allowed to cool and the 10.9 g of X, mp 78–81°, which precipitated, was collected by filtration. Evaporation of the solvent afforded an additional 7 g of product, mp 65–75°, which was recrystallized from benzene. The total yield of X was 17.9 g (98.8%).

Anal. Calcd for $C_9H_{11}NOS$: C, 59, 64; H, 6.11; N, 7.72. Found: C, 59.70; H, 6.15; N, 7.96.

p-Tolyl 2,4-Dimethylthioallophanate (XI). A. From p-Tolyl Methyl Carbamate (X) and Methyl Isocyanate.—A solution of 0.035 g (0.5% by weight) of potassium *t*-butoxide and 7 g (0.04 mole) of X in 20 ml of benzene was heated to reflux and a solution of 2.28 g (0.04 mole) methyl isocyanate in 10 ml of benzene was added during 6 min. The mixture was allowed to reflux for 20 min. Benzene (100 ml) was added and the 1.1 g (48.3%) of trimethyl isocyanurate, mp 174–175°, which precipitated, was removed by filtration. Evaporation of the solvent and recrystallization of the residue from methanol afforded 4.5 g (42.2%) of XI, mp 89–90°.

Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.43; H, 5.93; N, 11.75. Found: C, 55.51; H, 5.81; N, 11.80.

B. From p-Toluenethiol and 2,4-Dimethylallophanoyl Chloride.—To a solution of 6.1 g (0.41 mole) of 2,4-dimethylallophanoyl chloride[6] in 60 ml of benzene there was added 4.15 g (0.041 mole) of triethylamine and 5.1 g (0.041 mole) of *p*-toluenethiol. An exothermic reaction occurred immediately. The mixture was stirred for 30 min after which time the 4.75 g (84.3%) of triethylamine hydrochloride which had precipitated was removed by filtration. Evaporation of the solvent afforded 10.5 g of crude XI, mp 70–85°, which was recrystallized from benzene to give 5.9 g (60.5%) of XI, mp 89–91°. The infrared and nmr spectra were identical with those of the compound prepared by procedure A.

***n*-Dodecyl-2,4-Dimethylthioallophanate (XII).**—A solution of 6 g (0.105 mole) of methyl isocyanate in 10 ml of benzene was added dropwise and with stirring during 4 min at 28–43° to a solution of 0.1 g of potassium *t*-butoxide and 10.1 g (0.05 mole) of 1-dodecanethiol in 20 ml of benzene. Benzene (100 ml) was added and the very small amount of trimethyl isocyanurate which precipitated was removed by filtration. Evaporation of the solvent left 15.7 g (99.5%) of *n*-dodecyl 2,4-dimethylthioallophanate, a liquid.

Anal. Calcd for $C_{16}H_{32}N_2O_2S$: N, 8.84. Found: N, 8.70.

Reaction of Alcohols with Methyl Isocyanate. General Procedure.—The reaction of isopropyl alcohol with methyl isocyanate well exemplifies the procedure used for the products summarized in Table III. A solution of 22.8 g (0.4 mole) of methyl isocyanate in 20 ml of benzene was added dropwise and with stirring during 10 min to a solution of 0.12 g of potassium *t*-butoxide[13] and 12 g (0.2 mole) of isopropyl alcohol in 20 ml of benzene. The mixture was allowed to reflux for 30 min. Benzene (100 ml) was added and the 6.85 g (30%) of trimethyl isocyanurate which precipitated was removed by filtration. Evaporation of the solvent and fractional distillation of the residue afforded 7.2 g of isopropyl methylcarbamate [bp 42–46° (0.2 mm)]; 9.3 g of a mixture of isopropyl methylcarbamate (57%) and isopropyl 2,4-dimethylcarbamate (43%) [bp 46–63° (0.2 mm)]; and 7.5 g of pure isopropyl 2,4-dimethylallophanate, [bp 63–65° (0.2 mm)]. The total yields are listed in Table III.

The Synthesis of Unsaturated Esters by a Semicatalytic Reaction of Nickel Carbonyl

J. B. METTALIA, JR., AND E. H. SPECHT

Rohm and Haas Research Division, Philadelphia, Pennsylvania

Received July 7, 1967

Methyl 7-hydroxy-2,5-heptadienoate and dimethyl 2,5,8-decatriene-1,10-dioate were prepared from reactions of either *cis*-2-butene-1,4-diol or butadiene monoxide with acetylene, carbon monoxide, nickel carbonyl, and methanol in the presence of an acid and an inorganic halide. The reaction of butadiene monoxide was controlled to give high yields of the seven-carbon ester but the *cis*-2-butene-1,4-diol reaction could not be directed to this product alone. The isomeric distribution of products was established by a combination of polarography and ultraviolet and infrared absorption spectroscopy.

Chiusoli[1] has described a very facile technique for converting allylic compounds to 2,5-hexadienoates which involves the reaction of the allylic compound with acetylene, carbon monoxide, nickel carbonyl, and alcohol. It was of interest to us to apply this reaction to appropriately substituted butenes in order to prepare seven and ten carbon acids or esters of possible commercial importance.[2]

Diol Reaction.—The initial work was directed to converting the difunctionally allylic intermediates *trans*-1,4-dichloro-2-butene and *cis*-2-butene-1,4-diol by reaction at one allylic substituent to methyl 7-substituted-2,5-heptadienoate (I) or by reaction at both allylic substituents to dimethyl 2,5,8-decatriene-1,10-dioate (II) (eq 1). Compound I after hydrogenation and amidation could serve as an intermediate to enantholactam and nylon 7 while compound II on hydrogenation and saponification would give sebacic acid. Chiusoli[1a,c] has reported, however, that 1,4-dichloro-2-butene undergoes a rapid reaction with nickel carbonyl that results in the formation of *cis*-2-butene and butadiene but no carbonylation products. Our experience with this reaction verifies his observation. Over a wide variety of conditions, including the addition of *trans*-1,4-dichloro-2-butene to an established carbonylation reaction of allyl chloride, the *trans*-1,4-dichloro-2-butene reacts solely with nickel carbonyl to produce nickel chloride and butadiene.[3] The use of Chiusoli conditions in the reaction of *cis*-2-butene-1,4-diol[1b] also results in butadiene as the sole product even when the molar ratios of diol to hydrogen chloride or sulfuric acid are very high. The failure of these reactions is directly due to having halogen as both allylic

$$\left.\begin{array}{l}\mathrm{ClCH_2CH{=}CHCH_2Cl}\\ \quad\text{or}\\ \mathrm{HOCH_2CH{=}CHCH_2OH + HCl}\end{array}\right\}\xrightarrow[\mathrm{HC{\equiv}CH,\ CH_3OH}]{\mathrm{Ni(CO)_4,\ CO}}$$

$$\begin{array}{c}\mathrm{RCH_2CH{=}CHCH_2CH{=}CHCOOCH_3}\\ \mathrm{Ia,\ R = OH}\\ \mathrm{b,\ R = Cl}\end{array}$$

$$\Big\downarrow{\scriptstyle \mathrm{Ni(CO)_4,\ CO}\atop \scriptstyle \mathrm{HC{\equiv}CH,\ CH_3OH}}$$

$$\underset{\mathrm{II}}{\mathrm{H_3COOCCH{=}CHCH_2CH{=}CHCH_2CH{=}CHCOOCH_3}} \qquad (1)$$

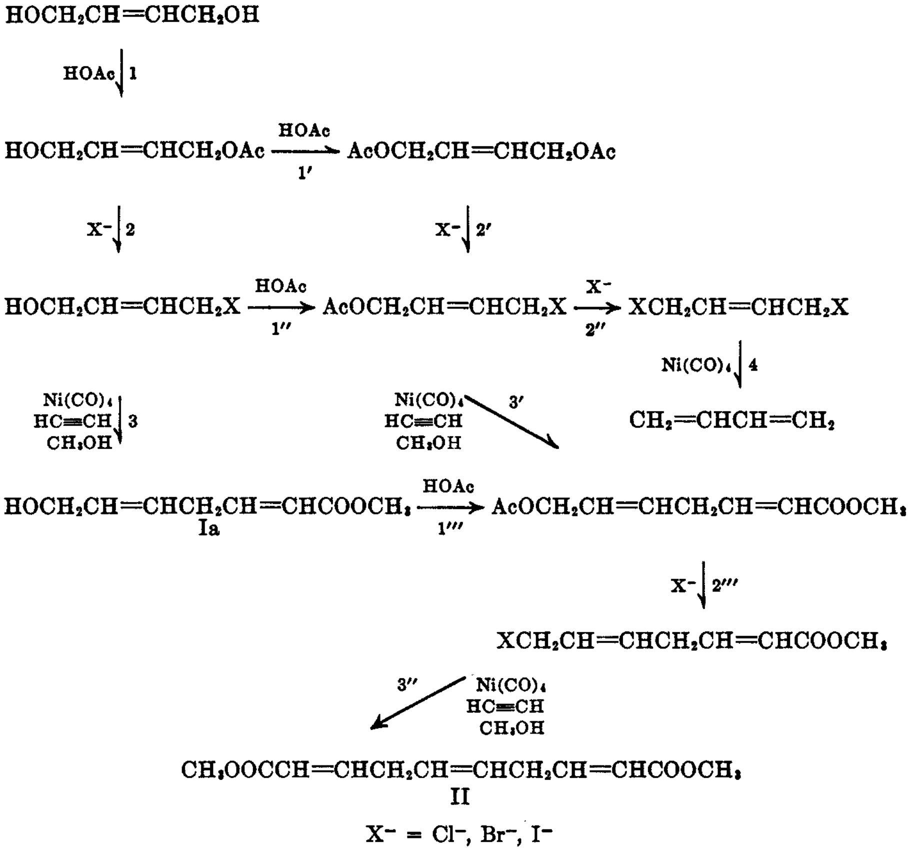
---

[1] (a) G. P. Chiusoli, *Chim. Ind.* (Milan), **41**, 506 (1959); (b) G. P. Chiusoli, *ibid.*, **41**, 762 (1959); (c) G. P. Chiusoli and L. Cassar, *Angew. Chem. Intern. Ed. Engl.*, **6**, 124 (1967); (d) G. P. Chiusoli and G. Bottaccio, Belgian Patent 630, 619 (1963).

[2] (a) Our interest in this particular area of nickel carbonyl chemistry stemmed from research at Rohm and Haas on the semicatalytic acrylate reaction.[2b] During studies on the application of various alcohols to the process, the reaction of allyl alcohol was independently observed to give the allyl ester of 2,5-hexadienoic acid. (b) H. T. Neher, E. H. Specht, and A. Neuman (Rohm and Haas Co.), U. S. Patent 2,582,911 (1952).

[3] Identification of butadiene was established by preparation of the maleic anhydride adduct which was compared with an authentic sample.

SCHEME I



substituents since the reactions of 4-chloro-2-buten-1-ol, 1-butoxy-4-chloro-2-butene, and N-(4-chloro-2-butenyl) benzamide all lead to the expected carbonylation products when an acid acceptor such as sodium carbonate is present. Chiusoli has also reported a normal carbonylation for 1-acetoxy-4-chloro-2-butene under these conditions.[1c,d] In the absence of acid acceptors butadiene formation predominates[4] in these reactions. Successful carbonylation of *cis*-2-butene-1,4-diol to a mixture of hydroxy ester (Ia) and diester (II) is achieved, however, when the intermediate monohalide is generated slowly *in situ* through the agency of a weak acid (acetic, formic, phosphoric acids)–inorganic halide (lithium chloride, sodium bromide) combination. In such a system we believe kinetic control favors carbonylation over butadiene formation because the rate of carbonylation is rapid compared to the nucleophilic displacement by halide ion on the esters derived from esterification of the diol. This prevents the formation of dihalide and butadiene. In order to be consistent with the data which will be presented the rate of 3′ must be faster than 2″ and, by analogy, it seems probable that 3,3″ are also faster than 2,2′2″ and 2‴. In support of Scheme I we have found that 1,4-diacetoxy-2-butene[5] can be converted to the ten-carbon diester II in the absence of any added acid but through the agency of inorganic halides. With strong mineral acids butadiene is the sole product and with weaker acids such as acetic and phosphoric in the absence of halide ion no reaction occurs at all. The diol is also inert when acetic and phosphoric acids are used in the absence of halide.

The diol reaction was studied in some detail as both a batch and a continuous process. Batch operation consisted in feeding nickel carbonyl, acetylene, methanol and halide to a mixture of acid and diol until no further reaction occurred while continuous operation involved feeding all reactants at constant conditions to a 1-l. continuous-flow, stirred tank reactor until a sufficient number of reactor turnovers had occurred to insure an equilibrium sample for work-up. Phosphoric and acetic acids were both employed, but phosphoric acid gave higher yields. The yields of Ia and II indicated in the various tables are predominantly the 2,5 and the 2,5,8 isomers respectively, unless otherwise noted. The reaction exhibited a very marked dependence on the halide employed as shown in Table I. In the reactions that were successful,

TABLE I
THE EFFECT OF HALIDE ON THE CARBONYLATION OF *cis*-2-BUTENE-1,4-DIOL[a]

	% yield on diol		
Halide, mole	Ia	II	Ia + II
LiCl,[b] 0.62	1	52	53
LiBr, 0.23	4	45	49
NaBr, 0.23	0.2	51	51.2
NaBr, 0.08	14	47	61
NaI, 0.23	0.02	51	51
$CaCl_2$, 0.46	Butadiene only		
$CaBr_2$, 0.30	Butadiene only		
CaI_2, 0.23	0.5	56	56.5
$NiCl_2$, 0.23	Butadiene only		

[a] Batch reaction; 0.95 mole of diol, 0.6 mole of H_3PO_4, excess $Ni(CO)_4$, C_2H_2, and CO at 45°. [b] The reaction temperature was 56°; this reaction could not be initiated below 50°.

---

[4] This is due to the production of hydrogen chloride in the carbonylation of allylic chlorides.

[5] (a) Allyl acetate and formate also reacted in the presence of lithium bromide to form methyl 2,5-hexadienoate. (b) In separate experiments it was demonstrated that allyl acetate can be converted to allyl chloride and bromide by treatment with lithium chloride and bromide in methanol at 50°.

nickel was isolated as an insoluble phosphate (Ni:P ratio 1.0 ± 0.2, indicating $Ni_2P_2O_7$) while the halide was recovered intact from an aqueous extract of the reaction mixture. The results with nickel chloride, calcium chloride, and calcium bromide may possibly be attributed to the initial formation of the strong acids hydrogen chloride and hydrogen bromide by the reaction of these salts with phosphoric acid prior to the nucleophilic displacement reaction. Based on these initial results the reaction was studied as a continuous process using sodium bromide and phosphoric acid. The effects of halide and acid concentration on product distribution are shown in Table II.

TABLE II
YIELD AS A FUNCTION OF THE ACID AND HALIDE FEED RATES[a]

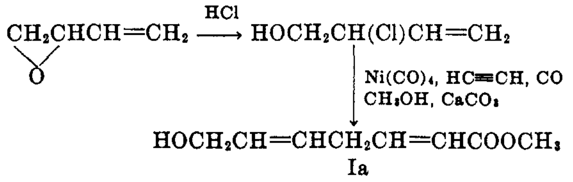
NaBr, moles/hr	H_3PO_4, moles/hr	% yield on diol Ia	II	Ia + II	Ia/II
0.27	0.10	17	2.4	19.4	7.1
0.25	0.20	40	18	58	2.2
0.27	0.30	18	28	46	0.64
0.28	1.0	6	38	44	0.16
0.007[b]	0.3	11	2.3	13	4.8
0.017	0.3	25	5.3	30	4.7
0.27	0.3	18	28	46	0.64
1.45	0.3	16	35	51	0.46

[a] Diol at 0.48 mole/hr, C_2H_2 at 1.03 moles/hr, no CO feed, at 45–50°. [b] At this level the reaction was unstable.

These data are consistent with the picture of the reaction previously given that the rate-determining step of the process involves a nucleophilic displacement by the halide ion. In the batch process the reaction is driven to high yields of II relative to Ia because an excess of reagents is employed and a sufficient time is allowed. In the continuous process the restricted time allowed for reaction causes an increase in diester II production relative to hydroxy ester Ia formation as both the acid and halide feed rates are increased. Further verification of an over-all low reaction rate was evidenced by the observations that attempts to decrease the reaction time or increase carbon monoxide incorporation into the products to levels approaching those obtained in normal allyl chloride carbonylations were unsuccessful. Since any attempts to increase the rate of reaction by increasing the rate of the slow halide displacement step were likely to result in a changeover of reaction to butadiene formation, no further work was done with *cis*-2-butene-1,4-diol.

Butadiene Monoxide Reaction.—Aside from the difficulty in obtaining high levels of catalytic activity and reasonable production rates for the diol reaction, the nature of this reaction is such that conditions which favor the formation of the intermediate hydroxy ester, Ia, necessarily result in low conversions on diol. This arises from the fact that the hydroxy ester possesses the same allylic functionality as the starting diol and hence should be equally reactive. This would not be the case if isomerization of the hydroxy ester to a 3,5 or 2,4 isomer were to occur rapidly under the conditions of reaction. Examination of the products, however, indicated that over the range of conditions studied the major product was the 2,5 isomer.[6] Since a process leading solely to the hydroxy ester was of interest, a search of the literature was made for potentially reactive compounds that might meet this requirement. The most interesting candidate found was butadiene monoxide.

Butadiene monoxide, recently synthesized in relatively high yield by the oxidation of butadiene,[7] is known to undergo facile ring opening with hydrogen chloride to a secondary allylic chloride, 2-chloro-3-buten-1-ol,[8] in good yield. Since Chiusoli[1a] has demonstrated that secondary allylic halides carbonylate to form linear products predominantly, a potential path exists for the direct conversion of the monoxide to the desired hydroxy ester, Ia (eq 2).



$$\text{CH}_2\text{CHCH}{=}\text{CH}_2 \xrightarrow{\text{HCl}} \text{HOCH}_2\text{CH(Cl)CH}{=}\text{CH}_2 \xrightarrow[\text{CH}_3\text{OH, CaCO}_3]{\text{Ni(CO)}_4\text{, HC}{\equiv}\text{CH, CO}} \underset{\text{Ia}}{\text{HOCH}_2\text{CH}{=}\text{CHCH}_2\text{CH}{=}\text{CHCOOCH}_3} \quad (2)$$

The initial experiments involved the preparation of the secondary allylic chloride and its separate conversion to the hydroxy ester. Over-all yield was about 50% and there was no evidence of vinyl group absorption and, hence, unrearranged product, in the infrared spectrum of the crude product. Attempts to generate the desired product in a one-step reaction with hydrogen chloride and butadiene monoxide gave only a small yield of the hydroxy ester; the predominant product was a methanol addition product of butadiene monoxide.[9] A series of screening, batch experiments was then made with a variety of reagents designed to determine the effect of various nucleophiles and differing conditions of acidity on the conversion of butadiene monoxide to the hydroxy ester. The results are shown in Table III. As expected, the use of active nucleophiles under weakly acidic conditions favored the production of hydroxy ester over side reactions such as the methanol addition to butadiene monoxide that was observed when hydrogen chloride was used. The formation of hydroxy ester was completely unexpected, however, in the reaction employing acetic acid without halide or in the reaction in which neither

TABLE III
CARBONYLATION OF BUTADIENE MONOXIDE[a]

Acid	Halide	Yield of Ia, %[b]
HCl	. . .	9.4
HCl	. . .	8.8
HOAc	. . .	21
HOAc	LiBr	32
HOAc	LiCl	47
H_2CO_3	LiCl	37
. . .	LiCl	(14)[c]
. . .	. . .	(8.8)[c]

[a] Batch reactions employing $Ni(CO)_4$, $HC{\equiv}CH$, CO, and CH_3OH under similar conditions. [b] On butadiene monoxide. [c] Product is predominantly the 3,5 isomer.

---

(6) This is discussed in greater detail in the section on isomer distribution.

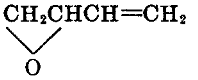
(7) (a) B. Phillips and P. S. Starcher (Union Carbide Corp.), British Patent 858,793 (1961); (b) M. Korach and W. H. Rideout (Columbia Southern Chemical Corp.), British Patent 846,534 (1960); (c) Imperial Chemical Industries, French Patent 1,323,787 (1963).

(8) (a) A. A. Petrov, *J. Gen. Chem. USSR*, **11**, 991 (1941); (b) R. K. Kadesch, *J. Am. Chem. Soc.*, **68**, 41 (1946).

(9) Analytical data did not allow differentiation between 1-methoxy-3-buten-2-ol and 2-methoxy-3-buten-1-ol.

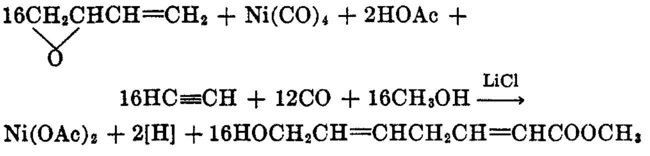
TABLE IV

CONVERSION OF BUTADIENE MONOXIDE TO METHYL 7-HYDROXY-2,5-HEPTADIENOATE (Ia)[a]

Run no.	1	2	3	4	5	6	7
Temp, °C	45	47	48	35	48	45	48
CO incorporation, %[b]	57	71	76	54	76	62	78
Feed rates, moles/hr							
 $\underset{\mathrm{O}}{\mathrm{CH_2CH}}\mathrm{CH{=}CH_2}$	0.935	0.53	0.52	0.50	0.50	3.04	0.51
$Ni(CO)_4$	0.275	0.156	0.046	0.078	0.052	0.36	0.056
HOAc	0.315	c	0.063	0.094	0.06	0.63	0.05
LiCl	0.50	0.50	0.50	0.52	0.50	0.79	0.50
CH_3OH	15.6	20.4	17.0	17.2	17.0	13.0	17.2
C_2H_2	1.10	0.60	0.52	0.52	0.52	3.12	0.52
CO	0.60	0.30	0.35	0.25	0.38	1.80	0.41
Production rate, moles/hr							
Base[d]	...	...	0.0023	...	...	...	0.004
Acid[d]	0.128	...	...	0.008	0.02	0	...
Ni^{2+}(titration)	0.091	...	0.026	...	...	0.264	0.024
Ni^{2+}(gravimetric)	0.10	0.03	0.029	0.052	0.028	...	...
$CH_2{=}CHCOOCH_3$	0.073	0	0	0	0	0	0
$CH_2{=}CHCH{=}CH_2$	Present	0	0	0	0	0	0
Ia[e]	0.58	0.32	0.38	0.39	0.36	2.14	0.39
% yield of Ia[f]	62	61	73	77	72	71	75

[a] Reaction run as continuous process for minimum of four reactor volume turnovers. [b] See footnote 13 for definition; values determined from CO gas consumed and Ni^{2+} formed. [c] H_2CO_3 at 0.10 mole/hr. [d] Determined from potentiometric titration. [e] Determined from vpc analysis of the product stream. [f] Based on butadiene monoxide.

acid nor halide was present. Since allylic acetates are completely inert to carbonylation[10] in the absence of the halide ion, it would appear that a direct ring opening of the epoxide by nickel carbonyl is occurring and that the intermediate formation of an allylic halide is not required. In the reactions in which no acid was employed, the reaction mixture became basic; a methanol addition product of butadiene monoxide was formed and the hydroxy ester produced was the 3,5 isomer rather than the 2,5 isomer. No attempt was made in these initial runs to optimize the yield and as many as 35 distinct peaks were observed when these samples were programmed on a vapor phase chromatograph. A few of these components were trapped off the chromatograph and identified. The major, low boiling by-products proved to be methyl 5-hydroxy-3-pentenoate[11] and a methanol addition product of butadiene monoxide. Lesser amounts of methyl 2-vinyl-3-hydroxypropionate,[11] butadiene and methyl acrylate were also found. Butadiene formation was greatest in the runs in which hydrogen chloride was used. The system involving acetic acid and lithium chloride appeared to be the most promising, and this system was studied as a continuous process with the results as shown in Table IV. In none of these runs was any diester II produced. Maximum yields of 70–77%[12] and carbon monoxide incorporations into product of 60–78% were realized when the acid feed was adjusted to maintain the product stream close to neutrality. Acid consumption in these runs was 81–98% of theory based on



$$16\underset{\mathrm{O}}{\mathrm{CH_2CH}}\mathrm{CH{=}CH_2} + Ni(CO)_4 + 2HOAc + 16HC{\equiv}CH + 12CO + 16CH_3OH \xrightarrow{LiCl} Ni(OAc)_2 + 2[H] + 16HOCH_2CH{=}CHCH_2CH{=}CHCOOCH_3$$

(written arbitrarily for a condition of 75% carbon monoxide incorporation).[13] Production rate changes from 0.38 to 2.14 moles of product/hr were achieved without significant loss in yield or loss in carbon monoxide incorporation into the product. Catalytic activity (carbon monoxide incorporation) observed compared very favorably with the semicatalytic acrylate reaction[14] and was very much superior to that observed in the diol reaction.[15]

Isomer Distribution.—Chiusoli has characterized the major product of the reaction of allylic halides with acetylene, carbon monoxide, nickel carbonyl, and alcohols as 2-*cis*-5-*trans*-hexadienoates and has reported[16] that under mild basic conditions this 2,5 product iso-

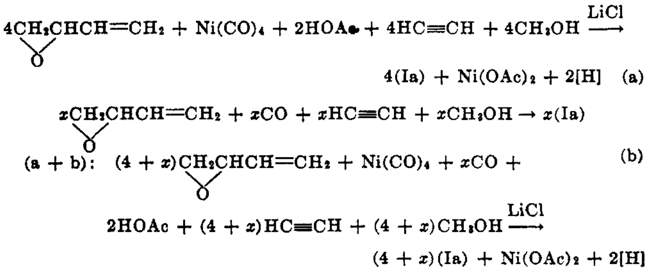
---

(10) Allyl acetate, allyl formate, and 1,4-diacetoxy-2-butene were inert to carbonylation in the absence of halide ion.

(11) These products are the expected ones for a reaction of butadiene monoxide with nickel carbonyl and methanol in which acetylene is not incorporated.

(12) Neither unreacted butadiene monoxide nor any of the low boiling products reported earlier were found in these reaction mixtures. Treatment of the crude, stripped product with methanol in the presence of sulfuric acid for 8 hr at 100° in an autoclave did not result in any increase in hydroxy ester yield which indicated that the heptadienoate product was all in the form of the methyl ester.

(13) For purposes of stoichiometric calculations, the semicatalytic reaction can be written as the sum of a reaction a involving nickel carbonyl and a reaction b involving carbon monoxide.



$$4\underset{\mathrm{O}}{\mathrm{CH_2CH}}\mathrm{CH{=}CH_2} + Ni(CO)_4 + 2HOAc + 4HC{\equiv}CH + 4CH_3OH \xrightarrow{LiCl} 4(Ia) + Ni(OAc)_2 + 2[H] \quad (a)$$

$$x\underset{\mathrm{O}}{\mathrm{CH_2CH}}\mathrm{CH{=}CH_2} + xCO + xHC{\equiv}CH + xCH_3OH \rightarrow x(Ia) \quad (b)$$

$$(a + b):\quad (4 + x)\underset{\mathrm{O}}{\mathrm{CH_2CH}}\mathrm{CH{=}CH_2} + Ni(CO)_4 + xCO + 2HOAc + (4 + x)HC{\equiv}CH + (4 + x)CH_3OH \xrightarrow{LiCl} (4 + x)(Ia) + Ni(OAc)_2 + 2[H]$$

Per cent of carbon monoxide incorporation is then defined as $\frac{100x}{4 + x}$.

(14) (a) Reference 2b. (b) J. E. Ehrreich, R. G. Nickerson, and C. E. Ziegler, *Ind. Eng. Chem., Process Design Develop.*, **4**, 77 (1965). Carbon monoxide incorporations into acrylates of 70–85% are claimed in both references.

(15) The maximum carbon monoxide incorporation in the diol reaction was 25%.

(16) (a) G. P. Chiusoli and S. Merzoni, *Chim. Ind.* (Milan), **43**, 256 (1961); (b) G. P. Chiusoli, A. G. Agnes, C. A. Ceselli, and S. Merzoni, *ibid.*, **46**, 21 (1964); G. P. Chiusoli, *Angew. Chem.*, **72**, 750 (1960).

merizes to a 3,5-hexadienoate, whereas, at higher temperatures or under more strongly basic conditions, the 2,4 isomer is produced. Since the conditions employed in both the diol and butadiene monoxide reactions were somewhat different from those employed by Chiusoli, it was of interest to determine the relative percentages of these isomers in the hydroxy ester fraction. The three isomers were separated on a Carbowax 20M vapor phase chromatographic column when properly temperature programmed, and it was possible to isolate both the 2,5 and 3,5 isomers from the column. Quantitative analysis of the three isomers was accomplished by comparing chromatographic peak areas. The qualitative identification of the three peaks rested on the following evidence. Treatment of the hydroxy ester fraction with triethylamine at room temperature resulted in a decrease in the size of the first peak, a major increase in the second peak, and a small increase in the very small third peak. The infrared spectrum showed a decrease in the 820-cm^{-1} band (Chiusoli[1a] and others[17] have related this band to a conjugated *cis* double bond), the band at 970 (*trans*, unconjugated double bond) disappeared, a band at 990 (*trans*, conjugated double bond) appeared, and the band at 1720 shifted to 1735 (conjugated ester to saturated ester); the polarogram showed a shift in half-wave potential (mercury pool reservoir) from -2.0 (ethyl acrylate $= -1.9$ v) to -2.6 (pure 3,5 isomer $= -2.6$ v) and -1.7 (ethyl sorbate $= -1.7$ volts); the ultraviolet absorption maximum in methanol shifted from 215 to 228 mμ. On treatment of the hydroxy ester fraction with triethylamine at elevated temperature, the first two peaks were greatly reduced and the third peak increased. The sample showed strong ultraviolet absorption maxima in methanol at 230 and 263 mμ and an increase in the polarographic half wave potential at -1.7 v.[18] The changes that occurred on treatment with base were therefore 2,5 (peak 1) → 3,5 (peak 2) → 2,4 (peak 3). The results of the quantitative determination of the isomer distribution of a variety of reaction mixtures are shown in Table V.

TABLE V
ISOMER DISTRIBUTION

Reacn conditions	% of isomers 2,5	3,5	2,4
cis-2-Butene-1,4-diol			
Excess H_3PO_4	66	26	7
Stoichiometric H_3PO_4	96	0	4
	97.5	1	1.5
Deficient H_3PO_4	96	2	2
Butadiene monoxide			
Excess HOAc	82	18	0
	80	20	0
Stoichiometric HOAc	77	23	0
	80	20	0
	76	24	0
	78	22	0
H_2CO_3	86	14	0
No Acid	39	61	0
	57	43	0
	64	36	0
4-Chloro-2-buten-1-ol			
$CaCO_3$	69	31	0

Although there are more variables in these runs than acid levels, there does appear to be the expected relationship of acidity to product distribution. In systems in which the reaction medium was close to neutrality, 80% of the 2,5- and 20% of the 3,5 isomer were formed, while in basic systems the distribution was 40–65% of the 2,5- and 35–60% of the 3,5 isomer. A few polarographic and infrared spectra checks on isomer distribution were in close agreement with the values obtained by vapor phase chromatography so that only a negligible amount of isomerization took place on the gas chromatograph column. The 2,5 product of the reactions of *cis*-2-butene-1,4-diol, *cis* and *trans*-4-chloro-2-butene-1-ol, and butadiene monoxide is the 2-*cis*-5-*trans* product. The infrared spectra of all three products are identical and agree with the infrared data obtained by Chiusoli on similar reaction products. The diester products from the reactions of 1,4-diacetoxy-2-butene, 4-chloro-2-buten-1-ol, and *cis*-2-butene-1,4-diol are predominantly dimethyl or diethyl 2-*cis*-5-*trans*-8-*cis*-decatriene-1,10-dioate as determined from their infrared and ultraviolet spectra as well as their polarographic half-wave potentials. This is in agreement with Chiusoli's published data on the dimethyl ester prepared from 1-chloro-4-acetoxy-2-butene.[1d] Saponification of the diethyl ester produced 3,5,7-decatriene-1,10-dioic acid in agreement with the same product prepared by Chiusoli.[19]

Experimental Section

All melting and boiling points are uncorrected. The nmr spectra were obtained on a Varian HR-60, the infrared spectra from a Perkin-Elmer Model 21, the ultraviolet spectra from a Perkin-Elmer Model 202, the polarographic data from a Leeds and Northrup Electrochemograph Type E,[20] and potentiometric titrations from a Leeds and Northrup Model 7644. Butadiene monoxide was custom synthesized by Medical Research Consultants; *cis*-2-butene-1,4-diol was purchased from General Aniline and Film Corp. All other intermediates were synthesized by known routes.

The apparatus employed for the carbonylations was a 1-l., continuous-flow, stirred, glass-tank reactor equipped with automatic temperature and liquid level controls. The gases (acetylene, carbon monoxide, nitrogen, and hydrogen chloride) were monitored into the reactor through calibrated rotameters equipped with automatic pressure controls which ensured delivery to within two per cent of the desired flow. The solutions of the other reactants in methanol were fed to the reactor by means of positive displacement pumps with an accuracy of 5%. Operation was at atmospheric pressure and on some occasions a slight positive nitrogen bleed had to be maintained to avoid a partial vacuum. The composition of the gas vent was determined by analysis on a Fisher Gas Partitioner. This analysis coupled with a determination of divalent nickel content was the basis for calculations of carbon monoxide incorporation into the product. Previous work in our laboratory on the semicatalytic acrylate reaction[14a] had demonstrated that maximum levels of carbon monoxide incorporation in carbonylation reactions could only be achieved in continuous-flow apparatus and only with close control of the variables of reactant molar ratios and temperature.

Methyl 7-Hydroxy-2,5-heptadienoate (Ia). A. From 4-Chloro-2-buten-1-ol.—A mixture of 71.2 g (0.67 mole) of 4-chloro-2-buten-1-ol,[21] 40 g (0.4 mole) of calcium carbonate,

---

(17) R. G. Sinclair, A. F. McKay, G. S. Myers, and R. N. Jones, *J. Am. Chem. Soc.*, **74**, 2578 (1952).

(18) With the exception of the polarographic data similar evidence has been cited by Chiusoli and coworkers in their identification of the isomeric hexadienoates.[1a–c,16]

(19) G. P. Chiusoli and G. Agnes, *Chim. Ind.* (Milan), **46**, 25 (1964).

(20) The polarographic data were obtained by Mr. R. LaCoste. Conditions follow: 25°, 60-cm high mercury reservoir, 2 to 5 sec capillary, 0.1 *M* methyl tributyl ammonium chloride in 10% water, 50% ethanol and 40% benzene as supporting electrolyte, dropping mercury cathode and a mercury reservoir as reference electrode.

(21) J. Colonge and G. Poilane, *Bull. Soc. Chim. France*, 953 (1955).

and 400 ml of anhydrous methanol was charged to a 1-l., continuous-flow, stirred tank reactor. The reactor was flushed with nitrogen and then a mixture of acetylene and carbon monoxide gases was fed at rates of 0.23 mole/hr and 0.07 mole/hr, respectively. After 6 min a solution of nickel carbonyl in anhydrous methanol was fed at a rate of 0.18 mole of nickel carbonyl/hr. The reaction was initiated 8 min after the start of the nickel carbonyl feed, as evidenced by the production of a reddish color and the complete absorption of the feed gases. Temperature was maintained at 35°. Reaction occurred for 2 hr at which time the reaction mixture became green and a high gas vent was observed. The product solution was filtered and stripped of nickel carbonyl and methanol under reduced pressure. The residue was extracted with ether and water, and the ether layer was dried with sodium sulfate, filtered, stripped of ether, and then distilled in a 36 in. × 10 mm spinning-band column. A pure cut was isolated which had bp 79° (0.15 mm), $n^{20}\text{D}$ 1.4868.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75; O, 30.73. Found: C, 61.16; H, 7.75; O, 30.81.

The infrared spectrum (neat) showed strong bands at 3350, 1720, 1640, 1438, 1400, 995, 968, and 818 cm^{-1}. The ultraviolet absorption spectrum in methanol did not exhibit any maxima above 212 mμ.

B. From *cis*-2-Butene-1,4-diol.—A solution of 44 g (0.5 mole) of *cis*-butenediol (General Aniline and Film Corp. purified grade) and 29.4 g (86%, 0.3 mole) of phosphoric acid made up to 240 ml with methanol was charged to the 1-l. reactor. The reactor was flushed with nitrogen and maintained at 45° while a solution of nickel carbonyl in methanol was fed at a rate of 0.31 mole of nickel carbonyl/hr and a solution of sodium bromide in methanol was fed at a rate of 0.27 mole of sodium bromide/hr. Initially acetylene and carbon monoxide were fed at 0.56 mole/hr and 0.14 mole/hr, respectively. After the reaction had initiated, the feeds were maintained at the following rates: nickel carbonyl at 0.31 mole/hr, sodium bromide at 0.27 mole/hr, acetylene at 1.03 mole/hr, carbon monoxide at 0.20 mole/hr, butenediol at 0.50 mole/hr, phosphoric acid at 0.31 mole/hr, and methanol at 20 mole/hr. The reaction was maintained for 8 hr at which time a sufficient number of reactor turnovers (eight) had occurred to ensure an equilibrium sample. The material in the reactor was then filtered and stripped of nickel carbonyl and methanol under reduced pressure, and the residue was extracted with ether and water. Analysis of the aqueous layer showed 0.15 mole of Ni^{2+} per 0.5 mole of butenediol reacted. The ether layer was dried with sodium sulfate, filtered and stripped to a residue. The ether residue was analyzed by vpc (Apiezon L at 240°, helium flow rate at 120 cc/min) to contain methyl 7-hydroxy-2,5-heptadienoate (29% conversion based on butenediol) and dimethyl 2,5,8-decatriene-1,10-dioate[22] (34% conversion based on butenediol). The identification of the dimethyl 2,5,8-decatriene-1,10-dioate was based on isolation of a sample by distillation and comparison of its infrared spectrum with that of an authentic sample. The identification of methyl 7-hydroxy-2,5-heptadienoate was based on isolation and analysis of a distilled sample which had bp 90° (0.4 mm), $n^{20}\text{D}$ 1.4870.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75; O, 30.73. Found: C, 61.40; H, 7.67; O, 31.25.

The infrared spectrum (neat) was identical with that of the previously prepared sample.

C. From Butadiene Monoxide.—A solution of 21 g of lithium chloride (0.5 mole) in 300 ml of anhydrous methanol was charged to the reactor, which was flushed with nitrogen. Acetylene was fed at the rate of 0.25, butadiene monoxide at 0.5, nickel carbonyl at 0.15, and acetic acid at 0.125 mole/hr. Temperature was maintained at 45°. After initiation occurred the temperature was reduced to 35° and the following feed rates were maintained: butadiene monoxide at 0.5, nickel carbonyl at 0.078, acetic acid at 0.0935, lithium chloride at 0.52, acetylene at 0.52, carbon monoxide at 0.25, and methanol at 17 moles/hr. After four reactor turnovers the material in the reactor was worked up as described previously. Vpc analysis gave a yield of 77% of methyl 7-hydroxy-2,5-heptadienoate. A consumption of 0.053 mole of Ni^{2+} per 0.5 mole of butadiene monoxide had occurred, based on elemental nickel determination. A pure distillation cut had bp 90–98° (0.5 mm), $n^{20}\text{D}$ 1.4904.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75; O, 30.73. Found: C, 61.98; H, 7.74; O, 30.26.

The infrared spectrum (neat) was identical with those of the two previous samples. A sample of the crude butadiene monoxide reaction product was hydrogenated using Raney nickel at 100–150°, 1000 psig of H_2 to give methyl 7-hydroxyheptanoate, bp 95–100° (0.5 mm), $n^{20}\text{D}$ 1.4410. Recovery was 95% of the amount predicted by vpc analysis of Ia.

Anal. Calcd for $C_8H_{16}O_3$: C, 59.97; H, 10.07; O, 29.96. Found: C, 60.13; H, 10.29; O, 29.51.

The methyl 7-hydroxyheptanoate was treated with an excess of concentrated NH_4OH at 25° for 8 days. After cooling, the precipitate which formed was filtered, washed, and dried. No further purification was made. The 7-hydroxyheptanoic acid amide had mp 112–114°. Isolated yield was 86%.

Anal. Calcd for $C_7H_{15}NO_2$: C, 57.90; H, 10.41; O, 9.64; N, 22.03. Found: C, 57.86; H, 10.29; O, 9.45; N, 22.32.

Dimethyl 2,5,8-Decatriene-1,10-dioate.—A suspension of 20 g (0.19 mole) of sodium carbonate in 200 ml of anhydrous methanol was charged to the reactor. The reactor was flushed with nitrogen and the following compounds were fed: 4-chloro-2-buten-1-ol at 0.56, nickel carbonyl at 0.20, acetylene at 0.60, carbon monoxide at 0.20, and methanol at 8 moles/hr. The reaction initiated 5 min after the start of the nickel carbonyl feed and was held at 38° for a period of 1 hr at which time the reaction mixture became green and the gases vented. The reaction mixture was then held at 35° and anhydrous hydrogen chloride was fed at a rate of 0.18 along with acetylene at 0.60 and carbon monoxide at 0.20 mole/hr. After 40 min the nickel carbonyl feed was resumed at 0.20 mole/hr. After 60 min the hydrogen chloride rate was increased to 0.60 mole/hr. In an additional 10 min the reaction initiated, becoming a dark red color, and the reaction continued for 65 min at which time the mixture became green and a high gas vent occurred. The total reaction mixture was worked up as previously described. From the mixture 0.34 mole of methyl acrylate and 0.24 mole of Ni^{2+} were recovered. Part of the ether extract was distilled to give a pure sample of dimethyl 2,5,8-decatriene-1,10-dioate, bp 96° (0.1 mm), $n^{20}\text{D}$ 1.4896 (lit.[1d] bp 140° (5 mm), $n^{20}\text{D}$ 1.4911).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19; O, 28.54. Found: C, 64.30; H, 7.22; O, 28.91.

The infrared spectrum (neat) exhibited strong bands at 1715–1730, 1640, 1435, 1400, 968, and 815 cm^{-1}. The ultraviolet spectrum did not exhibit any bands above 212 mμ. The sole polarographic half wave potential at −2.0 v had an intensity 1.6 times the intensity of the same wave in methyl 7-hydroxy-2,5-heptadienoate. The ether extract from above was hydrogenated with PtO_2 at 900 psig and at 25°. The product was distilled to give a pure cut of dimethyl sebacate. Yield of dimethyl sebacate based on 4-chloro-2-buten-1-ol was 38%.

Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63; O, 27.79. Found: C, 62.94; H, 9.85; O, 27.38.

The infrared spectrum was identical with that of an authentic sample of dimethyl sebacate. Saponification of the sample gave a solid which after recrystallization from water had mp 133–135° and which did not depress the melting point of authentic sebacic acid (mmp 131–133°).

Diethyl 2,5,8-Decatriene-1,10-dioate.—A solution of 10.4 g (0.12 mole) of lithium bromide in 250 ml of anhydrous ethanol was charged to the reactor. The reactor was flushed with nitrogen and the following compounds were fed: 1,4-diacetoxy-2-butene[23] at 0.3, nickel carbonyl at 0.2, acetylene at 0.6, carbon monoxide at 0.16, and ethanol at 7 moles/hr. Initiation did not occur until the temperature was raised to 55°. A total of 0.6 mole of 1,4-diacetoxy-2-butene was fed and the reaction sustained itself for 2.5 hr. Potentiometric titration of the reaction product gave two end points, one for acetic acid (0.458 mole) and the other for nickel acetate (0.27 mole). The total reaction mixture was worked up as previously described. A total of 0.42 mole of ethyl acrylate was produced. The product could not be distilled from the ether residue because of decomposition but a pure sample was trapped from an Aerograph Autoprep A700 (20 ft × 3/8 in. column of 15% Apiezon L on

---

[22] The formation of this product is further evidence that the intermediate hydroxy ester is allylic and hence predominantly a 2,5-heptadienoate. The vpc analyses were checked by means of spiking experiments and were found to be accurate to within 5% of the reported values.

[23] W. J. Bailey and R. Barclay, Jr., *J. Org. Chem.*, **21**, 328 (1956).

Chromosorb W programmed from 80 to 295°). Yield by vpc analysis was 65%.

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.60; H, 7.95. Found C, 66.31; H, 7.94.

The remainder of the ether extract was saponified with sodium hydroxide and the product recrystallized twice with water to give the isomerized product 3,5,7-decatriene-1,10-dioic acid.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.16. Found: C, 61.36; H, 6.31.

Nmr analyses showed a doublet at τ 6.48 ($>C{=}CCH_2C(=O)-$) with a 3:2 ratio in intensity of vinyl protons to methylene protons; ultraviolet spectrum showed $\lambda_{max}^{H_2O}$ 260, 270, and 280 mμ (Chiusoli[19] reports 258, 267, and 276 mμ in ethanol).

7-Benzamido-2,5- (3,5-) heptadienoic Acid.—A mixture of 11 g (0.1 mole) of sodium carbonate, 45 ml of water, and 150 ml of acetone was charged to the reactor. A solution of N-(4-chloro-2-butenyl) benzamide[24] (42 g, 0.2 mole) in 340 ml of acetone and 20 ml of water was fed at a rate of 0.1 mole of amide/hr. Nickel carbonyl was fed at a rate of 0.05 as an acetone solution, acetylene at 0.133, and carbon monoxide at 0.06 mole/hr. Reaction occurred at 35° and lasted 2 hr. The reaction mixture was stripped and extracted with chloroform, and a precipitate isolated from the chloroform extract after cooling was recrystallized twice from chloroform, mp 122–123°.

Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; Acid No. 228.7; Br_2 No. 128. Found: C, 67.82; H, 6.39; Acid No. 228.3; Br_2 No. 128.5.

The infrared spectrum (Nujol mull) exhibited strong bands at 3280, 2890, 1695, 1625, 1600, 1530, 1458, 1440, 977, 970, and 818 cm^{-1}. Ultraviolet absorption spectrum in methanol exhibited a strong band 210–228 mμ. Polarographic data gave $E_{1/2} = -2.4$ (butadiene, −2.5) and $E_{1/2} = -2.0$ (methyl acrylate, −2.0). Intensity ratio indicated 90% of the 3,5 and 10% of the 2,5 isomer.

Methyl 7-butoxy-2,5-heptadienoate was prepared from the reaction of 1-butoxy-4-chloro-2-butene[25] with nickel carbonyl, acetylene, carbon monoxide, methanol, and calcium carbonate. A sample of the product was isolated from an Aerograph Autoprep A700 (Apiezon L, 190°).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.98; H, 9.50; 0, 22.61. Found: C, 67.69; H, 9.69; O, 22.50.

Infrared spectrum (neat) exhibited strong bands at 1725, 1642, 1438, 1100–1118, 968, and 818 cm^{-1}. No ultraviolet maxima appeared above 212 mμ.

Methyl 5-hydroxy-3-pentenoate was isolated from an Aerograph Autoprep A700 (5 ft × $^3/_8$ in. column 10% Carbowax 20M terminated with terepthalic acid on 70–80 mesh, acid-washed Chromosorb W, programmed 80–235°, 200 cc of helium/min) separation of a butadiene monoxide reaction product.

Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75; O, 36.88. Found: C, 55.58; H, 7.78; O, 36.47.

The infrared spectrum (neat) showed strong bands at 3400, 1730, 1430, 1085, 1005, and 971 cm^{-1}. The nmr spectrum showed a doublet at τ 5.97 ($HOCH_2CH{=}$) and a doublet at 6.97 ($>CH{=}CHCH_2COOCH_3$).

Methyl 2-vinyl-3-hydroxypropionate was isolated as above.

Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75; O, 36.88. Found: C, 55.44; H, 7.81; O, 36.89.

The infrared spectrum (neat) showed strong bands at 3400, 1730, 1650, 1440, 1040, 990, and 925 cm^{-1}.

Methyl 7-hydroxy-3,5-heptadienoate was isolated as above.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75; O, 30.73. Found: C, 61.47; H, 7.76; O, 30.50.

The infrared spectrum (neat) showed strong bands at 3400, 1740, 1440, 1010 (shoulders), and 990 cm^{-1}. The nmr spectrum showed a doublet at τ 5.91 ($HOCH_2CH{=}CH-$) and a doublet at 6.93 ($CH{=}CHCH_2COOCH_3$). The two doublets were of equal intensity. Polarographic data gave $E_{1/2}$ (*vs.* mercury reservoir) at −2.6 and no waves at −1.7 or −2.0 v.

1(2)-Methoxy-3-buten-1(2)-ol was isolated as above.

Anal. Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87; O, 31.33. Found: C, 58.71; H, 9.83; O, 31.87.

The infrared spectrum (neat) showed strong bands at 3400, 1070, 1040, 990, and 925 cm^{-1}. Available data did not distinguish which isomer was isolated.

Registry No.—Ia, 14565-10-7; II, 14565-19-6; methyl 7-hydroxyheptanoate, 14565-11-8; 7-hydroxyheptanoic acid amide, 14565-12-9; diethyl 2,5,8-decatriene-1,10-dioate, 14565-13-0; 7-benzamido-2,5-heptadienoic acid, 14565-14-1; methyl 7-butoxy-2,5-heptadienoate, 14565-15-2; methyl 5-hydroxy-3-pentenoate, 14565-16-3; methyl 2-vinyl-3-hydroxypropionate, 14565-17-4; methyl 7-hydroxy-3,5-heptadienoate, 14565-18-5; 7-benzamido-3,5-heptadienoic acid, 14565-33-4.

Acknowledgment.—Analytical data were obtained by various members of the Rohm and Haas analytical groups. We wish to thank Mr. R. A. Thomas, Jr. and Mr. A. Ziga for assistance in performing the experimental work.

---

[24] A. Fleury, *Compt. Rend.*, **241**, 808 (1955).

[25] A. A. Petrov, *J. Gen. Chem. USSR*, **19**, 1046 (1949).

The Synthesis of α-Hydroxy Esters from α-Keto Acetals

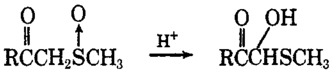
JAMES E. THOMPSON

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Received May 10, 1967

α-Keto acetals have been found to rearrange in the presence of water and Lewis acid catalysts, stannic chloride in particular, to give high yields of α-hydroxy esters. The mechanism of this rearrangement was shown to involve initial complexation of the keto acetal with stannic chloride followed by hydride transfer. Together with recently reported syntheses leading to α-keto acetals, this reaction comprises a convenient means of converting a carboxylic ester to an α-hydroxy ester with one more carbon in the chain. An especially attractive feature of this over-all process is that it appears to be the first of its kind which has been successfully applied to the synthesis of aliphatic hydroxy esters.

Since the discovery that β-keto sulfoxides can be conveniently prepared from carboxylic esters and methylsulfinyl carbanion,[1] considerable interest has developed in the chemistry of these compounds. Of particular bearing on the present work have been studies on the Pummerer rearrangement[2] of β-keto sulfoxides. Russell and co-workers[1b] have shown that a number of β-keto sulfoxides, primarily aromatic ones, rearrange in the presence of dilute mineral acid to give excellent yields of α-keto hemimercaptals (eq 1).



$$RC(=O)CH_2S(\rightarrow O)CH_3 \xrightarrow{H^+} RC(=O)CH(OH)SCH_3 \qquad (1)$$

---

[1] (a) H.-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963); (b) H.-D. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963); (c) E. J. Corey and M. Chaykovsky, *ibid.*, **86**, 1639 (1964); **87**, 1345 (1965).

[2] R. Pummerer, *Chem. Ber.*, **42**, 2282 (1909); **43**, 1401 (1910).