

Reactions of 1,3-Dienes with Acrylates by Means of Transition Metal Complex Catalysts

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The reactions of 1,3-dienes with acrylates by the use of catalyst systems composed of transition-metal acetylacetonates and triethylaluminum were studied. Butadiene and isoprene react with acrylates to give hepta-2,5-dienoates and 5- or 6-methylhepta-2,5-dienoates respectively, by means of the binary catalyst system consisting of cobalt(III) or iron(III) acetylacetonate and triethylaluminum. The effects on this reaction of changing the catalyst concentration, the molar ratio of triethylaluminum to the transition-metal acetylacetonates, and the mixing order of the reagents were examined, as was the difference in catalytic activities between cobalt and iron catalyst systems.

A number of catalyst systems for the dimerization and trimerization of butadiene have been reported, most of them consisting of a transition-metal complex and an organoaluminum compound. The systems containing cobalt are excellent catalysts for the linear dimerization of butadiene to 3-methylhepta-1,4,6-triene and octa-1,3,6-triene.¹⁾ Dodeca-1,4,6,10-tetraene, a butadiene trimer, has been prepared by an analogous iron catalyst system.²⁾

The coupling of a diene with an olefinic compound, for example, ethylene, styrene and an acrylate has been realized using catalyst systems similar to those used for butadiene oligomerizations.^{3,4)}

We wish now to report on the reaction of butadiene or isoprene with acrylates; we thereby obtained products different from those reported previously.^{3a,4)} We wish also to discuss the nature of the reaction.

Experimental

Reactor. Glass tubes with a capacity of 30 ml, a 200 ml glass autoclave, and a 100 ml SUS 27 autoclave were used.

Reagents. Diluted triethylaluminum (Ethyl Corporation, U. S. A.) was used. The toluene was purified

by conventional methods. The metal acetylacetonates were prepared by usual methods.

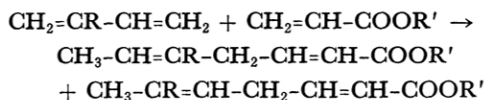
Reaction Procedures. In a small-scale reaction, 0.25 mmol of metal acetylacetonate, 25 mmol of 1,3-diene, 3 ml of toluene, and 0.25 g of a triethylaluminum toluene solution (15 wt%) were charged, in this order, into a glass ampoule. Acrylate (25 mmol) was added to the solution after the solution had shown a dark red color which was presumably due to the low-valent transition-metal complex. In a large-scale reaction, 2.5 mmol of metal acetylacetonate, 250 mmol of 1,3-diene, 30 ml of toluene, 2.5 g of a triethylaluminum toluene solution, and 250 mmol of acrylate were charged into a glass autoclave or a SUS 27 autoclave in the same way as in the small-scale reaction. All these operations were carried out under a nitrogen stream. The reactions were carried out at 50°C for 3 hr.

Analysis. For the separation of the products, the reaction mixture from the large-scale experiment was washed with dilute hydrochloric acid and with water several times, and then fractionally distilled. The products were identified by elemental analysis, by the measurement of the molecular weight and by a study of the infrared, nuclear magnetic resonance, and ultraviolet spectra. For the detection and quantitative analysis of the products, the reaction mixture was directly analyzed by means of gas chromatography, using a 2 m stainless-steel column 4 mm in diameter packed with 20% poly-diethyleneglycol succinate on Shimalite, at a helium gas flow rate of 30 ml/min at 160°C.

Hydrogenation. The number of C=C double bonds was determined by means of hydrogenation, using palladium black as a catalyst, at the atmospheric pressure of hydrogen and at room temperature.

Results and Discussion

The reaction of butadiene and isoprene with acrylates yielded hepta-2,5-dienoates and 5- or 6-methylhepta-2,5-dienoates respectively:



1) a) S. Ohtsuka, T. Taketomi and T. Kikuchi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1094 (1963); *J. Am. Chem. Soc.*, **85**, 3709 (1963). b) T. Saito, T. Ohno, Y. Uchida and A. Misono, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1099 (1963). c) S. Tanaka, K. Mabuchi and N. Shimazaki, *J. Org. Chem.*, **29**, 1626 (1964).

2) M. Hidai, Y. Uchida and A. Misono, *This Bulletin*, **38**, 1243 (1965).

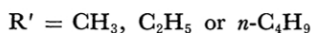
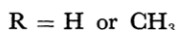
3) a) D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963). b) G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964). c) H. Mueller, D. Wittenberg, H. Seibt and E. Sharf, *Angew. Chem.*, **77**, 318 (1965).

4) B. A. S. F., Japanese Pat. 19354 (1964).

TABLE 1. CHARACTERISTIC VALUES OF METHYL HEPTA-2,5-DIENOATE (I), METHYL HEPTA-3,5-DIENOATE (II), ETHYL HEPTA-2,5-DIENOATE (III) AND BUTYL HEPTA-2,5-DIENOATE (IV)

I		II	
Mol wt	142	145	
Elem. Anal.	Found: C, 68.83; H, 8.89%. Calcd for C ₈ H ₁₂ O ₂ : C, 68.53; H, 8.63%	Found: C, 68.81; H, 8.46%	Calcd for C ₈ H ₁₂ O ₂ : C, 68.53; H, 8.63%
UV Abs.† λ_{max}	215 m μ	230 m μ	
ϵ_{max}	8.37×10^3	1.53×10^4	
bp	50—53°C/5 mmHg		
III		IV	
Elem. Anal.	Found: C, 69.76; H, 9.32%. Calcd for C ₉ H ₁₄ O ₂ : C, 70.10; H, 9.15%	Found: C, 72.26; H, 10.10%	Calcd for C ₁₂ H ₁₈ O ₂ : C, 72.49; H, 9.94%
UV Abs.† λ_{max}	215 m μ	215 m μ	
ϵ_{max}	1.01×10^4	9.83×10^3	
bp	100—105°C/15 mmHg		96—100°C/1.5 mmHg

† Cyclohexane was used as solvent.



The catalyst system composed of iron(III) acetylacetonate and triethylaluminum required a larger amount of triethylaluminum than did the cobalt catalyst system in order to catalyze the reaction with a comparable efficiency. 3-Methylhepta-1,4,6-triene, which is the main product of the butadiene homooligomerization using cobalt catalyst systems,¹⁾ was not detected.

Identification. *Products of the Reaction of Butadiene with Methyl Acrylate.* The reaction of butadiene with methyl acrylate by means of the cobalt catalyst system yielded methyl hepta-2,5-dienoate (I) in about a 20–30% yield (based on the charged monomers). The other products were methyl hepta-3,5-dienoate (II) (2–3%) and the higher oligomers. The characteristic values and the nuclear magnetic resonance spectra of I and II are given in Tables 1 and 2 respectively.

With the iron catalyst system, the ratio of the products differed from that found with the cobalt catalyst system, and an unidentified product (bp 60–65°C/8 mmHg, mol wt, 142), which is probably another type of adduct of butadiene and methyl acrylate, was formed in about half the amount of I.

The structures of I and II were determined as follows. The molecular weight and the elemental analysis of I fit the empirical formula $C_8H_{12}O_2$. The broad absorption peak at about 215 m μ in the ultraviolet spectrum of I indicates that I has a C=C double bond conjugated with C=O, while the absorption at about 230 m μ of II indicates that II has a conjugation between two C=C double bonds. The absorption peaks at 1728 cm⁻¹ in the infrared spectrum of I and at 1748 cm⁻¹ in that of II also indicate that I is an α , β -unsaturated ester, while II is not. Neither I nor II has the

band characteristic of a vinyl group. From the nuclear magnetic resonance spectra, it is evident that these compounds have a methyl group adjacent to -CH=. The presence of two C=C double bonds is confirmed by the results of the hydrogenation of I and II. From these facts, I and II were determined to be methyl hepta-2,5-dienoate and methyl hepta-3,5-dienoate respectively.

Products of the Reaction of Butadiene with Ethyl Acrylate or Butyl Acrylate. The reaction of butadiene with ethyl acrylate or butyl acrylate by means of the cobalt catalyst system afforded ethyl hepta-2,5-dienoate (III) (25–30%) and butyl hepta-2,5-dienoate (IV) (25–30%) respectively. The infrared and nuclear magnetic resonance spectra of III and IV showed the same absorption peaks as those of I, except for the peaks attributable to the ethyl group or butyl group. The characteristic values of III and IV are given in Table 1.

Products of the Reaction of Isoprene with Ethyl Acrylate. In the reaction of isoprene with ethyl acrylate, two adducts were obtained according as which site of isoprene coupled with ethyl acrylate. These two products were obtained in somewhat higher yields (35–45% in total) than that of I in the reaction of butadiene with methyl acrylate. They are ethyl 5-methylhepta-2,5-dienoate (V) (bp 103–105°C/6 mmHg) and ethyl 6-methylhepta-2,5-dienoate (VI) (bp 106–108°C/6 mmHg) obtained in a ratio of 3:1 to 2:1. V and VI were separated by fractional distillation. The structures of V and VI were determined in the same way as that of I. The elemental analysis of V and VI is as follows:

V Found: C, 71.98; H, 9.70%.

VI Found: C, 71.69; H, 9.70%.

Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%.

The nuclear magnetic resonance spectra of V and VI are shown in Table 2.

TABLE 2. NMR SPECTRA OF I, II, V and VI†

τ -Value	Assignment	Relative intensities
I		
8.35 (doublet)	$\text{CH}_3^*-\text{CH}=\text{}$	2.94
7.05 (triplet)	$=\text{CH}-\text{CH}_2^*-\text{CH}=\text{}$	3
6.28 (singlet)	CH_3^*-O	3
2.7-4.8	Olefinic protons	3.93
II		
8.20 (doublet)	$\text{CH}_3^*-\text{CH}=\text{}$	2.87
6.85 (doublet)	$=\text{CH}-\text{CH}_2^*-\text{CO}$	2.19
6.30 (singlet)	CH_3^*-O	3
2.9-4.7	Olefinic protons	4.35
V		
8.75 (triplet)	$\text{O}-\text{CH}_2-\text{CH}_3^*$	3.3
8.50	$\text{CH}_3^*-\text{CH}=\text{}$	6
8.35	$\text{CH}_3^*-\text{CH}=\text{}$, $\text{C}=\text{C}-\text{CH}_3^*$	
7.15 (doublet)	$=\text{C}-\text{CH}_2^*-\text{CH}=\text{}$	1.9
5.90 (quartet)	$\text{O}-\text{CH}_2^*-\text{CH}_3$	2.1
3.0-5.0	Olefinic protons	3.1
VI		
8.75 (triplet)	$\text{O}-\text{CH}_2-\text{CH}_3^*$	3.3
8.30, 8.40	$\text{CH}_3^* \text{ } \diagup \text{C}=\text{CH}-$ $\text{CH}_3^* \text{ } \diagdown$	6
7.15 (triplet)	$=\text{CH}-\text{CH}_2^*-\text{CH}$	2.1
5.90 (quartet)	$\text{O}-\text{CH}_2^*-\text{CH}_3$	2.4
3.0-5.0	Olefinic protons	3.1

† Tetramethylsilane was used as an internal reference and carbon tetrachloride as solvent.

The Reaction of Butadiene with Methyl Acrylate. The reaction of butadiene with methyl acrylate was quite fast at 50°C, and the yields and conversions reached constant values about two hours after the beginning of the reaction (Fig. 1).

The Effect of the Catalyst Concentration on the Reaction. The effect of the metal acetylacetonate concentration on this reaction was also studied. It was found that there was a marked difference between cobalt and iron catalyst systems in this respect. The yield of I reached a constant value in a reaction by either a cobalt or an iron catalyst system about two hours after the beginning of the reaction. The relation between the catalyst concentration and the yield of I in the reaction time of 3 hr is shown in Fig. 2. In the case of the iron catalyst, although the yield of I was low, it was proportional to the amounts of iron(III) acetylacetonate in the concentration range investigated. On the other hand, in the case of the cobalt catalyst system, it rather decreased as the concentration of cobalt(III) acetylacetonate increased.

The Effect of the Mixing Order of the Reagents. For both cobalt and iron catalyst systems, the

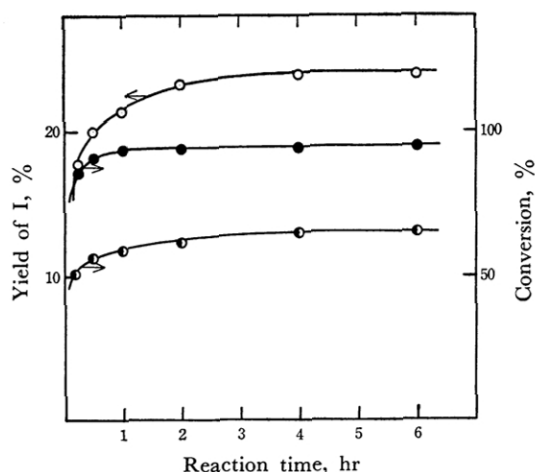


Fig. 1. The reaction of butadiene with methyl acrylate by the cobalt catalyst.

—○— Yield of I
—●— Conversion of butadiene
—◐— Conversion of methyl acrylate
Co(acac)₃/monomer mol. ratio=1/100
AlEt₃/Co(acac)₃ mol. ratio=2.7
Co(acac)₃, 0.25 mmol
Reaction temperature: 50°C
Solvent: toluene, 3 ml

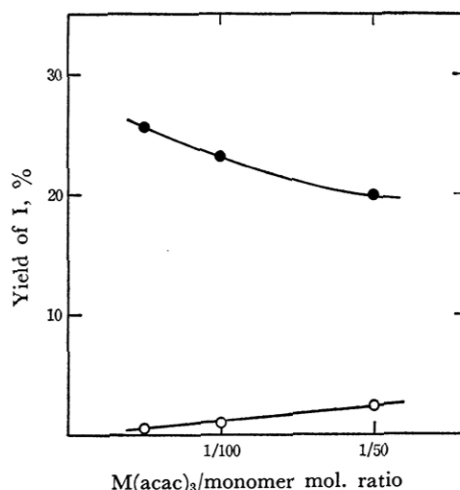


Fig. 2. The effect of catalyst concentration.

—●— Yield of I (for Co catalyst)
—○— Yield of I (for Fe catalyst)
Monomers: 25 mmol
AlEt₃/metal acetylacetonate mol. ratio=2.8
Reaction time: 3 hr
Reaction temperature: 50°C
Solvent: toluene, 3 ml

activity of the catalyst was markedly suppressed when the catalyst solution was prepared in the presence of methyl acrylate without butadiene. When triethylaluminum was added last in the presence of iron(III) acetylacetonate, butadiene,

and methyl acrylate, only a trace of I was formed; by the use of the cobalt catalyst system, however, the yield and the conversions were not different from those found with the usual mixing order (the mixing order of (1) in Table 3).

TABLE 3. THE EFFECT OF THE MIXING ORDER ON THE YIELD OF I

Mixing order	Yield of I	Mixing order	Yield of I
(1) Co-BD-Al-MA	22%	Fe-BD-Al-MA	1.3%
(2) Co-BD-MA-Al	26	Fe-BD-MA-Al	t
(3) Co-MA-Al-BD	2	Fe-MA-Al-BD	t

Co: cobalt(III) acetylacetonate

Fe: iron(III) acetylacetonate Al: triethylaluminum

BD: butadiene MA: methyl acrylate

Metal acetylacetonate, 0.25 mmol

Al/metal acetylacetonate mol. ratio=2.8

Metal acetylacetonate/monomer mol. ratio=1/100

Reaction time: 3 hr Reaction temperature: 50°C

Solvent: toluene, 3 ml

The Effect of Triethylaluminum on the Reaction.

The effect of the molar ratio of triethylaluminum to metal acetylacetonates (the Al ratio) on the reaction was also examined. Figure 3 gives the results on the reactions conducted at a constant concentration of metal acetylacetonates and with a variation in the concentration of triethylaluminum. In the case of the cobalt catalyst, the Al ratio of about 3–6 gave the maximum yield of I, whereas in the case of the iron catalyst the yield of I increased almost linearly with the Al ratio in the range investigated.

Figure 4 shows the results of the reactions at a constant concentration of triethylaluminum and with a variation in the concentration of the metal acetylacetonates. The yield of I decreased with the decrease in cobalt acetylacetonate, while in the case of the iron catalyst an increase in the yield of I was observed as the concentration of iron acetylacetonate decreased.

These results reveal the importance of the Al ratio and of the concentration of triethylaluminum in the reactions, especially in those with the iron catalyst.

The catalyst solutions are prepared by the reaction of triethylaluminum with a transition-metal compound in the presence of a diene. It is very probable that low valent transition metals act as the reaction centers just as in the case of butadiene oligomerization, and that the reaction proceeds between dienes and acrylates which are coordinated to low-valent transition metals.

The structure of the products of the present study shows that a hydrogen transfers from an acrylate to a diene during the reaction, and that the reaction is not the dienylation of acrylates reported by Wittenberg^{3a)} for reactions performed

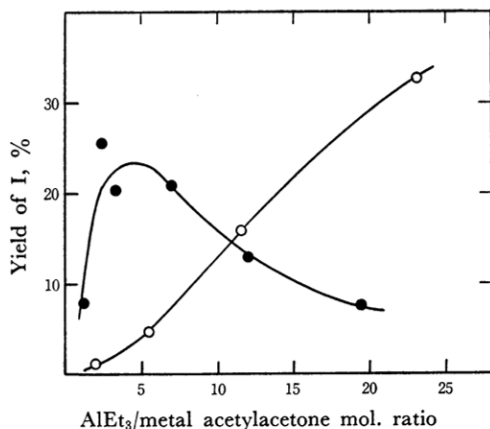


Fig. 3. The effect of mol. ratio of triethylaluminum to transition metal acetylacetonate.

—●— Yield of I (for Co catalyst)

—○— Yield of I (for Fe catalyst)

Metal acetylacetonate: 0.25 mmol

Metal acetylacetonate/monomer mol. ratio=1/100

Reaction time: 3 hr

Reaction temperature: 50°C

Solvent: toluene, 3–6 ml

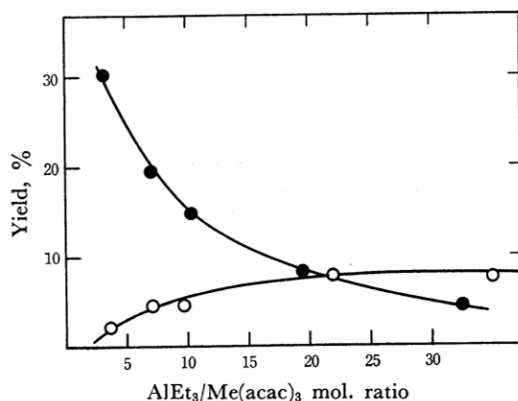


Fig. 4. The effect of mol. ratio of triethylaluminum to transition metal acetylacetonate.

—○— Fe catalyst

—●— Co catalyst

50°C, 3 hr AlEt₃: 0.8 mmol

Monomers: 25 mmol Solvent: toluene, 6 ml

under conditions which do not seem to be essentially different from ours.

The great influence of an excess of triethylaluminum on the reaction with an iron catalyst system suggests that it plays another role in addition to reducing a transition metal to a low-valent state. In the oligomerization of butadiene with the catalyst systems composed of nickel tetracarbonyl or dicobalt octacarbonyl and triethylaluminum,^{1a,5)}

5) S. Ohtsuka, H. Mori, T. Kikuchi, F. Imaizumi and I. Nagaoka, *Shokubai*, **7**, 50 (1965).

triethylaluminum is considered to play the role of expelling the carbonyl ligand from the zerovalent transition metal, and then, by coordinating itself loosely to the transition metal, to facilitate the coordination of butadiene to the transition metal.

Also in this reaction, triethylaluminum seems to facilitate the exchange reaction of ligands by coordinating to the low-valent transition metal, so promoting the reaction.
