

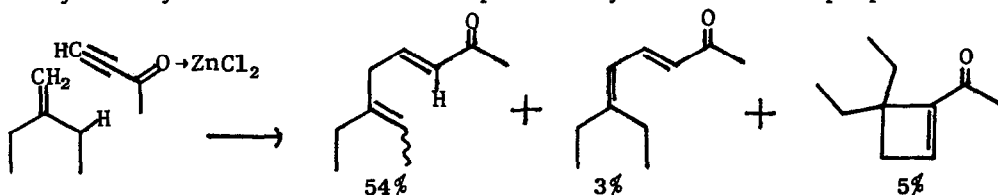
THE LEWIS ACID CATALYZED REACTION OF 3-BUTYN-2-ONE WITH ALKENES

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We have recently shown that the aluminum chloride catalyzed reaction of propiolate esters with alkenes yields stereospecific [2+2] cycloadducts and/or ene adducts, depending on the degree of substitution of the double bond.<sup>1,2</sup> Unlike other aluminum chloride catalyzed [2+2] cycloaddition reactions of acetylenes,<sup>3</sup> this reaction appears to involve complexation of the Lewis acid with the carbomethoxy group rather than the acetylene. It should, therefore, be generalizable to acetylenes containing other electron withdrawing groups capable of complexing with Lewis acids.

In this paper, we report the Lewis acid catalyzed reaction of 3-butyn-2-one<sup>4</sup> with alkenes to provide a variety of interesting 2,5-dienones, 2,4-dienones, and 1-cyclobutenyl methyl ketones which were previously difficult to prepare. The



optimal catalyst/solvent system was determined using the reaction of 3-butyn-2-one and 2-ethyl-1-butene. The maximum yield of crude adduct is obtained with 0.5 equiv. of anhydrous zinc chloride, bromide, or iodide in methylene chloride for 4 days at 25°. <sup>4,5</sup> The expected ene adduct<sup>6</sup> (see Table 1) is obtained in 54% yield along with 5% of the cyclobutenyl methyl ketone<sup>7</sup> and 3% of the conjugated dienone. The conjugated dienone presumably arises from acid catalyzed conjugation of the 2,5-dienone. All further work was carried out with zinc chloride as catalyst and methylene chloride as solvent. Reactions were run for 3-7 days at 25°. The results are shown in Table 1.

1,1-Di, tri, and tetrasubstituted alkenes react similarly to 2-ethyl-1-butene and yield ene adducts (2,5-dienones) as the major products, cyclobutenyl methyl

ketones as the minor products, and varying amounts of the conjugated dienone. The ene adduct derived from 2,3-dimethyl-2-butene cannot isomerize, and is isolated in 45% yield. It had previously been prepared in 17% yield by a six step process.<sup>9</sup> The ene reaction with 1-methylcyclopentene was investigated as a model for a prostaglandin synthesis.<sup>10</sup> The desired adduct with an exocyclic methylene group is obtained in 27% yield.

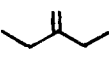
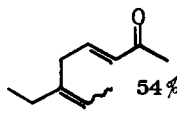
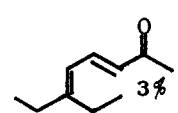
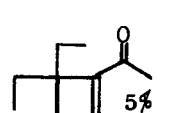

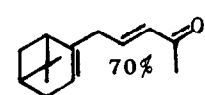

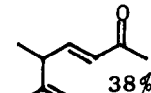
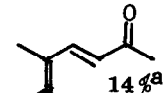
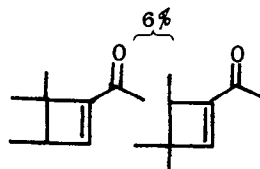

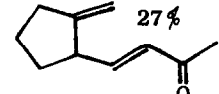
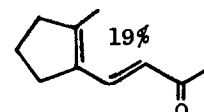
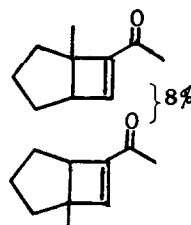

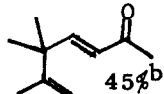
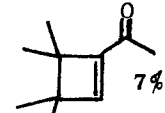

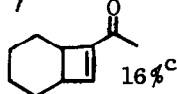

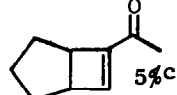

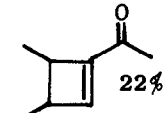
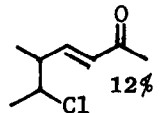

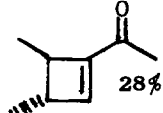
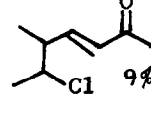
With 1,2 disubstituted alkenes, [2+2] cycloaddition to give cyclobutenes becomes the major process. This is in contrast to photolytic conditions in which olefins add across the carbonyl of 3-butyne-2-one giving alkynyl oxetanes.<sup>13</sup> The [2+2] cycloaddition of 3-butyne-2-one with trans or cis-2-butene is stereospecific. Trans-2-butene gives only the trans-3,4-dimethylcyclobutenyl methyl ketone in 28% yield, while cis-2-butene gives only the cis-3,4-dimethyl isomer in 22% yield. Both reactions also provide similar mixtures of  $\delta$ -chloroenones which appear to contain primarily one of the two possible diastereomers.<sup>14</sup> Presumably these arise from ring opening of the cyclobutenyl methyl ketone, although addition of hydrochloric acid to the ene adduct cannot be ruled out.

The mechanism of this cycloaddition reaction is open to question. The two extremes are a polar two-step sequence or a concerted [2s + 2a] cycloaddition. Although the latter is possible when one of the addends is an acetylene,<sup>5</sup> a variety of two-step polar cycloadditions are also known to proceed stereospecifically.<sup>16</sup> It is clear that in these 3-butyne-2-one cycloadditions the stabilization of negative charge by the complexed carbonyl group is important.

The procedures described above make a variety of unusual and reactive molecules readily available by an easy one-pot reaction.

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Table 1. Reaction of 3-Butyn-2-one with Alkenes

Alkene	Ene Adduct Yield	Conjugated Dienone Yield	Cyclobutenyl Methyl Ketone Yield	Chloroenone Yield
	 54%	 3%	 5%	
	 70%			
	 38%	 14% <sup>a</sup>	 6%	
	 27%	 19%	 8%	
	 45% <sup>b</sup>		 7%	
			 16% <sup>c</sup>	
			 5% <sup>c</sup>	
			 22%	 12%
 <sup>d</sup>			 28%	 9%

a. M. Trolliet, R. Longerey and J. Dreux, *Tetrahedron*, **30**, 163 (1974).

b. See ref. 9. c. Several minor unidentified products were also obtained.

d. Trans-4-octene gave similar results.

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4. The 3-butyn-2-one was purchased from Farchan Co. and used without further purification. The zinc bromide and zinc iodide were used as purchased from ROC/RIC. Zinc chloride was dried by refluxing in thionyl chloride. Methylene chloride was dried by filtration through natural alumina, activity grade I.
5. Use of 1,2-dichloroethane as solvent gave comparable yields but use of carbon disulfide, toluene, or ether gave much lower yields. Very poor yields were obtained when boron trifluoride etherate, titanium tetrachloride, or stannic chloride were employed as the catalyst in several solvent systems.
6. All compounds were isolated by preparative GC on a DEGS column and were characterized by NMR, IR and mass spectroscopy and gas chromatography.
7. The methyl cyclobutenyl ketones undergo ring opening reactions fairly readily. The IR spectra show characteristic absorptions at 1590 and 1680  $\text{cm}^{-1}$ . The olefinic hydrogen absorbs as a multiplet ( $J \approx 1\text{Hz}$ ) at about 6.8  $\delta$  in the NMR spectra in  $\text{CDCl}_3$ .<sup>8</sup>
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