 3 H), 2.40 (m, 2 H), 3.20 (t, J = 7 Hz, 2 H) 4.02 (q, J = 8 Hz, 2 H), 4.75 (t, J = 6 Hz, 2 H), 7.85 (s, 5 H). Anal. Calcd for $C_{12}H_{16}NOBF_4$: C, 52.02; H, 5.82; N, 5.06. Found: C, 51.63; H, 6.06; N, 4.96.

2-Ethyl-3-phenyl-2*H*-5,6-dihydro-1,2-oxazine (7). A cold (–65 °C) solution of Me_3N (56 mg, 1 mmol) in 5 mL of $CHCl_3$ was added at once to a stirred solution of 276 mg (1 mmol) of **6** in 5 mL of $CHCl_3$ at –65 °C. The reaction was allowed to proceed over 1 min under N_2, the $Me_3NH^+BF_4^-$ was filtered off at –30 °C. The oil, obtained after removal of the solvent at –10 °C, was identified as **7**: IR (neat) 3050, 2980, 1640, 1610, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 2.95 (q, J = 7 Hz, 2 H), 3.1–3.6 (m, 2 H), 3.92 (t, J = 6 Hz, 2 H), 5.16 (t, J = 4 H, 1 H), 7.4 (m, 5 H). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.09; H, 7.80; N, 7.61.

Thermal Decomposition of 7. Solutions of **7** (0.5 M in $CDCl_3$) were allowed to decompose thermally, and the reaction was followed by ^1H NMR spectroscopy. ^1H NMR spectrum of the product (obtained after total disappearance of signals characteristic for **7**): δ 1.10 and 1.22 (2 t, J = 3 and 7 Hz and J = 4.5 Hz, 5:2, together 3 H), 3.16 and 3.55 (2 q, J = 3.7, 4.5 Hz, 5:2, together 2 H), 4.86–6.8 (m, 3 H), 7.1–7.5 (m, 5 H); IR $CHCl_3$) 3070, 1670, 1600 cm^{-1}. The first-order reaction rate constants at 40.5,

(6) For arguments supporting this observation see ref 1, and on the role of N–O lone pair–lone pair interactions see also: Müller, K.; Eschenmoser, A. *Helv. chim. Acta* **1969**, *52*, 1923. Müller, K. **Ibid. 1970**, *53*, 1112. Compare also: Gygax, P. Ph.D. Thesis, ETH Zürich 5901, 1977.

(7) Brannock, K. C.; Burpitt, R. D.; Goodlett, V. W.; Thweat, J. G. *J. Org. Chem.* **1963**, *28*, 1464.

(8) Melting points are uncorrected. Ultraviolet spectra were measured on a Cary 14 instrument. Infrared spectra were taken on Perkin-Elmer 251 instrument. NMR spectra were taken on a Bruker HX 90E instrument in $CDCl_3$ and are in δ values.

at 34.5 and 23.5, and at 23.5 °C were 1.41×10^{-3}, 7.36×10^{-4}, 1.46×10^{-4} s^{-1}, respectively ($E^{\ddagger}$ = 24.0 ± 2.7 kcal/mol).

Reaction of 7 with DMAD. DMAD (284 mg, 2 mmol) was added to a 10-mL solution of 378 mg (2 mmol) of **7** in $CHCl_3$, acetone, or acetaldehyde at 16 °C and was allowed to react over 10 h. The solvent was evaporated, and the residue was chromatographed over Al_2O_3 to give 496, 402, and 331 mg of **8** (75%, 61%, and 50% yield) respectively: mp 72 °C; IR (KBr) 2980, 1740, 1700, 1605 cm^{-1}; UV (hexane) λ_{max} 289 (ϵ 19500); ^1H NMR (CCl_4) δ 0.97 (t, J = 7 Hz, 3 H), 3.3 (q, J = 7 Hz, 2 H), 3.57 (s, 3 H), 3.93 (s, 3 H), AB q at 4.10 and 4.39 (J = 14 Hz, 2 H), ABX system with δ(A) 5.36, δ(B) 5.50, and δ(X) 5.99 (J_{AB} = 1.5 Hz, J_{AX} = 16 Hz, J_{BX} = 10 Hz), 7.43 (br s, 5 H); ^{13}C NMR 16.1 (q), 43.3 (t), 50.1 (q), 52.8 (q), 59.6 (t, C-6), 90.9 (s, C-5), 97.7 (s, C-2), 119.6 (t), 128.0 (d), 128.5 (d), 128.9 (d), 136.3 (d), 138.6 (s), 147.4 (s, C-4), 164.9 (s), 165.4 (s) ppm; ^{13}C NMR assignments are tentative and are based on chemical shifts and off-resonance decoupled spectra; mass spectrum, m/e (relative intensity) 331 (M^+, 10). Anal. Calcd for $C_{18}H_{21}NO_5$: C, 65.26; H, 6.34; N, 4.23. Found: C, 65.55; H, 6.37; N, 4.07.

Crystal Structure Analysis of 8. Suitable single crystals of the compound were obtained by slow evaporation from a hexane solution. Accurate cell constants were obtained by a least-squares procedure applied to 25 reflections with $12° < \theta \leq 18°$ automatically centered on an Enraf-Nonius CAD4 diffractometer at the beginning of data collection. Crystal data: $C_{18}H_{21}NO_5$, M_r = 331.4, monoclinic, a = 7.834 (1) Å, b = 13.334 (2) Å, c = 16.595 (2) Å, β = 95.06 (1)°, V = 1726.7 Å^3, Z = 4, d_c = 1.275 g cm^{-3}, $F(000)$ = 704; Mo Kα radiation, λ_{mean} = 0.71069 Å, μ(MoKα) = 1.1 cm^{-1}; space group $P2_1/n$.

The intensities of all reflections within $1° < \theta < 27°$ were measured by using graphite-monochromatized Mo Kα radiation and an ω–2θ scan technique with a scan width of 1.2 + 0.35 tan θ. The scan rate varied according to the detected intensity between 1.0 and 4.0° min^{-1}. Three intensity-control reflections, monitored frequently, showed no decay of the crystal. The intensities were corrected for Lorentz and polarization effects and variable measuring time but not for absorption or secondary extinction. A total of 3127 unique reflections were collected, of which 2074 reflections had intensities above a threshold of three standard deviations of the intensity and were used in the final refinement.

The structure was solved by direct methods using the MULTAN system of computer programs. Refinement was carried out by full-matrix least-squares methods, including the atomic coordinates of all atoms, anisotropic thermal parameters of the nonhydrogen atoms, and isotropic thermal parameters of the hydrogens. All hydrogen atom positions could be found from difference maps. Refinement of the structural model converged to R = 0.039; the quantity minimized was $\sum w(\Delta F)^2$ with $w = 1/\sigma^2(F_0)$. There were no significant features in the difference map after the refinement was complete; the highest peak and deepest trough were 0.26 and −0.17 e Å^{-3}, respectively. Positional and thermal atomic parameters and lists of observed and calculated structure factors are available as supplementary material.

Reaction of 8 with HCl. A solution of 331 mg (1 mmol) of **8** in 5 mL of $CHCl_3$ was stirred with 0.5 mL of concentrated HCl for 15 min. The acid was neutralized with solid K_2CO_3, and the aqueous solution extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were dried (K_2CO_3) and filtered, and the solvents were removed in vacuum to give 330 mg of crude **12**. Recrystallization (hexane) gave the product: 298 mg (81%); mp 89 °C; IR (KBr) 2920, 1740, 1700, 1605 cm^{-1}; UV (hexane) λ_{max} 287.4 (ϵ 11000); ^1H NMR (CCl_4) δ 1.13 (t, J = 7 Hz, 3 H), 2.6 (t, J = 7.5 Hz, 2 H), 3.13 (q, J = 7 Hz, 2 H), 3.48 (s, 3 H), 3.77 (s, 3 H), 3.5 (m, 2 H), AB q at 3.81 and 4.21 (J = 14.k Hz, 2 H), 7.27 (s, 5 H); ^{13}C NMR δ 16.2 (q), 39.0 (t), 40.2 (t), 42.9 (t), 51.1 (q), 52.9 (q), 59.1 (t, C-6), 90.5 (s, C-5), 97.9 (s, C-2), 127.1 (d), 128.6 (d), 128.9 (d), 138.4 (s), 147.3 (s, C-4), 164.9 (s), 165.3 (s) ppm; mass spectrum, m/e (relative intensity) 368 (M^+, 12). Anal. Calcd for $C_{18}H_{22}NO_5Cl$: C, 58.78; H, 6.03; N, 3.81; Cl, 9.64. Found: C, 58.43; H, 6.24; N, 3.67; Cl, 9.83.

Hydrogenation of 8. Compound **8** (331 mg, 1 mmol) in 25 mL of methanol reacted in the presence of 10 mg of 10% Pd/C with 24 mL of H_2. The catalyst was filtered off (Celite), and the solvents were removed under vacuum. The product was crystallized (hexane) to give **9**: 310 mg (93%); mp 75 °C; IR (KBr) 2920, 1735, 1705, 1605 cm^{-1}; UV λ_{max} 289.5 (ϵ 30000); ^1H NMR δ 0.82 (t, J = 7.5 Hz, 3 H), 1.01 (t, J = 6 Hz, 3 H), 2.1 (q, J = 7.5 Hz, 2 H), 3.15 (q, J = 6 Hz, 2 H), 3.48 (s, 3 H), 3.75 (s, 3 H), AB q at 3.87 and 4.18 (J = 15 Hz, 2 H); ^{13}C NMR 7.9 (q), 16.4 (q), 29.1 (t), 42.6 (t), 51.0 (q), 52.8 (q), 59.3 (t, C-6), 91.6 (s, C-5), 98.1 (s, C-2), 127.5 (d), 128.5 (d), 128.8 (d), 139.4 (s), 147.7 (s, C-4), 165.4 (s) 165.9 (s) ppm; mass spectrum, m/e (relative intensity) 333 (M^+, 33). Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.63; H, 6.73; N, 4.29.

Hydrolysis of 12. A solution of 100 mg (0.27 mmol) of **12** in 5 mL of $CHCl_3$ was stirred with 5 mL of concentrated HCl for 4 h. The acid was neutralized with solid K_2CO_3, the $EtNH_2$ evolved was trapped in CCl_4, the aqueous layer was extracted with $CHCl_3$ (3 × 50 mL), the combined $CHCl_3$ solutions were dried (K_2CO_3) and filtered, and the solvent was removed under vacuum. The crude product was separated on preparative TLC (silica gel, TLC 7731 Merck), eluting with 3:7 $CHCl_3$/hexane. The less polar fraction (R_f 8–9) was identified as 3-chloro-1-phenyl-1-propanone (57 mg). The second fraction (R_f 5–7) was unreacted **12**, and the lower layer (R_f 2–3) consists of a mixture of alcohols which was not separated. When **10** was treated similarly the same products mixture was obtained.

Hydrolysis of 9. Compound **9** (100 mg, 0.3 mmol) was hydrolyzed analogously to **12** and gave the following: Ethylamine (trapped in CCl_4), a crude oil, was separated on preparative TLC (silica gel acc to stahl for TLC 7731 Merck), eluting with 3:7 $CHCl_3$/hexane. The less polar fraction (R_f 8.1–9.7) was identified as 1-phenyl-1-propanone. The second fraction (R_f 4–7.8) was unreacted **11**, and the lower layer (R_f 2–3.5) consists of a mixture of alcohols which were not separated.

Registry No. **4**, 3308-98-3; **5**, 75343-42-9; **6**, 81096-81-3; **7**, 81096-82-4; **8**, 81096-83-5; **9**, 81096-84-6; **12**, 81096-85-7; DMAD, 762-42-5.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and isotropic and anisotropic thermal parameters for **8** (4 pages). Ordering information is given on any current masthead page.

Highly Stereoselective Synthesis of Allenic Halides by means of Halocuprate-Induced Substitution in Propargylic Methanesulfonates

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Received November 6, 1981

For the preparation of racemic allenic halides several methods are available, but the number of routes to optically active allenic halides is rather restricted.[1] Hitherto optically active allenes have been synthesized mainly via S_N2'-like reactions in propargylic substrates (cf. ref 1). Of special interest in this connection is the difference in stereochemistry observed for halocuprate-induced formation of allenic halides from propargylic alcohols and chlorides. Thus the conversion of a propargylic alcohol by a halocuprate species prepared from HX and CuX into the allene preferentially follows the syn 1,3-substitution mode,[2] while that of 3-chloro-3-phenyl-1-propyne by tet-

(1) See for a comprehensive review: Patai, S., Ed. "The Chemistry of Ketenes, Allenes, and Related Compounds"; Wiley: Chichester, 1980.
(2) Landor, S. R.; Demetriou, B.; Evans, R. J.; Grzeskowiak, R.; Davey, P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1995.

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