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## Aluminum Chloride Catalyzed Reactions of Methyl Chloropropiolate with Unactivated Alkenes

Sir:

We have recently reported that methyl propiolate undergoes aluminum chloride catalyzed ene reactions and/or stereospecific [2 + 2] cycloadditions with unactivated alkenes.[1] We report that this reaction can be extended to methyl chloropropiolate which gives rise stereospecifically to (Z)-3-chloro-2,5-alkadienoates via a regioselective ene reaction and to 2-chlorocyclobutene carboxylates via a stereospecific [2 + 2] cycloaddition (Figure 1). The resulting adducts are versatile synthetic intermediates which are not readily accessible by other routes.

Methyl chloropropiolate (**1**) can be prepared in a single step from *trans*-1,2-dichloroethylene, methyllithium, and methyl chloroformate in 60–70% yield by a modification of Viehe's procedure,[2] making this versatile reagent readily available.[3,4] The products from the aluminum chloride catalyzed reactions of **1** with alkenes are shown in Table I. Cyclobutenes are the major products in most cases, while with methyl propiolate cyclobutenes are formed only from mono- and 1,2-disubstituted alkenes. The most significant effect of the chlorine is observed in the reactions of 2,3-dimethyl-2-butene (**10**) which gives exclusively ene adduct with methyl propiolate and 95% cyclobutene with **1**.

A possible explanation for this follows from an examination of the transition state required for a concerted ene reaction (Figure 1). If R = CH$_3$ and X = Cl, severe steric strain retards the reaction. For methyl propiolate (X = H), the steric hindrance is apparently not severe. Reactions 13 and 14 were carried out to test this hypothesis. If the mechanism shown in Figure 1 is correct, then the hydrogen on the carbon trans to olefinic hydrogen should be transferred preferentially. In both cases the major ene adduct is the one expected from the less hindered transiton state (Figure 1: R = H, R′ = CH$_3$). The minor isomer may result from isomerization of the starting alkene. As predicted, 1:1 mixtures of regioisomers are obtained from the reaction of **13** or **14** with methyl propiolate. Similar interactions may be responsible for the formation of a single ene adduct in case 9. This is a novel example of synthetically useful regioselectivity in an ene reaction, which should be ap-

Table I. Reaction of Methyl Chloropropiolate with Alkenes

ALKENE	MOLE %AlCl$_3$	REACTION TIME DAYS,(°C)	PRODUCTS (% YIELD)^a
2	32	3 (25)	2a (16), 2b (8)
3	50	2 (25)	3a (65)
4	70	2 (25)	4a (74)
5	76	3 (25)	5a (51)
6	50	2 (25)	6a^b (41), 6b^c (28)
7	47	5 (4) 1 (25)	7a (52)
8	45	3 (4) 1 (25)	8a^d (46), 8b (20)
9	22	27 (25)^e	9a (23), 9b (53)
10	42	3 (4)	10a (76), 10b (4)
11	70	2 (25)	11a^f (3), 11b^f (8), 11c (66)
12	38	5 (4) 2 (25)	12a^g (37), 12b^g (16)
13	66	3 (4) 1 (25)	13a (47), 13b^h (28), 13c^h (4)
14	66	3 (4) 1 (25)	14a (53), 13b^h (9), 13c^h (29)

^{a} Methyl chloropropiolate is added to a stirred suspension of sublimed aluminum chloride in anhydrous benzene under nitrogen. After the aluminum chloride has dissolved, 1.1 equiv of alkene is added and the reaction is stirred for the time shown. The reaction is quenched in dilute hydrochloric acid. Cyclobutenes (less polar) are easily separable from ene adducts by chromatography on silica gel. All yields are for isolated pure compounds unless otherwise specified. Products were characterized by NMR, IR, and mass spectroscopy and elemental analysis. ^{b} Contains ~85–90% **6a** and 10–15% **13a** and **14a**. ^{c} Contains ~85–90% **6b** as a 1:1 mixture of isomers and 10–15% **13b** and **13c**. ^{d} Regiochemistry determined by conversion to **18**. ^{e} Similar yields are obtained in 2–3 days using more aluminum chloride. ^{f} Determined by analysis of NMR spectrum of a mixture **11a** and **11b**. ^{g} Small amounts of an unidentified compound, which may have a structure analogous to **11b**, were also formed. For similar results in the thermal reaction of chloropropiolonitrile with norbornadiene, see T. Sasaki, S. Eguschi, M. Sugimoto, and F. Hibi, *J. Org. Chem.*, **37**, 2317 (1972). ^{h} Determined by analysis of the NMR spectrum of a mixture of **13b** and **13c**.

plicable to the ene reactions of a variety of disubstituted acetylenes.

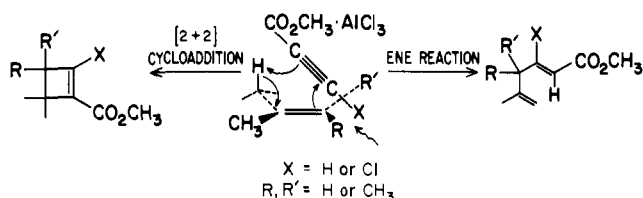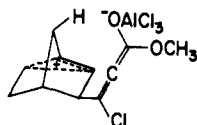In addition to the regioselectivity studies which support a

Figure 1.

Figure 2.

concerted mechanism for the ene reaction, the propylene reaction (case 2) in which both cyclobutenes are formed and cases 3 and 4 which are stereospecific suggest that the cycloaddition reaction is also concerted. A polar two-step sequence for the formation of the minor isomer (**2b**) in case 2 requires a primary carbenium ion as an intermediate. A stereospecific $[_{\pi}2_s + _{\pi}2_a]$ cycloaddition of the vinyl cation resonance form of the 1-AlCl$_3$ complex is consistent with the steric and electronic effects observed in this reaction.[5]

The reaction of norbornene with **1** (case 11), which gives the three products expected from a 2-norbornyl cation (Figure 2), clearly goes through a two-step pathway. However, norbornene may well be a special case since an ene reaction cannot occur, the intermediate carbenium ion is especially stable, and the transition state required for a $[_{\pi}2_s + _{\pi}2_a]$ cycloaddition is sterically hindered.[6,7]

An NMR study of the reaction of **1** with 0.18 equiv of AlCl$_3$ and 2-methyl-2-butene (case 8) showed complex behavior (percent conversion, time in hours: 55, 0.25; 62, 1; 68, 2; 75, 4; 84, 7; and 93, 21) that is consistent with the expected second-order rate in 1-AlCl$_3$ and 2-methyl-2-butene[8] only if the product complexes much more strongly than **1** with AlCl$_3$. Since ethynyl is more electron withdrawing than alkenyl,[9,10] **1** should be less basic than the products. Similar kinetic studies with methyl propiolate (**15**) indicate that **1** is three–four times as reactive as **15**. Chlorine, an electron-withdrawing group,[11] makes **1** less basic than **15** giving rise to a more reactive aluminum chloride complex. This reactivity difference is also seen in the reaction of **15** with norbornene which gives mainly the unrearranged [2 + 2] adduct and in the reaction of **1** with easily rearranged alkenes such as β-pinene which give complex mixtures derived from acid-catalyzed rearrangement of the alkene.

The products shown in Table I are useful synthetic intermediates. Treatment of **3a**, **7a**, or **11c** with lithium dimethylcuprate results in replacement of the chlorine with a methyl group in yields of 93, 81, and 95% respectively.[12] Treatment of **8a** with excess sodium methoxide in methanol gives a mixture of **16** and **17** which on acid hydrolysis is converted cleanly to **18**.[13] Similarly **3a** and **4a** are converted to dimethyl *threo-*
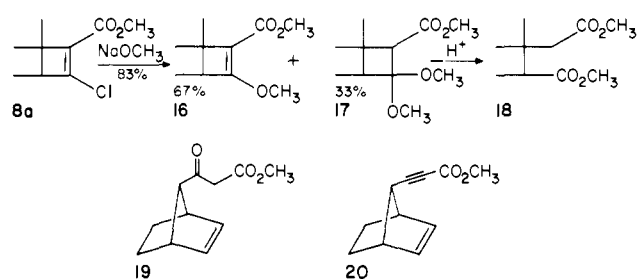
and *erythro*-2,3-dimethylglutarate[14] in 64 and 68% yield, respectively. Treatment of **11c** under similar conditions gives **19** in 72% yield which we believe will be a useful intermediate in the synthesis of tricyclic sesquiterpenes. Dehydrochlorination of **11c** to give **20** in 84% yield is accomplished by treatment with tetraethylammonium fluoride and potassium carbonate in acetonitrile.[15]

The reactions of methyl chloropropiolate with alkenes provides a versatile route to a variety of novel highly functionalized cyclobutenes and ene adducts with considerable regio- and stereoselectivity. We are presently investigating the synthetic utilization of these products and extension of this reaction to other acetylenes.[16]

References and Notes

(1) B. B. Snider, *J. Org. Chem.*, **41**, 3061 (1976).
(2) H. G. Viehe, *Chem. Ber.*, **92**, 1950 (1959). Lithium chloroacetylide in ether (prepared from *trans*-1,2-dichloroethylene and low halide methyllithium) is added via a double tipped needle to 1.5–2 equiv of methyl chloroformate at −80 °C. After stirring for 1 h at −80 °C, the mixture is quenched with dilute hydrochloric acid and washed with brine and dried. The ether is removed at 25 °C (≥150 mm) and the residue distilled at 40–45 °C (15 mm) giving 64–70% methyl chloropropiolate. *Methyl chloropropriolate is a very potent lachrymator. Lithium chloroacetylide is shock sensitive (especially when dry).*
(3) Halopropiolates have seen little synthetic use. For examples see (a) K. Alder, R. Hartmann, and W. Roth, *Justus Liebigs Ann. Chem.*, **613**, 6 (1958); (b) J. F. Normant, A. Commercon, and J. Villieras, *Tetrahedron Lett.*, 1465 (1975).
(4) As a dienophile, **1** can function as a ketene equivalent, giving ketones whose regiochemistry is opposite to that obtained from α-substituted acrylonitriles. The Diels–Alder reaction of chloropropiolic acid and cyclopentadiene has been reported.[3a] Isoprene and **1** in the presence of hydroquinone at 100 °C give a complex mixture. In the presence of aluminum chloride at −80 °C in toluene, isoprene is polymerized. With milder Lewis acids a 3:2:1 mixture of Diels–Alder adduct, ene adduct and cyclobutene is formed in ~50% yield. Anthracene and **1** undergo an aluminum chloride catalyzed Diels–Alder reaction in 66% yield (CH$_2$Cl$_2$, 25 °C, 4 days).
(5) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). It has been proposed that for polar [2 + 2] cycloadditions Woodward–Hoffmann rules need not apply: N. D. Epiotis, "Theory of Organic Reactions", Springer-Verlag, Berlin, 1978.
(6) Dichloroketene reacts poorly with norbornene: L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).
(7) For a similar polar ene reaction in which norbornene is a special case, see H. M. R. Hoffmann and T. Tsushima, *J. Am. Chem. Soc.*, **99**, 6008 (1977).
(8) The aluminum chloride catalyzed Diels–Alder reactions of methyl acrylate are second order; see T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 872 (1967).
(9) See J. Dale in "Chemistry of Acetylenes", H. Viehe, Ed., Marcel Dekker, New York, 1969, p 71.
(10) For a discussion of the relative stability of allyl and propargyl cations, see H. G. Richey, and J. M. Richey in "Carbonium Ions", Vol. II, G. Olah, P. v. R. Schleyer, Eds., Wiley, New York, 1970, pp 940–941.
(11) The $\sigma_p{}^+$ for Cl$^-$ is 0.035: C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968).
(12) C. P. Casey, D. F. Marten, and R. H. Boggs, *Tetrahedron Lett*, 2071 (1973), S. Kobayashi, H. Takei, and T. Mukaiyama, *Chem. Lett.*, 1097 (1973); C. P. Casey and D. F. Marten, *Synth. Commun.*, **3**, 321 (1973).
(13) V. Jäger and H. G. Viehe in Houben-Weyl, "Methoden Der Organischen Chemie", Band V/2a, George Thieme Verlag, Stuttgart, 1977, pp 738–740.
(14) A. R. Parikh and K. A. Thaker, *J. Inst. Chem. Calcutta*, **43**, 228 (1971); A. Michael and J. Ross, *J. Am. Chem. Soc.*, **52**, 4598 (1930).
(15) F. Naso and L. Rozini, *J. Chem. Soc., Perkin Trans. 1*, 340 (1974), and references cited therein.
(16) Methyl bromopropiolate[17] reacts with 2-methyl-2-butene similarly to methyl chloropropiolate. Methyl tetrolate, methyl phenylpropiolate, and methyl trimethylsilylpropiolate do not react with 2-ethyl-1-butene in the presence of aluminum chloride in benzene or methylene chloride.
(17) W. Chodkiewicz, *Ann. Chim. (Paris). Ser. 13*, **2**, 819 (1957).

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