for the separation of dicyanoacetylene and benzene and a Dow-Corning XF-1150 silicone oil column for detection of carbon disulfide. The contents of trap 2 were allowed to evaporate in the hood. Before reuse, the sulfur and dark deposits were removed by passing air through the shielded pyrolysis tube at 600–800°; the sulfur ignited. Pure oxygen had been used in place of air for a number of times, but an explosion occurred in one instance.

Pyrolysis of 4,5-Dicyano-1,3-dithiol-2-thione (6).—The apparatus was the same as that used for the pyrolysis of 4,5-dicyano-1,3-dithiol-2-one. The flask was charged with 5.400 g of 4,5-dicyano-1,3-dithiol-2-thione.[18c,d] The pyrolysis was carried out at 650° tube temperature; the bath temperature was 100–160°, the pressure 0.2 mm. Only part of the thione (1.625 g) sublimed into the pyrolysis tube during 5 hr. The contents of both traps, on flash distillation, gave 310 mg of a mixture of dicyanoacetylene (42%; 19% yield) and carbon disulfide (54%) as determined by gas chromatography (conditions as above).

Registry No.—1, 1071-98-3.

Synthetic Reactions by Complex Catalysts. VIII. Copper-Catalyzed Reactions of Thiol and Alcohol with Diazoacetate

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The reactions of thiols and alcohols with diazoacetate by copper compound catalysts were examined, in which R of RSH (thiol) and ROH (alcohol) were $n\text{-}C_4H_9$, $C_6H_5CH_2$, and $CH_2{=}CHCH_2$. All the products were isolated and identified, the total yields of the products based on diazoacetate being almost quantitative. In the reaction with thiols, the carbene from ethyl diazoacetate was inserted into the sulfur–hydrogen linkage to produce ethyl alkylthioacetate (IV) in a high yield and a high selectivity. In addition, diethyl alkylthiosuccinate (V) and diethyl thiodiglycolate (VI) were isolated as the by-products. On the other hand, the reaction of alcohol with ethyl diazoacetate afforded the insertion reaction products in low selectivity. The O analogs corresponding to V and VI as well as triethyl 1-alkoxypropane-1,2,3-tricarboxylate (X), triethyl propene-1,2,3-tricarboxylate (XIII), diethyl fumarate, and diethyl maleate (XII) were formed. In the allyl alcohol–diazoacetate reaction, the cyclopropane derivatives were also formed.

We have reported a series of reactions of isocyanide with amines,[1] alcohols,[2,3] and thiols[4] to produce formamidine (I), formimidate (II), and thioformimidate (III), respectively (see eq 1–3). These reactions are all

$$RN{\equiv}C: + NHR'R'' \longrightarrow \underset{\text{I}}{RN{=}CHNR'R''} \qquad (1)$$

$$RN{\equiv}C: + HOR' \longrightarrow \underset{\text{II}}{RN{=}CHOR'} \qquad (2)$$

$$RN{\equiv}C: + HSR' \longrightarrow \underset{\text{III}}{RN{=}CHSR'} \qquad (3)$$

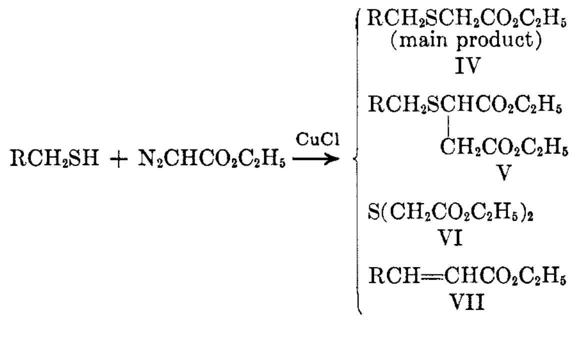
catalyzed by copper compounds and are characterized by the common feature that the isocyanide carbon atom having lone-pair electrons is inserted into N–H, O–H, and S–H linkages.

The carbene produced by the decomposition of diazoalkane is another species having the lone-pair electrons of carbon, which resembles isocyanide also in the property of coordinating with copper compounds.[5] These facts prompted us to explore the copper-catalyzed reactions of diazoacetate. We have hitherto found that the carbene carbon is inserted quite selectively into N–H linkage in the copper-catalyzed reactions of ethyl diazoacetate with amines.[6]

$$RR'N{-}H + N_2CHCOOC_2H_5 \xrightarrow{\text{Cu compounds}} RR'NCH_2COOC_2H_5 \qquad (4)$$

The present paper describes the reactions of thiols and alcohols with ethyl diazoacetate in the presence of copper compounds as catalysts.

The reaction of thiols with ethyl diazoacetate without a catalyst was once studied by Müller and Freytag,[7] and it was reported that benzenethiol reacted with ethyl diazoacetate to form ethyl phenylthioacetate, whereas aliphatic thiols did not react even at 80°. It has now been found that, in the presence of cuprous chloride as catalyst, aliphatic thiols (alkane and aralkane thiols) react satisfactorily with ethyl diazoacetate at 80–90° to produce the corresponding thioacetate (IV) as the main product along with three by-products (V, VI, and VII).



$$RCH_2SH + N_2CHCO_2C_2H_5 \xrightarrow{\text{CuCl}} \left\{ \begin{array}{c} RCH_2SCH_2CO_2C_2H_5 \\ \text{(main product)} \\ \text{IV} \\ RCH_2S\underset{|}{C}HCO_2C_2H_5 \\ CH_2CO_2C_2H_5 \\ \text{V} \\ S(CH_2CO_2C_2H_5)_2 \\ \text{VI} \\ RCH{=}CHCO_2C_2H_5 \\ \text{VII} \end{array} \right.$$

Each product was isolated by means of preparative glpc and was identified by elemental analysis and infrared and nmr spectra. Typical results are shown in Table I. Both diethyl maleate and fumarate were formed only in quite small yields in these reactions.

It is clearly indicated that the carbon having lone-pair electrons of the carbene from diazoacetate is inserted between sulfur and hydrogen of thiol to form the main product (IV). The insertion of carbene into the S–H linkage may be compared with the corresponding

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(1) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Letters*, 6121 (1966).

(2) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *ibid.*, 521 (1967).

(3) T. Saegusa, Y. Ito, S. Kobayashi, N. Takeda, and K. Hirota, *ibid.*, 1273 (1967).

(4) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and Y. Okumura, Abstracts, Annual Meeting of Chemical Society of Japan, Tokyo, April 1967.

(5) H. Nozaki, S. Moriuchi, H. Tanaka, and R. Noyori, *Tetrahedron Letters*, 5239 (1966).

(6) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and T. Shimizu, *ibid.*, 6131 (1967).

(7) E. Müller and A. Freytag, *J. Prakt. Chem.*, **146**, 56 (1931).

insertions into O–H in the reactions of alcohol with diazoacetate. The selectivity of the formation of IV was much higher than that of the alkoxyacetate in the alcohol–diazoacetate reaction by a copper catalyst, as will be described later.

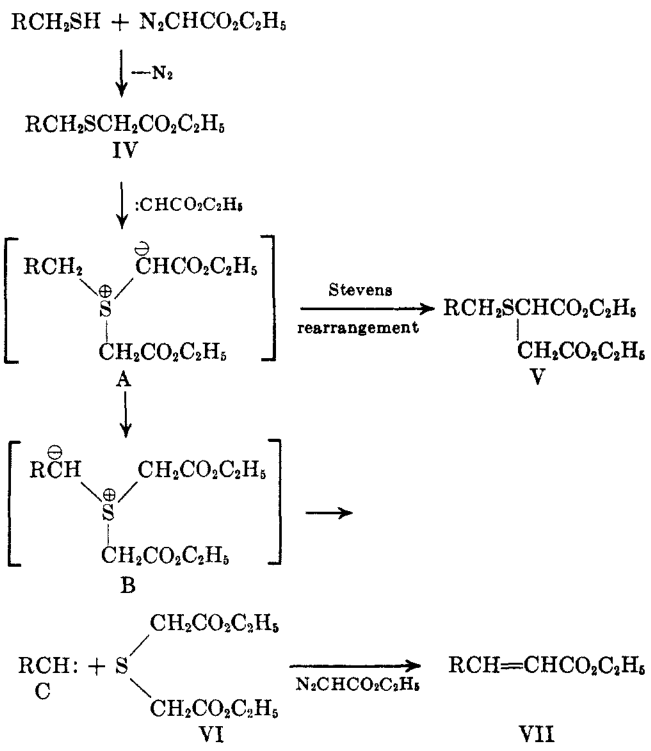
TABLE I
REACTION OF THIOL WITH ETHYL DIAZOACETATE BY CUPROUS CHLORIDE CATALYST[a]

Thiol (RCH_2SH)	Reaction time, hr	Products,[b] yield, % IV	V	VI	VII
n-C_4H_9SH	30	85	2	8	
$CH_2{=}CHCH_2SH$	9	63	20	7	
$C_6H_5CH_2SH$	6	86	2	9	1

[a] A mixture of 60 mmoles of thiol, 60 mmoles of ethyl diazoacetate, and 1 mmole of CuCl was heated at 80–90°. [b] The compound numbers, IV, V, VI, and VII, represent, respectively, $RCH_2SCH_2CO_2C_2H_5$, $RCH_2SC(CH_2CO_2C_2H_5)HCO_2C_2H_5$, $S(CH_2CO_2C_2H_5)_2$, and $RCH{=}CHCO_2C_2H_5$.

The formations of three by-products may reasonably be explained by the reactions depicted in Scheme I.

SCHEME I



The reaction of alkylthioacetate (IV) with the carbene from diazoacetate will lead to an S-ylide (A) which by Stevens rearrangement[8] produces alkylthiosuccinate (V). The proton shift in the S-ylide A, on the other hand, will afford the carbene (C) and diethyl thiodiglycolate (VI) through the intermediate (B). The carbene (C) in turn reacts with diazoacetate to afford the third by-product (VII).

An alternative route could also be considered for the formation of VI and VII. Proton abstract from thiol by S-ylide A and the subsequent attack of the resulting thiol anion on the resulting sulfonium ion will lead to the formation of VI. In this case, VII will be formed by the insertion of carbethoxy carbene into the methylene C–H bond of toluene thiol followed by the loss of hydrogen sulfide.

It might be assumed that alkylthiosuccinate (V) resulted from the reaction of thiol with maleate or with fumarate which could be formed from diazoacetate. This possibility, however, has been eliminated by control experiments which have shown that thiol did not react with maleate and with fumarate under the same conditions. The formation of VI, by the reaction of diazoacetate and hydrogen sulfide has also been ruled out by a control experiment.

The reaction of alcohols with ethyl diazoacetate catalyzed by cupric chloride led to a more rapid decomposition of diazoacetate than with thiols and amines. At room temperature in alcohol, the evolution of nitrogen by the decomposition of diazoacetate ceased in 3 hr. The reaction products were analyzed and isolated by glpc techniques.

The results of the reactions of 1-butanol, benzyl alcohol, and allyl alcohol, respectively, with ethyl diazoacetate in the presence of cupric chloride as catalyst are given in Tables II, III, and IV. All the products were identified; the total yield based on ethyl diazoacetate was almost quantitative. No significant difference in the catalyst activity was observed among cuprous and cupric compounds of various ligands. Except for the cyclopropane derivatives produced in

TABLE II
REACTION OF 1-BUTANOL WITH ETHYL DIAZOACETATE BY CUPRIC CHLORIDE[a]

Products	Yield, %[b]
n-$C_4H_9OCH_2CO_2C_2H_5$ (VIIIb)	15
n-$C_4H_9OCHCO_2C_2H_5$ (IXb) | $CH_2CO_2C_2H_5$	16
n-$C_4H_9OCHCO_2C_2H_5$ (Xb) | $CHCO_2C_2H_5$ | $CH_2CO_2C_2H_5$	14
$O(CH_2CO_2C_2H_5)_2$ (XI)	7
trans-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (XIIb)	12
cis-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (XIIc)	11
$C_2H_5O_2CCH{=}CCO_2C_2H_5$ (XIII) | $CH_2CO_2C_2H_5$	16
	91 (total yield)

[a] Reaction conditions were n-C_4H_9OH, 35 mmoles; $N_2CHCO_2C_2H_5$, 17 mmoles; $CuCl_2$, 1 mmole; at 25°; 3 hr. [b] Based on ethyl diazoacetate.

TABLE III
REACTION OF BENZYL ALCOHOL WITH ETHYL DIAZOACETATE BY CUPRIC CHLORIDE[a]

Products	Yield, %[b]
$C_6H_5CH_2OCH_2CO_2C_2H_5$ (VIIIc)	49
$C_6H_5CH_2OCHCO_2C_2H_5$ (IXc) | $CH_2CO_2C_2H_5$	13
$O(CH_2CO_2C_2H_5)_2$ (XI)	5
trans-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (XIIb)	7
cis-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (XIIc)	8
$C_2H_5O_2CCH{=}CCO_2C_2H_5$ (XIII) | $CH_2CO_2C_2H_5$	11
	93 (total yield)

[a] Reaction conditions were $C_6H_5CH_2OH$, 35 mmoles; $N_2CHCOOC_2H_5$, 17 mmoles; $CuCl_2$, 1 mmole; at 25°; 3 hr. [b] Based on ethyl diazoacetate.

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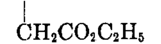
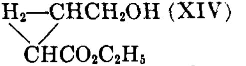
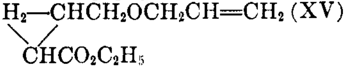
[8] T. Thompson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932).

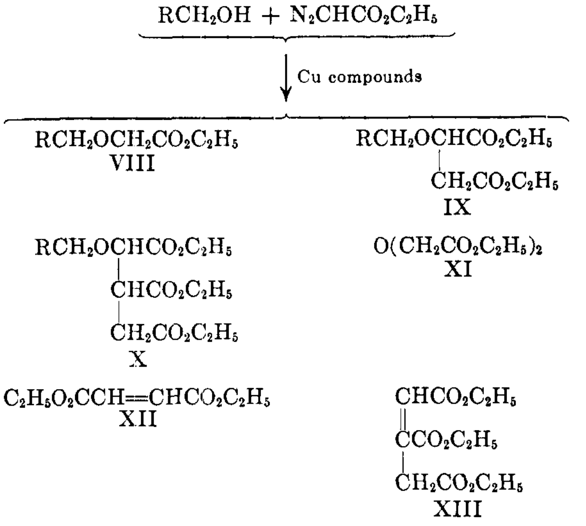
TABLE IV

REACTION OF ALLYL ALCOHOL WITH ETHYL DIAZOACETATE BY CUPRIC CHLORIDE[a]

Products	Yield, %[b]
$CH_2{=}CHCH_2OCH_2CO_2C_2H_5$ (VIIId)	17
$O(CH_2CO_2C_2H_5)_2$ (XI)	9
trans-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (XIIb)	15
cis-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (XIIc)	16
 $C_2H_5O_2CCH{=}\underset{CH_2CO_2C_2H_5}{\underset{\vert}{C}}CO_2C_2H_5$ (XIII)	24
 (XIV)	8
 (XV)	5
	94 (total yield)

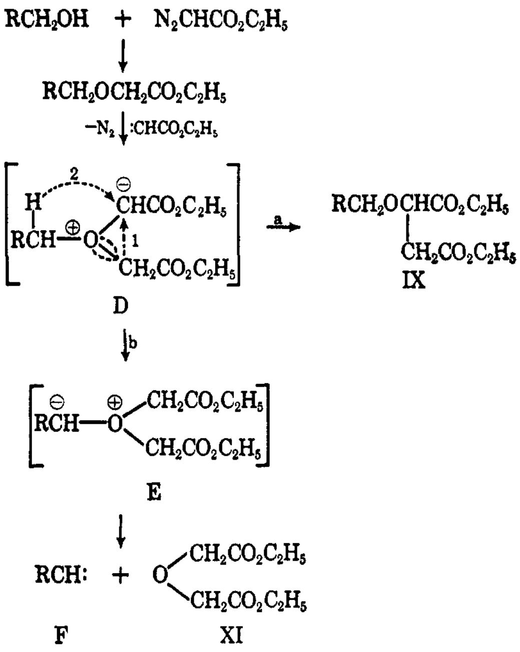
[a] Reaction conditions were $CH_2{=}CHCH_2OH$, 17.6 mmoles; $N_2CHCOOC_2H_5$, 8.8 mmoles; $CuCl_2$, 1 mmole; at 25°; 3 hr. [b] Based on ethyl diazoacetate.

the allyl alcohol–diazoacetate reaction, the products of the alcohol–diazoacetate reaction are summarized below. In the thiol–diazoacetate reaction, the sulfur compounds of the structures corresponding to VIII, IX, and XI were formed. The selectivity of the formation of VIII in the alcohol–diazoacetate reaction was, however, much lower than that of the alkylthioacetate in the thiol–diazoacetate reaction.



It has been shown in reference experiments that the reaction of VIII with ethyl diazoacetate actually affords IX and X. In a way similar to the thiol–diazoacetate reaction, the following mechanism *via* the intermediate O-ylides, D and E, may be postulated for the formations of IX and XI, *i.e.*, as shown in Scheme II. In the O-ylide D, the transfer of $CH_2CO_2C_2H_5$ group to the carbanion center (reaction a) will afford IX, whereas the hydrogen migration will give another O-ylide (E) (reaction b). Then, E in turn gives XI. Alternatively, it may also be assumed that XI is formed by the reaction of diazoacetate with water which is possibly produced in the condensation of 2 moles of alcohol to ether.

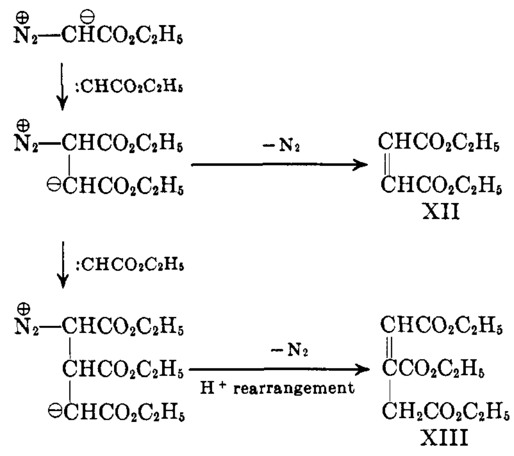
SCHEME II



The by-products of X and XIII contain three units of the carbethoxycarbene group. Reference experiments have shown that X is actually formed in the reaction of VIII with ethyl diazoacetate but it is not formed in the reaction of XIII with alcohol under the same reaction conditions. The formation of X would be explained by considering an intermediate similar to that shown in the course of VIII → IX.

On referring to the mechanism proposed for the formations of diethyl fumarate and maleate from ethyl diazoacetate,[9] the reactions given in Scheme III are now tentatively assumed to explain the production of XIII.

SCHEME III



Experimental Section

Reaction of 2-Propenethiol with Ethyl Diazoacetate.—To a stirred mixture of 4.5 g (60 mmoles) of 2-propenethiol and 0.1 g (1 mmole) of cuprous chloride, 6.9 g (60 mmoles) of ethyl diazoacetate was added dropwise at room temperature during 30 min. Stirring was then continued for additional 9 hr at 80–90°. After insoluble salt was removed by filtration, the filtrate was distillated *in vacuo* to give the distillate (9.2 g) boiling at 55–120° (26 mm). The distillate was analyzed by glpc. Three products were formed, which were isolated by preparative glpc.

Ethyl 2-propenylthioacetate (IVa) had an infrared spectrum that showed ν_{max} 1710 (vs), 1620 (w), 1270 (vs), 1120 (vs), 1020 (vs), 985 (s), and 910 cm^{-1} (s). The nmr with TMS (in $CDCl_3$) showed τ 8.74 (3 H, triplet, CH_3CH_2O–), 6.90 (2 H, singlet, SCH_2CO), 6.78 (2 H, doublet, $={}CHCH_2S$), 5.87 (2 H, quartet, CH_3CH_2O–), 4 ~ 5 (3 H, multiplet, $CH_2{=}CH$—).

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[9] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

Anal. Calcd for $C_7H_{12}O_2S$: C, 52.47; H, 7.66. Found: C, 52.14; H, 7.48.

Diethyl α-(2-propenyl)thiosuccinate (Va) possessed an nmr (in CCl_4) spectrum of τ 8.75 (6 H, triplet, CH_3CH_2O–), 7.56 (2 H, multiplet, >CH–CH_2CO), 6.78 (2 H, doublet, =$CHCH_2S$—), 6.65 (1 H, triplet, $SCHCH_2$–), 5.92 (4 H, quartet, CH_3CH_2O–), 4.0 ~ 5.2 (3 H, multiplet, CH_2=CH–).

Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.64; H, 7.37. Found: C, 53.48; H, 7.26.

Diethyl dithioglycolate (VI) was identified by the comparisons of glpc retention time and infrared spectrum with those of the authentic sample.

In the reaction of α-toluenethiol with ethyl diazoacetate, a small amount of trans ethyl cinnamate was formed in addition to the main product IV and two by-products (V and VI).

Reaction of 2-Propenethiol with Diethyl Fumarate or Diethyl Maleate.—A mixture of 1.5 g (20 mmoles) of 2-propenethiol, 3.5 g (20 mmoles) of diethyl fumarate or maleate, and 30 mg (0.3 mmole) of cuprous chloride was stirred at 80–90° for 9 hr. After the insoluble salt was removed by filtration, the filtrate was analyzed by glpc. Two starting compounds were recovered almost quantitatively and no trace of Va could be detected.

Reaction of 1-Butanol with Ethyl Diazoacetate.—To a mixture of 2.6 g (35 mmoles) of 1-butanol and 0.13 g (1 mmole) of cupric chloride, 2.0 g (17 mmoles) of ethyl diazoacetate was added dropwise with stirring at 25° during 30 min. An exothermic reaction proceeded with the evolution of nitrogen gas. When the reaction mixture was stirred for an additional 3 hr, the infrared absorption band of diazo group ($\nu_{N\equiv N}$ at 2100 cm^{-1}) disappeared. Then the reaction mixture was freed from insoluble residue by filtration and was distilled *in vacuo* to give 4.2 g of the distillate boiling from 40° (18 mm) to 160° (18 mm). The distillate was analyzed by glpc (PEG 20000, 200°C) and all the products were isolated by preparative glpc. Ethyl *n*-butoxyacetate (VIIIb), diethyl diglycolate (XI), diethyl fumarate (XIIb), and diethyl maleate (XIIc) were identified by the comparisons of the glpc retention times and the infrared spectra with those of the corresponding authentic samples.

The following three products were identified by infrared and nmr spectra and elemental analysis.

Diethyl *n*-butoxysuccinate (IXb) had an infrared spectrum that showed ν_{max} 1725 (vs), 1260 (vs), 1160 (vs), 1120 (vs), and 1020 cm^{-1} (vs); nmr with TMS (in CCl_4) showed peaks at τ 9.10 (3 H, triplet, $CH_3(CH_2)_3O$), 8.77 and 8.75 (6 H, two triplets, CH_3CH_2O–), 7.49 (2 H, doublet, >$CHCH_2CO$), 6.58 (2 H, multiplet, $CH_3(CH_2)_2CH_2O$), 5.99 (1 H, triplet, >$CHCH_2$–), 5.98 and 5.93 (4 H, two quartets, CH_3CH_2O–).

Anal. Calcd for $C_{12}H_{22}O_5$: C, 58.51; H, 9.00. Found: C, 58.26; H, 8.83.

Triethyl 1-(*n*-butoxy)propane-1,2,3-tricarboxylate (Xb) had an infrared spectrum that showed ν_{max} 1730 (vs), 1300–1100 (broad, s), and 1020 cm^{-1} (vs); nmr (in CCl_4) showed peaks at τ 9.10 (3 H, triplet, $CH_3(CH_2)_3O$–), 8.76, 8.75, and 8.73 (9 H, three triplets, CH_3CH_2O–), 7.30 ~ 7.60 (2 H, multiplet, >CH-CH_2CO–), 6.30–7.00 (3 H, multiplet, $CH_3(CH_2)_2CH_2$– and –CH_2CH–CH–), 5.97, 5.96, and 5.91 (6 H, three quartets, CH_3-CH_2O–), 5.80–6.10 (1 H, doublet, *n*-C_4H_9OCH–C).

Anal. Calcd for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49. Found: C, 57.68; H, 8.42.

Triethyl propene-1,2,3-tricarboxylate (XIII) had an infrared spectrum that showed ν_{max} 1710 (vs), 1640 (w), 1270 (vs), 1170 (vs), 1090 (s), and 1020 cm^{-1} (vs); nmr (in CCl_4) peaks appeared at τ 8.78, 8.73, 8.71 (9 H, three triplets, CH_3CH_2O–), 6.21 (2 H, singlet, =CCH_2CO–), 5.70 ~ 6.20 (6 H, three quartets, CH_3-CH_2O–), and 3.20 (1 H, singlet, =$CHCO_2$–).

Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.79; H, 7.30. Found: C, 55.49; H, 7.16.

Reaction of Ethyl *n*-Butoxyacetate with Ethyl Diazoacetate.—To a stirred mixture of 3.2 g (20 mmoles) of ethyl *n*-butoxyacetate and 0.07 g (0.5 mmole) of cupric chloride, 2.3 g (20 mmoles) of ethyl diazoacetate was added dropwise at 25°. After the evolution of nitrogen gas ceased, the reaction mixture was analyzed by glpc. In addition to the starting *n*-butoxyacetate, IXb and Xb were isolated in yields of 27% and 19%, respectively.

Reaction of Benzyl Alcohol with Ethyl Diazoacetate.—The distillation of the reaction mixture gave 5.1 g of the distillate boiling from 80° (18 mm) to 150° (3 mm). By glpc, all the products were isolated. Ethyl benzyloxyacetate (VIIIc), diethyl diglycolate (XI), diethyl fumarate (XIIb), and diethyl maleate (XIIc) were identified by the comparison of the glpc retention times and infrared spectra with those of authentic samples.

Diethyl benzyloxysuccinate (IXc) was identified by infrared and nmr spectra and elemental analysis. The infrared spectrum showed bands at ν_{max} 1740 (vs) and 1300–1000 cm^{-1} (vs); nmr (in $CDCl_3$) peaks appeared at τ 8.78 and 8.71 (6 H, two triplets, CH_3CH_2O–), 7.19 (2 H, doublet, >$CHCH_2CO$–), 5.84 and 5.77 (4 H, two quartets, CH_3CH_2O–), 5.62 (1 H, triplet, –$OCHCH_2$-CO–), 5.48 and 5.18 (2 H, two doublets, $C_6H_5C(H_A)(H_B)O$–, $J_{H\text{-}H}^{gem}$ = 11.3 cps) and 2.68 (5 H, singlet, C_6H_5–).

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.37; H, 7.24.

Reaction of Allyl Alcohol with Ethyl Diazoacetate.—At 25°, the reaction was carried out using 1.0 g (17.6 mmoles) of allyl alcohol, 1.0 g (8.8 mmoles) of ethyl diazoacetate, and 0.13 g (1 mmole) of cupric chloride. The vacuum distillation of the reaction mixture gave 1.5 g of distillate boiling in the range from 60° (30 mm) to 150° (30 mm).

Ethyl allyloxyacetate (VIIId) was identified as follows. Infrared spectrum showed bands at ν_{max} 1730 (vs), 1630 (w), 1270 (vs), 1200 (s), 1120 (vs), 1020 (vs), 990 (s), and 910 cm^{-1} (s); nmr (in CCl_4) peaks appeared at τ 8.73 (3 H, triplet, CH_3-CH_2O–), 6.08 (2 H, singlet, –OCH_2CO–), 6.02 (2 H, doublet, CH_2=$CHCH_2O$–), 5.88 (2 H, quartet, CH_3CH_2O–), and 4.00–5.00 (3 H, multiplet, CH_2=CH–).

Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.14; H, 8.30.

2-Carbethoxycyclopropylcarbinol (XIV) had an infrared spectrum that showed bands at ν_{max} 3350 (vs), 1710 (vs), 1200 (s), 1180 (vs), and 1020 cm^{-1} (vs); nmr (in CCl_4) peaks appeared at τ 8.30–9.30 (4 H, multiplet, protons of cyclopropane ring), 8.71 (3 H, triplet, CH_3CH_2O–), 6.50 (2 H, multiplet, >$CHCH_2OH$), 6.18 (1 H, singlet, -OH), and 5.93 (2 H, quartet, CH_3CH_2O–).

Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.57; H, 8.51.

Allyl 2-carbethoxycyclopropylmethyl ether (XV) had an nmr spectrum (in CCl_4) with peaks at τ 8.30–9.20 (4 H, multiplet, protons of cyclopropane ring), 8.77 (3 H, triplet, CH_3CH_2O–), 5.70–6.20 (6 H, multiplet, –CH_2OCH_2– and CH_3CH_2O–), and 4.00–5.00 (3 H, multiplet, CH_2=CH–).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 68.15; H, 4.61. Found: C, 68.51; H, 4.92.

Registry No.—IVa, 15224-05-2; Va, 15224-06-3; VIIId, 15224-07-4; IXb, 15224-08-5; IXc, 15275-67-9; Xb, 15224-09-6; XIII, 5349-99-5; XIV, 15224-11-0; XV, 15224-12-1; ethyl diazoacetate, 623-74-5; 2-propenethiol, 870-23-5; 1-butanol, 71-36-3; benzyl alcohol, 100-51-6; allyl alcohol, 107-18-6; cuprous chloride, 7758-89-6; cupric chloride, 7447-39-4.

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