Ethynyl Ortho Esters as Precursors of Propargyl Cations. The Low-Temperature, Ionic Diels-Alder Addition of Ethyl Propiolate to 1,3-Dienes via Ethynyl Ortho Esters Paul G. Gassman* and Subhash P. Chavan Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Summary: 3,3,3-Triethoxypropyne (triethyl orthopropiolate) was added to a series of 1,3-dienes at low temperature in the presence of trimethylsilyl triflate to yield the $4\pi + 2\pi$ products of the formal addition of ethyl propiolate to the 1,3-dienes.

The use of allyl cations¹ and propargyl cations² as powerful low-temperature dienophiles in the Diels-Alder reaction is becoming well established. An extension of this concept has been made which involves the addition of acrolein acetals³ and vinyl ortho esters⁴ to 1,3-dienes in low-temperature cycloadditions.⁵ In general, the carbocation is the most powerful, carbon-based electron-withdrawing group that



can be generated. Thus, it is not surprising that the conversion of 1 and 2 into 3 and 4, respectively, results in the formation of extremely powerful low-temperature dienophiles. We now wish to report that this concept can be extended to the low-temperature addition of ethyl propiolate to a variety of 1,3-dienes *via* the intermediacy of propargyl cations generated from triethyl orthopropiolate.

In a general procedure, triethyl orthoacrylate⁶ (3,3,3-triethoxypropene, 2) was treated with one equivalent of bromine at 0 °C in chloroform. After removal of the solvent, the crude product was dehydrohalogenated with powdered potassium hydroxide (5 equivalents) in heptane containing 18-crown-6 to yield 61% of 5.⁸ When 5 was exposed to trimethylsilyl triflate in methylene chloride at -78 °C in



the presence of two equivalents of 1,3-cyclohexadiene, followed by slow warming to -15 $^{\circ}$ C over a 1.5-h period, **6** was obtained in 78% yield after purification by column chromatography.

In terms of mechanistic detail, it seems apparent that treatment of 5 with trimethylsilyl triflate results in the formation of 7. Considerable evidence supports this hypothesis. When 5 was treated with trimethylsilyl triflate in deuteriochloroform in the absence of 1,3-cyclohexadiene at -78 °C, the methylene protons of 5, which appeared at δ 3.69 in its ¹H NMR spectrum, disappeared and were replaced by a quartet (J = 7.1 Hz) at δ 4.75 indicative of the attachment of an -OCH₂CH₃ to a cationic center at low temperature. When this experiment was repeated with 1,3-cyclohexadiene in the reaction mixture, an ¹H NMR study failed to show the intermediacy of 7. Instead, spectral data consistent with the rapid formation of 8 at low temperature was obtained: ¹H NMR (CDCl₃) δ 8.03 (dd, 1 H, J = 6.6 and 1.9 Hz), 6.45 (t, 1 H, J = 6.8 Hz), 6.24 (t, 1 H, J = 6.8 Hz), plus a multiplet centered at δ 4.89 resulting from the overlap of a 32-peak system due to the ether methylenes, each of which is an AB quartet with different chemical shifts. A related pattern, which was centered at δ 3.53, was observed for 9.¹⁰

At low temperature, 7 decomposed to give ethyl propiolate and 8 decomposed to produce 6. Ample precedent exists for the decomposition of dialkoxy-substituted carbocations to esters.⁹ In an

attempt to trap 8 prior to its decomposition to 6, trimethylsilyl cyanide was added to the reaction mixture after a 25-min reaction time at -78 °C. This resulted in the formation of 17% of 9^{10} and 28% of 6.

The isolation of esters rather than ortho esters from this reaction raised the question of whether 7 merely decomposed to ethyl propiolate, followed by the addition of ethyl propiolate to 1,3-cyclohexadiene under the reaction conditions. Control reactions demonstrated that ethyl propiolate would not add to 1,3-cyclohexadiene under the reaction conditions either with acid catalysis or in the presence of trimethylsilyl triflate. This is consistent with the concept that 7 should be an exceptionally powerful dienophile.

The data listed in Table 1 illustrate the versatility of the use of 7 as a highly reactive intermediate. In the addition to acyclic 1,3-dienes, the reaction was complicated by the aromatization of the initially formed 1,4-cyclohexadienes.

In summary, a method has been developed for the formal low-temperature addition of ethyl propiolate to 1,3-dienes *via* the intermediacy of propargyl cations.

Table 1.	Addition of Ethyl Propiol	ate to 1,3-Dienes via 7 ge	enerated from 5 and Tr	imethylsilyl Triflate
Diene	Product	<u>Temperature</u> ^c	Time (h)	<u>Yield (%)</u>
\bigcirc	CO ₂ C ₂ H ₅	-78 °C to -15 °C	1.6ª	78
	CO2C2H5	-78 °C to 0 °C	2.0ª	57
Ę	CO2C2H5	0 °C	0.3 ^b	46
Ę	С02 С2 Н5	-78 °C to 0 °C	2.2ª	73 ^d
Ľ	CO2C2H5	0 °C	0.5 ^b	56 ^d
K	CO2C2H5	0 °C	0.5 ^b	37 ^d

(a) Trimethylsilyl triflate was used in 50 mol %. (b) Trimethylsilyl triflate was used in 75 mol %. (c) The reactions which show a temperature range were started at the lower temperature and allowed to warm slowly to the higher temperature. (d) The product was prone to undergo aromatization on standing.

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References and Footnotes

- Gassman, P. G.; Singleton, D. A. J. Am. Chem. Soc. 1984, 106, 6086. Gassman, P. G.; Singleton, D. A. J. Am. Chem. Soc. 1984, 106, 7993. Gassman, P. G., Singleton, D. A. J. Org. Chem. 1986, 51, 3075. Poutsma, M. L. J. Org. Chem. 1968, 33, 4080. Escher, A.; Übersax, B.; Neuenschwander, M. Chimia 1981, 35, 251. Hoffmann, H. M. R.; Vathke-Ernst, H. Chem. Ber. 1981, 114, 1182, 1464, 1548, 2208. Giguere, R. J.; von Ilsemann, G.; Hoffmann, H. M. R. J. Org. Chem. 1982, 47, 4948. Lazlo, P.; Lucchetti, J. Tetrahedron Lett. 1984, 25, 2147 and references therein.
- Gassman, P. G.; Singleton, D. A. Tetrahedron Lett. 1987, 28, 5969. See also: Mayr, H.; Bauml, E. Tetrahedron Lett. 1983, 24, 357. Mayr, H.; Halberstadt, I. K. Angew. Chem. 1980, 92, 840. Mayr, H.; Klein, H. Chem. Ber. 1982, 115, 3528. Mayr, H.; Schulz, F.; Halberstadt-Kausch, I. K. Chem. Ber. 1982, 115, 3516. Mayr, H.; Halberstadt-Kausch, I. K. Chem. Ber. 1982, 115, 3479.
- Gassman, P. G.; Singleton, D. A.; Wilwerding, J. J.; Chavan, S. P. J. Am. Chem. Soc. 1987, 109, 2182.
- 4. Gassman, P. G.; Chavan, S. P. J. Org. Chem. in press.
- 5. For mechanistic precedents, see: Roush, W. R.; Gillis, H. R.; Essenfeld, A. P. J. Org. Chem. 1984, 49, 4674.
- 6. Triethyl orthoacrylate⁴ was prepared in 82% yield through the dehydrobromination of triethyl α bromoorthopropionate⁷ with potassium <u>tert</u>-butoxide in dimethyl sulfoxide at room temperature.
- 7. Walters, P.; McElvain, S. J. Am. Chem. Soc. 1940, 62, 1482. Beyerstedt, F.; McElvain, S. J. Am. Chem. Soc. 1937, 59, 2266.
- Stetter, H.; Uerdingen, W. Synthesis 1973, 207. Boche, G.; Bigalke, J. Tetrahedron Lett. 1984, 25, 955.
- Perst, H. Oxonium Ions in Organic Chemistry; Verlag Chemie: Weinheim, 1971. Kabus, S. Angew. Chem., Int. Ed. Engl. 1966, 675. Pindur, U.; Muller, J.; Flo, C.; Witzel, H. Chem. Soc. Rev. 1987, 16, 75.
- Satisfactory elemental analysis and/or exact mass molecular weights were obtained on all new compounds. In all cases ¹³C NMR, ¹H NMR, and IR data were consistent with the assigned structure.

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