pentane. Fractional recrystallization from diethyl ether yielded 15 mg (1%) of compound **2a** at 15 °C and 620 mg (37%) of compound **7**-OH at −20 °C.

Compound **2a:** mp 247–248 °C; ir (KBr) 3535, 2950, 2865, 1699, 1468, 1450, 1258, 1229, 1141, 1000, 983, 965 cm^{-1}; mass spectrum *m/e* (rel abundance) 336 (M$^+$, 45), 318 (7), 308 (7), 290 (45), 169 (100). Compound **7**-OH: mp 169–170 °C; ir (KBr) 3450, 2950, 2870, 1702, 1622, 1470, 1220, 1191, 1140, 1080, 1043 cm^{-1}; ^{1}H NMR (pyridine-d_5) δ 1.10–2.90 (m, 28 H), 3.22 (br m, 1 H) 7.05 (s, 1 H); uv (ethanol) λ_{max} 247 nm (log ϵ 3.9); ^{13}C NMR (CDCl$_3$) 20.4, 20.9, 21.8, 22.5, 23.2, 24.2, 24.7, 25.6, 25.8, 26.7, 37.4, 41.8, 51.1, 85.6, 138.2, 161.0, 164.8, 169.3 ppm; mass spectrum *m/e* (rel abundance) 318 (M$^+$, 100), 300 (12), 290 (18), 151 (16).

Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.29; H, 9.56.

Preparation of 7-OMs. To a frozen solution of compound **7**-OH (318 mg, 1.0 mmol) in pyridine (3.0 ml) was added a cool (−5 °C) solution of methanesulfonyl chloride (228 mg, 2.0 mmol) in pyridine (2.0 ml). The mixture was immediately frozen, then slowly allowed to warm to −20 °C. After storing at −20 °C for 2 days the reaction mixture was poured over 15 g of ice, then extracted with two 15-ml portions of diethyl ether. The ethereal layer was separated and washed with water, 1 N HCl, 5% $NaHCO_3$, and brine, then dried, filtered, and concentrated in vacuo. Preparative layer chromatography (benzene elution) of the white residue resulted in the isolation of 322 mg (81%) of compound **7**-OMs: mp 138–139 °C; R_f (Bz) 0.46; ir (CHCl$_3$) 2940, 2879, 1719, 1700 (sh), 1620, 1470, 1350, 1330, 1173, 960, 932, 852 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.00–2.30 (m, 24 H), 2.38 (m, 4 H), 3.30 (s, 3 H), 3.89 (m, 1 H); mass spectrum *m/e* (rel abundance) 396 (M$^+$, 0.4), 317 (25), 300 (100).

Anal. Calcd for $C_{21}H_{32}O_5S$: C, 63.60; H, 8.13. Found: C, 63.51; H, 8.14.

Acknowledgment. This work was generously supported by USPHS-NIH Grant 5 R01 AI 11690. The technical assistance of Rodney Erkes is also gratefully acknowledged. The ^{13}C spectra were obtained with the help of Dr. David Behnke, U. C. School of Medicine.

Registry No.—**1a,** 96-01-5; **1b,** 3008-41-1; **1c,** 23427-68-1; **2a,** 59654-89-6; **2b,** 59654-90-9; **2c,** 59654-91-0; 7-OH, 59654-92-1; 7-OMs, 59654-93-2; *cis*-cyclododecane-1,2-diol, 4422-05-3; methanesulfonyl chloride, 124-63-0.

References and Notes

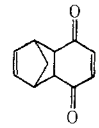
(1) (a) $n = 7$: A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *J. Am. Chem. Soc.*, 74, 3636 (1952). (b) $n = 9$: V. Prelog and M. Speck, *Helv. Chim. Acta*, **38,** 1786 (1955). (c) $n = 11$: T. Mori, T. Nakahara, and H. Nozaki, *Can. J. Chem.*, **47,** 3266 (1969).

(2) D. P. Bauer and R. S. Macomber, *J. Org. Chem.*, **40,** 1990 (1975).

(3) H. Meier, *Synthesis*, 235 (1972).

(4) J. G. Vinter and H. M. R. Hoffmann, *J. Am. Chem. Soc.*, **95,** 3051 (1973). Compound **5** is stereochemically rigid, giving a single C═O ir stretch. Its cis,syn,cis isomer is fluxional and shows two C═O bands in solution.

(5) A. Wasserman [*J. Chem. Soc.*, 1511 (1935)] lists the λ_{max} (ethanol) for the enedione below as 225 nm (log ϵ 4.11). Using Woodward's rules, two



i

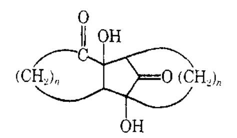
substituents (one α + one β) would add 22 nm: calcd 247 nm; observed 247 nm. The position and intensity of this band further argue for the near-planarity of the enedione moiety in **7-X**.

(6) For a leading reference, see H. O. Krabbenhoft, J. R. Wiseman, and C. B. Quinn, *J. Am. Chem. Soc.*, **96,** 258 (1974).

(7) W. Huckel, "Theoretical Principles of Organic Chemistry", Vol. I, American Elsevier, New York, N.Y., 1955, p 461.

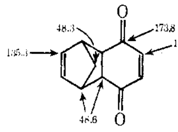
(8) The systematic names for these dimers follow: **2a,** 1,10-dihydroxytricyclo[9.7.1^{2,10}]eicos-19,20-dione; **2b,** 1,12-dihydroxytricyclo[11.9.1.1^{2,12}]-tetracos-23,24-dione; **2c,** 1,14-dihydroxytricyclo[13.11.1.1^{2,14}]octacos-27,28-dione; **7**-OH, 1-hydroxytricyclo[9.7.1.1^{2,10}]eicos-10-ene-19,20-dione.

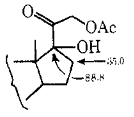
(9) One referee has suggested the structure below as an alternate of **2.** We

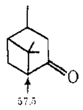


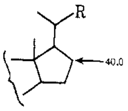
had considered this possibility, but eliminated it on the basis of the compounds' ir spectra. The structure below would show two carbonyl bands, one at ca. 1745 cm^{-1}. None of the compounds in this study exhibited a second C═O stretch, and none came above 1709 cm^{-1}.

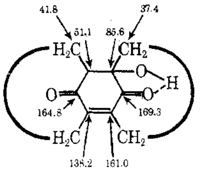
(10) Analogues for the ^{13}C chemical shifts can be found in L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, N.Y., 1972, and the spectrum of i in footnote 5 (determined in this work). The substantial difference in chemical shift between the olefinic carbons in **7**-OH may be caused by internal hydrogen bonding in the neighboring carbonyl:









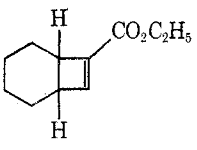


Communications

The Stereospecific Aluminum Chloride Catalyzed [2 + 2] Cycloaddition of Propiolate Esters with Unactivated Alkenes

Summary: The aluminum chloride catalyzed reaction of alkenes with propiolate esters at 25 °C produces either ene adducts and/or stereospecific [2 + 2] cycloadducts depending on the substitution pattern of the alkene.

Sir: We have previously shown that aluminum chloride catalyzes the reaction of methyl acrylate with 1,1-disubstituted olefins at 25 °C, giving good yields of ene adducts.[1,2] Since acetylenes are known to be more reactive than the corresponding alkene as enophiles,[1] we decided to examine Lewis acid catalyzed reactions of propiolate esters with alkenes. With 1,2-disubstituted olefins or monosubstituted double bonds an unexpected reaction occurs. With cyclohexene two products are obtained on treatment with ethyl propiolate and 0.5 equiv of aluminum chloride in benzene for 7 days at 25 °C. The expected ene adduct **17** is isolated in 15% yield.[3,4] The major product isolated in 72% yield is assigned structure **1** based on ir, NMR, and mass spectral considerations. The cis fusion is assigned based on steric considerations and the nature of the cycloaddition (vide infra). This type of cycloaddition has precedent in the cycloaddition of propiolate esters with enamines.[6] It has not been observed previously in nonphotochemical reactions of propiolates with unactivated olefins. In order to test the specificity of the addition, methyl propiolate was treated with excess *cis*- or *trans*-2 butene in the presence of 0.5 equiv of aluminum chloride for 2 days. In neither case is any ene adduct detected. The *cis*- and *trans*-3,4-dimethylcyclobutenecarboxylates, **2** and **3,** are obtained stereospe-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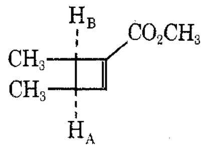
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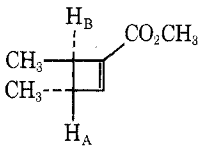
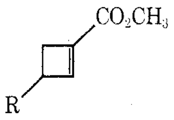
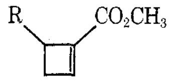

3

cifically with retention in 35 and 31% yields,[7] respectively and are >98% isomerically pure based on GC analysis. The stereochemistry is assigned by analysis of NMR coupling constants.[8] These compounds are identical by spectral comparison with those prepared by an alternate synthesis.[9] With propene the 1:1 adducts are obtained in 64% yield.[7] The ene adduct **13** is obtained as 24% of these adducts. Two other products are obtained as 43 and 33% of the mixture. These are isolated by gas chromatography and are assigned the structures **4** and **5**, respectively. Similarly, 1-butene gives a 74% yield of 1:1 adducts[7] which consists of 14.7% ene adduct **14** and 31 and 25% cyclobutene adducts **6** and **7**, respectively.[10]


4, R = CH_3
6, R = C_2H_5


5, R = CH_3
7, R = C_2H_5

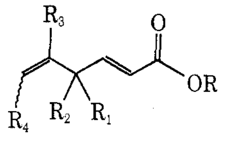
The mechanism of these cycloaddition reactions is open to question. The two mechanistic extremes are a concerted [$2_s + 2_a$] cycloaddition or a polar two-step sequence. It is possible for these cycloadditions to go by the [$2_s + 2_a$] route since one of the addends is an acetylene.[11] On the other hand, a variety of polar two-step cycloadditions are known to proceed stereospecifically.[12] From the mixtures of cyclic products obtained with monosubstituted olefins it is clear that the dominant feature is the great stabilization of at least a partial negative charge on the carbon α to the complexed ester in either a transition state or intermediate. On the other hand, if there is an intermediate, it must collapse very rapidly since no isomerization is observed. It should be noted that in similar uncatalyzed thermal reactions no cycloadducts are observed.[13]

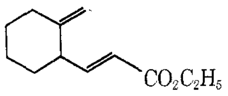
With olefins containing two substituents on one end of the double bond no cycloaddition product can be detected. Addition of a slight excess of β-pinene to a solution of ethyl propiolate in benzene containing 0.2 equiv of aluminum chloride gives after 2 days the expected ene adduct **8** in 82% yield (Scheme I). As one would expect with a six-membered-ring transition state the α,β-unsaturated ester is formed stereospecifically trans. Furthermore, NMR spectra of the crude product indicates that no conjugation of the δ,ϵ double bond, has occurred. This is somewhat surprising given the length of time and very acidic conditions of the reaction. Similarly, isobutylene gives the corresponding ene adduct **9**[14] in 61% yield after 5 days with 0.5 equiv of aluminum chloride and 2-ethyl-1-butene gives a 60:40 mixture of olefin isomers **10** in 56% yield after 6 days[7] with 0.33 equiv of $AlCl_3$. 3-Methyl-2-butene and ethyl propiolate containing 0.85 equiv of $AlCl_3$ gives rise to the ene adduct **11** in 74% yield. Similarly 1-methylcyclohexene gives a 70:30 mixture of adducts **15** and **16** in 90% yield while 2,3-dimethyl-2-butene gives only the expected ene adduct **12** in 92% yield.

Scheme I

8

The reactions described here provide ready access to a variety of 2,5-dienoates and cyclobutenecarboxylates which were previously difficult to prepare. We are investigating the use of these compounds in synthesis, intramolecular versions of these reactions, and the extension of this reaction to acetylenes with other electron-withdrawing substituents.


9, $R_1, R_2, R_4 = H$; $R_3 = CH_3$
10, $R_1, R_2 = H$; $R_3 = C_2H_5$; $R_4 = CH_3$
11, $R_1, R_3 = CH_3$; $R_2, R_4 = H$
12, $R_1, R_2, R_3 = CH_3$; $R_4 = H$
13, $R_1, R_2, R_3, R_4 = H$
14, $R_1, R_2, R_3 = H$; $R_4 = CH_3$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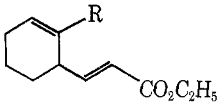
16, R = CH_3
17, R = H

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Princeton University for support of this research.

References and Notes

(1) For a review of the ene reaction, see H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).
(2) B. B. Snider, *J. Org. Chem.*, **39**, 255 (1974).
(3) All new compounds were characterized by NMR, ir, and mass spectra and exact mass determination.
(4) Typically the reactions are run at 25 °C in benzene (1.5 ml/mmol of acetylene) with excess olefin present. The amount of aluminum chloride used varies from 0.2 to 0.85 equiv depending on the reactivity of the olefin. If more than 1 equiv of $AlCl_3$ is used, facile Friedel–Crafts reactions take place. The reaction time varies from 2 to 7 days and is determined by chromatographic analysis of reaction mixtures. The choice of benzene as solvent and aluminum chloride as catalyst is important.[5] Reactions are worked up by quenching with bicarbonate solution, filtration through Celite, and extraction with ether.
(5) T. Inuki and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965), describe the use of this system for Diels–Alder reactions. We have found that solvents like methylene chloride give rise to extensive double-bond isomerization while other aromatic solvents like chlorobenzene or toluene give results similar to those obtained in benzene. Aromatic solvents form weak complexes with aluminum chloride which presumably deactivate it sufficiently to allow these reactions to take place cleanly. Strongly complexing solvents like ether give only traces of product.
(6) R. Fuks, and H. G. Viehe in H. G. Viehe, "Chemistry of Acetylenes", Marcel Dekker, New York, N.Y., 1969, pp 435–440.
(7) The other products in these reactions are traces (~5%) of telomerized olefin and Friedel–Crafts reaction of the olefin on benzene. Most of the remaining material is unreacted starting material. Aluminum chloride also catalyzes the isomerization of olefins at a rate competitive with ene reaction so that in the case of 2-ethyl-1-butene one obtains an 8% yield of ene adducts of methyl propiolate with 3-methyl-2-pentene.
(8) For the cis isomer **2**, $J_{AB} = 4.5$ Hz. For the trans isomer **3**, $J_{AB} = 1.4$ Hz. This is consistent with predictions based on the Karplus equation: I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967); E. A. Hill and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2047 (1967).
(9) The author thanks Maitland Jones, Jr., and R. Galucci for communicating these results prior to publication.
(10) The remaining 30% consisted of 15% *sec*-butylbenzene, (from Friedel–Crafts reaction), 4.9% methyl *trans*-3,4-dimethyl-1-cyclobutenecarboxylate and ~10% methyl *cis*-3,4-dimethylcyclobutenecarboxylate (from isomerization of 1-butene followed by the normal reaction expected for 2-butenes).
(11) R. B. Woodward and R. Hoffmann, *Ang. Chem., Int. Ed. Engl.*, **8**, 781,841 (1969).
(12) N. D. Epiotis et al., *J. Am. Chem. Soc.*, **98**, 453 (1976).
(13) K. Alder and H. v. Brachel, *Justus Liebigs Ann. Chem.*, **651**, 141 (1962).
(14) This material was identical by ir spectra with an authentic sample: G. P. Chuisoli et al., *Chim. Ind. Milan*, **46**, 21 (1964).

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