Photolysis of Diazocarbonyl Compounds in Allylic Alcohols. New Preparation of Bicyclo[3.1.0]lactones and the Nature of the Reactive Intermediate

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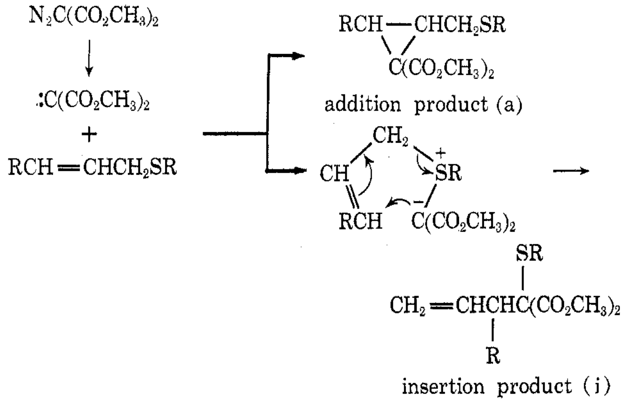
Carboalkoxycarbenes, generated photochemically from dimethyl diazomalonate or ethyl diazoacetate, react with allylic alcohols to form bicyclo[3.1.0]lactones and the insertion products of the carbene into the O–H bonds of allylic alcohols. Bicyclo[3.1.0]lactone is formed by the addition of the carbene to C=C double bond, followed by lactonization with elimination of methanol. Similar addition to the C=C bond and insertion into C—O bond by carboalkoxycarbenes were also observed in the reaction with allylic ethers. The product of insertion into C—O bond or O—H bond was not observed in the photosensitized reaction which is presumed to produce the triplet carbene. It is concluded that the singlet state of carboalkoxycarbene attacks the oxygen atom of the allylic alcohol or ether to give an intermediate oxygen ylide which rearranges to insertion product by 2,3-sigmatropic process or to O–H insertion product by hydrogen migration.

We recently reported a study of the reaction of carboalkoxycarbene with aliphatic sulfides[1-3] and allylic compounds containing sulfur, oxygen, and halides.[4-7] With an allylic compound such as allyl *n*-butyl sulfide the major processes were the insertion of the carboalkoxycarbene into the C—S bond, and addition of the carbene to the C=C bond. It was proposed that most of these reactions proceed through ylide formation by reaction of the singlet carbenes formed by the direct photolysis of diazocarbonyl compounds, and the insertion products were obtained *via* 2,3-sigmatropic allylic rearrangement of intermediate ylides.



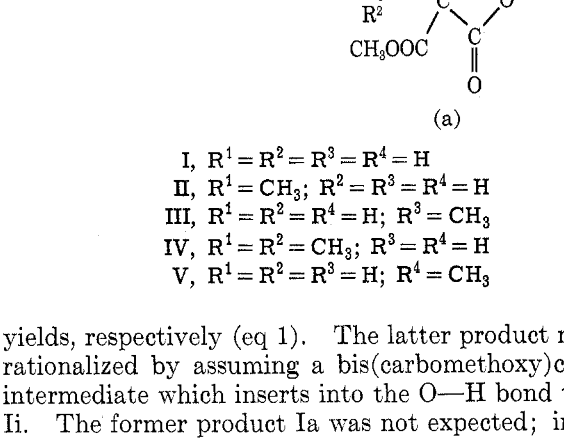
In the case of photosensitized decomposition of diazo compounds in allylic compounds, we found that such reaction with the C=C bond is prefered to the carbene insertion into the C—S, C—O, or C—Cl bond.

This study has now been extended to the direct and sensitized photolysis of diazocarbonyl compounds in allylic alcohols, and the results are compared with those obtained in allylic ethers.

Some of the reactions of the alcohols with diazoacetophenone[8] and ethyl diazoacetate[9] have been reported. Padwa has reported that the initially formed singlet diazoacetophenone decomposes to a hydrogen-bonded singlet ketocarbene which undergoes Wolff rearrangement. As the strength of the hydrogen bond decreases, more intersystem crossing to the triplet occurs and larger amounts of acetophenone are formed. Similar results in the reaction of carbethoxycarbene have been obtained with 2-propanol, which gives a product of carbethoxymethylene insertion into the tertiary C—H bond, a polar addition product with the O—H bond, and a rearrangement product.

Results and Discussions

Irradiation of solutions of dimethyl diazomalonate in allylic alcohols was carried out in a Pyrex vessel with a high pressure mercury lamp. The reaction of allyl alcohol I with bis(carbomethoxy)carbene produced by direct photolysis of dimethyl diazomalonate afforded the two principal products (Ia and Ii) in 24.5 and 31.9% yields, respectively (eq 1). The latter product may be rationalized by assuming a bis(carbomethoxy)carbene intermediate which inserts into the O—H bond to give Ii. The former product Ia was not expected; ir, nmr, and elemental analyses showed it to be the bicyclo[3.1.0]lactone. Its infrared spectrum showed bands indicative of an lactone and ester groups at 1800 and



(1)

I, $R^1 = R^2 = R^3 = R^4 = H$
II, $R^1 = CH_3$; $R^2 = R^3 = R^4 = H$
III, $R^1 = R^2 = R^4 = H$; $R^3 = CH_3$
IV, $R^1 = R^2 = CH_3$; $R^3 = R^4 = H$
V, $R^1 = R^2 = R^3 = H$; $R^4 = CH_3$

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[1] W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969).

[2] W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, 1979 (1969).

[3] W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, **37**, 1721 (1972).

[4] W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 5164 (1969).

[5] W. Ando, S. Kondo, and T. Migita, *ibid.*, **91**, 6516 (1969).

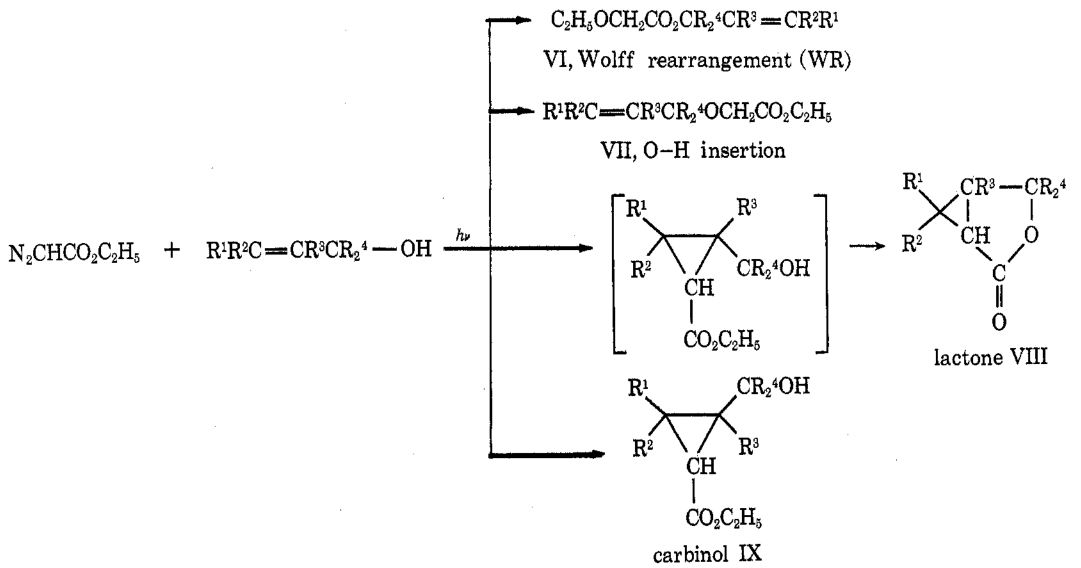
[6] W. Ando, T. Yagihara, S. Kondo, K. Nakayama, H. Yamato, S. Nakaido, and T. Migita, *J. Org. Chem.*, **36**, 1732 (1971).

[7] W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *J. Amer. Chem. Soc.*, **94**, 3870 (1972).

[8] A. Padwa and R. Layton, *Tetrahedron Lett.*, 2167 (1965).

[9] O. P. Strausz, T. Dominh, and H. E. Gunning, *J. Amer. Chem. Soc.*, **90**, 1660 (1968).

SCHEME I



1735, no bands above 3000, but weak absorption at 3050 cm^{-1}, indicative of a methylene group of cyclopropane. No vinyl proton resonances were present in the nmr spectrum.

Photolysis of dimethyl diazomalonate in γ,γ-dimethylallyl alcohol gave O—H insertion product as the major product in 69.2%, and bicyclo[3.1.0]lactone as the minor product. Both products could be isolated by tlc; analytical glpc was used to determine their yields. Examination of the products by tlc suggested that the bicyclo[3.1.0]lactones were not formed under the glpc conditions.

TABLE I
PHOTOLYSIS OF DIMETHYL DIAZOMALONATE IN ALLYLIC ALCOHOLS

	Direct		Ratio	Sensitized[a]
Alcohol	Lactone (a)	O-H (i)	of i/a	lactone (a)
$CH_2{=}CHCH_2OH$ (I)	24.5%	31.9%	1.3	38.7%
$CH_3CH{=}CHCH_2OH$ (II)	14.9	33.2	2.2	19.7
$CH_2{=}C(CH_3)CH_2OH$ (III)	34.1	21.2	0.6	39.4
$(CH_3)_2C{=}CHCH_2OH$ (IV)	11.5	69.2	6.0	7.2
$CH_2{=}CHC(CH_3)_2OH$ (V)	21.2	11.8	0.6	50.1

[a] No O-H insertion product was found in the sensitized reactions.

The formation of the bicyclo[3.1.0]lactones was of obvious interest. These products are presumably formed by lactonization with elimination of methanol from the initially formed cyclopropylcarbinols which arise by addition of the carbene to the C=C bond. In view of the reaction conditions, this lactonization is thought to occur by spontaneous intramolecular transesterification in the absence of particular acid or base catalyst. Such thermal transesterifications were found to occur also intermolecularly, as shown in the following Table II.

$$R^1CH_2CO_2R^2 + R^3OH \xrightarrow[5\text{ hr}]{160^\circ} \underset{A}{R^1CH_2CO_2R^3} + \underset{B}{CH_2(CO_2R^2)_2}$$

TABLE II
TRANSESTERIFICATION BETWEEN ESTER AND ALCOHOL IN THE ABSENCE OF CATALYST

Ester				
R^1	R^2	Alcohol, R^3	A, %	B, %
CO_2CH_3	CH_3	$CH_2{=}CHCH_2OH$	52	25
CO_2CH_3	CH_3	$CH_3CH_2CH_2OH$	37	49
$COCH_3$	CH_3	$CH_2{=}CHCH_2OH$	70	0
$COCH_3$	CH_3	$CH_3CH_2CH_2OH$	70	0
H	C_2H_5	$CH_2{=}CHCH_2OH$	0	0

This reaction may be more useful for preparation of bicyclo[3.1.0]lactones than the method reported previously.[10]

The most marked change in going from the direct photolysis to the sensitized one is in the relative ratio of the products of insertion and addition. The direct photolysis of diazomalonate in allyl alcohol gave 31.9% of O-H insertion product and 24.5% of bicyclo[3.1.0]lactone. In contrast, the benzophenone-photosensitized decomposition of diazomalonate gave 38.7% of bicyclo[3.1.0]lactone, but no O-H insertion product. Table I contrasts the results of the sensitized and direct irradiation. Appropriate control experiments showed that under the reaction conditions the products were neither isomerized nor destroyed. Since the relative extinction coefficients of the diazo compound and the benzophenone in the >3000-Å region allow more than 98% of the light to be absorbed by the sensitizer, it is concluded that the direct photolysis does produce an intermediate which gives both O-H insertion and addition products, but sensitization of the decomposition with benzophenone produces dramatic changes in the mode of reaction.[4-7,11,12]

Photolysis of ethyl diazoacetate in allylic alcohols gave similar products VII and VIII together with *trans*-cyclopropylcarbinol IX and VI (Scheme I). *trans*-Cyclopropylcarbinol IX cannot be converted to bicyclo[3.1.0]lactone under the reaction conditions be-

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[10] G. Gannic, G. Linstrumelle, and S. Julia, *Bull. Soc. Chim. Fr.*, 4913 (1968).

[11] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 1015 (1962).

[12] M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Lett.*, 1391 (1967).

TABLE III

PHOTOLYSIS OF ETHYL DIAZOACETATE IN ALLYLIC ALCOHOLS

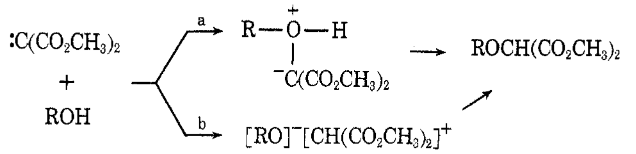
	Direct photolysis, %				Sensitized photolysis,[a] %	
Alcohols	WR	i	Lactone	Carbinol	Lactone	Carbinol
$CH_2{=}CHCH_2OH$	15.0	11.5	10.8	15.7	11.1	22.5
$CH_3CH{=}CHCH_2OH$	22.1	14.2	8.3	7.0	8.5	9.9
$CH_2{=}C(CH_3)CH_2OH$	24.0	12.0	7.0	12.8	11.9	17.1
$(CH_3)_2C{=}CHCH_2OH$	17.4	10.1	5.5	8.2	trace	15.4
$CH_2{=}CHC(CH_3)_2OH$	*b*	*b*	9.8	20.0	5.3	34.3

[a] "WR" and "i" products were not formed in the sensitized reactions. [b] "WR" and "i" products were not detected by gas chromatography.

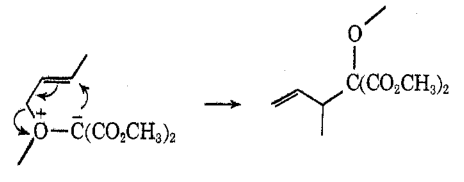
cause of the distance between the ester and O–H groups. The formation of VI involves a migration of the ethoxy group and most probably proceeds through an isomeric ketene analogous to that formed in the Wolff rearrangement (WR). Various allylic alcohols were allowed to react with ethyl diazoacetate and the results are shown in Table III.

The sensitized photodecomposition of ethyl diazoacetate in allylic alcohols produced a species showing little tendency to undergo the Wolff rearrangement. The carboalkoxycarbene generated under these conditions was relatively unreactive toward the O—H bond and gave mainly the C=C addition product. As is shown in Tables I and III, the product distribution is drastically changed by introducing a photosensitizer, which suggests that the singlet carbene is the precursor of the O–H insertion and Wolff rearrangement products.

With regard to the mechanism of insertion of carbene into the O—H bond, the reactions of diazomalonate with allylic alcohols gave some significant results. Two mechanisms can be considered: (a) electrophilic attack by carboalkoxycarbene at the oxygen atom of the alcohol to give an oxygen ylide, followed by the proton migration from oxygen to carbon, or (b) nucleophilic attack by the carbene at the proton of the alcohol. It is known that singlet carbenes are produced by direct photolysis of diazo compounds, and react with molecules bearing unshared electron pairs to give ylides. On the other hand, triplet carbenes produced by benzophenone-photosensitized photolysis do not lead to ylides. The fact that the O–H insertion was observed in the direct photolysis and not in the sensitized reaction suggests that the formation of these insertion products proceed through oxygen ylide intermediates derived by electrophilic attack of the carbenes on oxygen atoms of allylic alcohols. This is further supported by the fact that the relative reactivities of the O—H and C=C bonds toward the carbene correlated well with those of allylic ethers. Dimethyl diazomalonate was photolyzed with a high pressure mercury lamp in allylic methyl ethers. These reactions were found to give the "inverted insertion" product and the adduct of the carbene to the C=C bond. As shown in previous papers,[6,7] the "insertion" product can be considered to form through an intermediate oxygen ylide followed by 2,3-sigmatropic rearrangement. It can be seen that the ratio of the product (Table I) of O–H insertion to that of addition for allylic alcohols is in agreement with that of the products of *O*-allyl insertion to that of the addition for the corresponding allylic ethers (Table IV). Numerical coincidence was not observed for the γ,γ-dimethylallyl compounds, but a qualitative tendency of preference for insertion was observed in the reaction of both allylic compounds. This means that the O–H insertions into allylic alcohols proceed *via* quite similar rate controlling processes to those of *O*-allyl insertion into allylic ethers, since the reactivities of the C=C bonds of allylic system would not be significantly influenced by the structural change in going from alcohol to the corresponding methyl ether. Thus it may be concluded that the O–H insertion takes place by mechanism a.



$$:C(CO_2CH_3)_2 + ROH \begin{cases} \xrightarrow{a} R{-}\overset{+}{O}{-}H \ \text{with} \ {}^{-}C(CO_2CH_3)_2 \ \text{on O} \longrightarrow ROCH(CO_2CH_3)_2 \\ \xrightarrow{b} [RO]^{-}[CH(CO_2CH_3)_2]^{+} \nearrow \end{cases}$$



oxygen ylide intermediate (i)

TABLE IV

YIELDS OF PRODUCTS FROM THE PHOTOLYSIS OF DIMETHYL DIAZOMALONATE IN ALLYLIC ETHERS

Ether	i	a	Ratio of i/a
$CH_2{=}CHCH_2OCH_3$	31%	20%	1.6[a]
$CH_3CH{=}CHCH_2OCH_3$	37	17	2.2[a]
$CH_2{=}C(CH_3)CH_2OCH_3$	23	25	0.9
$(CH_3)_2C{=}CHCH_2OCH_3$	35	23	1.5
$CH_2{=}CHC(CH_3)_2OCH_3$	6.4	13	0.5

[a] See ref 7.

Dependence of the product ratio cited above seems to show the following tendencies (see Tables I and IV). Methyl substituent on a terminal carbon atom retards the addition of the bis(carbomethoxy)carbene, while the substituent on the α, or central, position retards the *O*-ylide formation. This implies that, in reactions of bis(carbomethoxy)carbene, the tendency for addition *vs.* *O*-ylide formation is largely controlled by steric factors. As shown in Table III, however, these effects are slight in the reactions of carbethoxycarbene. In this case the addition products (lactone and carbinol) always predominate, regardless of the structure of allylic alcohols. It is understandable that steric control is less important in the reaction of carbethoxycarbene than in that of bis(carbomethoxy)carbene. Results shown in Table III also show that the precursor of Wolff rearrangement products is a singlet carbene, although the reason that α,α-dimethylallyl alcohol does not give products of rearrangement and insertion is not yet clear.

In summary, allylic alcohols were found to react with a singlet carbene, mainly giving products of addition to C=C bonds and insertion into the O—H bonds, and with a triplet carbene to give only addition products. The most probable mechanism of the O–H insertion involves an *O*-ylide intermediate. Distribution of the products from the reaction of singlet bis(carbomethoxy)-carbene depends on the structure of the allylic alcohols, and seems to be controlled mainly by steric factors. It is noteworthy that the adducts of carboalkoxycarbenes with allyl alcohol lactonize spontaneously, giving bicyclo[3.1.0]lactones in high yields.

Experimental Section

General.—Infrared spectra were determined on a Japan Spectroscopic Co. LTD DS-21 instrument in chloroform, carbon tetrachloride, or neat. The nmr spectra were recorded on a Varian A-60D spectrometer using solutions in carbon tetrachloride with internal tetramethylsilane (TMS) as standard. Chemical shifts are reported in parts per million (ppm) downfield from TMS, with the parentheses designating the multiplicity of the signals: s, singlet; d, doublet; t, triplet; q, quartet, and m, multiplet. The number immediately following the parentheses indicates the number of protons causing the signal. Samples of diazo compound were added to clean 10 × 100 mm Pyrex tubes. The tubes were then corked (nondegassed) and placed in a water cooled bath for irradiation. The light source was a 400-W Rikosha high pressure mercury lamp having the maximum output at 3650–3660 Å with low intensities at 3126–2132 Å. Photolyses were carried to the disappearance of diazo band in infrared spectra. The solutions were analyzed on an Ohkura gas–liquid partition chromatography with a calibrated 5 ft × $^1/_4$ in. stainless steel column of 10% DC710 and 10% Carbowax 20M on C-22 firebrick. Hydrogen was used as the carrier gas. Peak areas were obtained by multiplying the height of the peak times the width at half-height. Absolute yields were then obtained relative to the area of the known amounts of internal standard.

Preparation of Starting Materials.—Dimethyl diazomalonate was prepared using the procedure in which a solution of dimethyl malonate and tosyl azide was treated with diethyl amine.[13] Ethyl diazoacetate[14] was prepared by treating ethyl glycinate hydrochloride with sodium nitrile, bp 36–36.5° (9 mm).

Research grade reagents of allyl alcohol, β-methylallyl alcohol, γ-methylallyl alcohol, and α,α-dimethylallyl alcohol (Tokyo Kasei) were used without further purification. γ,γ-Dimethylallyl alcohol was prepared by hydrolysis of γ,γ-dimethylallyl chloride with 10% NaOH,[15] bp 85–86° (89 mm), 32% yield. Allyl methyl ether, β-methylallyl methyl ether, γ-methylallyl methyl ether, and γ,γ-dimethylallyl methyl ether were prepared by converting the respective allylic chlorides with sodium metal in methanol.[16] α,α-Dimethylallyl methyl ether was prepared by converting the α,α-dimethylallyl alcohol with sodium in diethyl ether to the sodium allylalenoxide and then adding methyl iodide in excess and stirring at room temperature for 2 days, 32% yield, bp 66–69°.

Reaction of Dimethyl Diazomalonate with Allylic Alcohols. A. Allyl Alcohol (I).—A solution of 0.144 g (0.91 mmol) of dimethyl diazomalonate and 1.525 g (0.262 mol) of allyl alcohol was photolyzed for 15 hr. A large quantity of nitrogen gas was observed 1–2 min after the irradiation had begun. After the infrared spectrum of the reaction mixture showed no diazo band, the reaction mixtures were analyzed by glpc and showed two products Ii and Ia, yields given in Table I. Ii: nmr δ 3.75 (s, 6 H), 4.0–4.2 (m, 2 H), 4.48 (s, 1 H), 5.1–5.5 (m, 2 H), 5.5–5.9 (m, 1 H); ir 1750, 990, 930 cm^{-1}. *Anal.* Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.43; Found: C, 51.26; H, 6.79. Ia: nmr δ 1.2–1.5 (m, 1 H), 1.8–2.2 (m, 1 H), 2.5–2.9 (m, 1 H), 3.80 (s, 3 H), 4.10–4.4 (m, 2 H); ir 1800, 1735 cm^{-1}. *Anal.* Calcd for $C_7H_8O_4$: C, 53.84; H, 5.16. Found: C, 54.21; H, 5.40.

B. γ-Methyallyl Alcohol (II).—A similar procedure was followed in the reaction of 0.129 g (0.82 mmol) of diazomalonate in 0.71 g of γ-methylallyl alcohol for 20 hr. Glpc analysis showed that the products IIi and IIa were present in 33.2 and 14.9% yields. IIi: nmr δ 1.6–1.8 (m, 3 H), 3.75 (s, 6 H), 3.9–4.1 (m, 2 H), 4.35 (s, 1 H), 5.5–5.8 (m, 2 H); ir 1750 cm^{-1}. *Anal.* Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.65; H, 7.13. IIa: nmr δ 1.31 (d, 3 H), 1.4–1.8 (m, 1 H), 2.3–2.6 (m, 1 H), 3.80 (s, 3 H), 4.1–4.2 (m, 2 H); ir 1800, 1735 cm^{-1}. *Anal.* Calcd for $C_8H_{10}O_4$: C, 56.46; H, 5.92; Found: C, 56.14; H, 6.05.

C. β-Methylallyl Alcohol (III).—A solution of 1.15 mmol of dimethyl diazomalonate and 0.86 g of β-methylallyl alcohol were irradiated with a high pressure mercury lamp for 10 hr. Analysis by glpc showed two products IIIi and IIIa in 21 and 34% yields. Methanol was also found by glpc. IIIi: nmr δ 1.80 (s, 3 H), 3.78 (s, 6 H), 4.00 (s, 2 H), 4.36 (s, 1 H), 4.85 (s, 2 H); ir 1750 cm^{-1}. IIIa: nmr δ 1.37 (AB d, 1 H), 1.90 (AB d, 1 H), 1.42 (s, 3 H), 3.80 (s, 3 H), 4.10 (d, 2 H); ir 1800, 1735 cm^{-1}. *Anal.* Calcd for $C_8H_{10}O_4$: C, 56.46; H, 5.92. Found: C, 56.49; H, 6.28.

D. γ,γ-Dimethylallyl Alcohol (IV).—A similar reaction on the same scale was carried out. Glpc analysis of the reaction mixture showed the presence of IVi, IVa, and methanol. IVi: nmr δ 1.65–1.85 (m, 6 H), 3.75 (s, 6 H), 4.00–4.10 (m, 2 H), 4.36 (s, 1 H), 5.17–5.50 (m, 1 H); ir 1750 cm^{-1}. *Anal.* Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.31; H, 7.25. IVa: nmr δ 1.21 (s, 3 H), 1.23 (s, 3 H), 2.30–2.47 (m, 1 H), 3.75 (s, 3 H), 4.00–4.45 (m, 2 H); ir 1790, 1730. *Anal.* Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.39; H, 6.28.

E. α,α-Dimethylallyl Alcohol (V).—A 1-mmol-scale reaction was carried out using the same procedure. After the reaction was over, the reaction mixture was analyzed by glpc and Vi and Va were present in 11.8 and 21.1% yields, respectively. Vi: nmr δ 1.30 (s, 6 H), 3.73 (s, 6 H), 4.35 (s, 1 H), 4.93–5.35 (m, 2 H), 5.58–6.13 (m, 1 H); ir 1750, 930, 880 cm^{-1}. *Anal.* Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.21; H, 7.41. Va: nmr δ 1.35 (s, 3 H), 1.50 (s, 3 H), 1.70–2.00 (m, 1 H), 2.27–3.10 (m, 1 H), 3.80 (s, 3 H); ir 1790, 1735 cm^{-1}. *Anal.* Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.67; H, 6.84.

Photosensitized Reaction of Dimethyl Diazomalonate in Allylic Alcohols. A. Allyl Alcohol (I).—A solution of 0.41 g (2.2 mmol) of benzophenone and 0.136 g (0.86 mmol) of dimethyl diazomalonate in 1.4 g of allyl alcohol was irradiated in a Pyrex vessel at room temperature for 30 hr. The gas evolution had ceased and ir showed no diazo band at 2140 cm^{-1}. After irradiation, the solution was injected into the glpc and it was found that Ia was the only major product. Ii was not detected in glpc analysis. The yield is given in Table I.

B. γ-Methylallyl Alcohol (II), β-Methylallyl Alcohol (III), γ,γ-Dimethylallyl Alcohol (IV), and α,α-Dimethylallyl Alcohol (V).—The reactions were carried out in a similar manner on a 1-mmol scale. The glpc analyses gave only one major product, bicyclo[3.1.0]lactone, and the O–H insertion product was not detected. The bicyclolactones were identified on the basis of their retention time and infrared spectrum.

Photolysis of Ethyl Diazoacetate in Allylic Alcohols.—A photolysis of 0.97 mmol of ethyl diazoacetate in 1.3 g of allyl alcohol was carried out for 20 hr with a high pressure mercury lamp. Glpc analysis of the reaction mixture showed the presence of four major products, VI, VII, VIII, and IX, in 15, 11, 11, and 16% yields, respectively. On the other hand, sensitized photolysis of ethyl diazoacetate (1.13 mmol) in a solution of 3 mmol of benzophenone and 1.3 g of allyl alcohol was carried out for 25 hr. The glpc analysis of the reaction mixture showed the presence of only two products which correspond to VIII and IX in 11 and 23% yields, respectively.

Similarly, direct and sensitized photolyses were carried out for the other allylic alcohols, II, III, IV, and V, on the same scale. The glpc analysis of the reaction mixture in the direct photolysis showed the presence of four major products, Wolff rearrangement product, the O–H insertion product, bicyclo[3.1.0]lactone, and cyclopropylcarbinol, but analysis in the sensitized photolysis showed only the lactone and carbinol. The direct photolysis of ethyl diazoacetate in α,α-dimethylallyl alcohol gave only two products, the bicyclolactone and the carbinol in 10 and 20%

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[13] W. Ando, S. Kondo, and T. Migita, *Bull. Chem. Soc. Jap.*, **44**, 571 (1971).

[14] N. E. Seal, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 424.

[15] M. Jamele, C. J. Ott, K. E. Maple, and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

[16] W. T. Olson, *et al.*, *J. Amer. Chem. Soc.*, **69**, 2451 (1947).

TABLE V

ANALYTICAL DATA OF THE PRODUCTS OBTAINED FROM ALLYLIC ALCOHOLS AND DIAZOACETATE

Alcohol	Ir ($>$C=O), cm^{-1} (registry no.)	Nmr, ppm downfield from internal TMS	Calcd, % C	Calcd, % H	Found, % C	Found, % H
		A. Wolff Rearrangement Product				
I	1740 (22874-92-6)	1.22 (t, 3 H), 3.56 (q, 2 H), 3.99 (s, 2 H), 4.60 (d, 2 H), 5.08–5.48 (m, 2 H), 5.63–6.02 (m, 1 H)	58.31	8.39	58.24	8.45
II	1740 (35620-08-7)	1.20 (t, 3 H), 1.70 (d, 3 H), 3.53 (q, 2 H), 3.95 (s, 2 H), 4.41–4.62 (m, 2 H), 5.50–5.77 (m, 2 H)	60.74	8.92	60.70	8.73
III	1740 (35620-09-8)	1.20 (t, 3 H), 1.78 (s, 3 H), 3.57 (q, 2 H), 4.00 (s, 2 H), 4.52 (s, 2 H), 4.80–5.04 (m, 2 H)	60.74	8.92	60.44	8.69
IV	1740 (35620-10-1)	1.20 (t, 3 H), 1.72 (s, 6 H), 3.50 (q, 2 H), 3.91 (s, 2 H), 4.41–4.65 (m, 2 H), 5.10–5.40 (m, 1 H)	62.76	9.36	62.38	9.11
		B. O–H Insertion Product				
I	1750 (15224-07-4)	1.27 (t, 3 H), 3.93 (s, 2 H), 3.90–4.23 (m, 4 H), 5.00–5.40 (m, 2 H), 5.55–5.95 (m, 1 H)	58.31	8.39	58.29	8.32
II	1750 (35620-12-3)	1.30 (t, 3 H), 1.75 (s, 3 H), 3.90 (s + d, 4 H), 4.15 (q, 2 H), 5.50–5.77 (m, 2 H)	60.74	8.92	60.55	8.96
III	1750 (22874-89-1)	1.30 (t, 3 H), 1.78 (s, 3 H), 3.93 (s, 4 H, $=CCH_2O + OCH_2CO_2$), 4.17 (q, 2 H), 4.80–5.04 (m, 1 H)	60.74	8.92	60.67	8.67
IV	1750 (35620-14-5)	1.28 (t, 3 H), 1.70 (s, 6 H), 3.90 (s, 2 H), 3.77–4.28 (m, 4 H), 5.10–5.45 (m, 1 H)	62.76	9.36	62.48	9.21
		C. Bicyclo[3.1.0]lactone				
I	1785, 1730	0.73–1.00 (m, 1 H), 1.15–1.48 (m, 1 H), 1.83–2.40 (m, 2 H), 4.20 (d, 2 H)			Known compound[a]	
II	1780, 1745	1.05–1.55 (m, 1 H), 1.38 (d, 3 H), 1.65–2.30 (m, 2 H), 4.10–4.85 (m, 2 H)			Known compound[b]	
III	1785, 1730 (35589-61-8)	0.90–1.07 (m, 1 H), 1.02–1.30 (m, 1 H), 1.41 (s, 3 H), 1.63–2.11 (m, 1 H), 4.08 (d, 2 H)	64.27	7.19	64.22	7.09
IV	1780, 1740 (16860-52-9)	1.20 (s, 6 H), 1.63–2.11 (m, 2 H), 3.93–4.50 (m, 2 H)	66.64	7.99	66.45	7.87
V	1780 (15143-62-1)	0.60–1.30 (m, 2 H), 1.20 (s, 3 H), 1.30 (s, 3 H), 1.60–2.00 (m, 2 H)	66.64	7.99	66.48	7.91
	(–OH)	D. Cyclopropylcarbinol				
I	3420, 1730 (15224-11-0)	0.70–1.78 (m, 4 H), 1.28 (t, 3 H), 3.10 (s, 1 H), 3.33–3.62 (m, 2 H), 4.10 (q, 2 H)	58.31	8.39	58.42	8.44
II	3440, 1730 (35621-62-6)	1.10–1.65 (m, 6 H), 1.27 (t, 3 H), 2.80 (s, 1 H), 3.35–3.60 (m, 2 H), 4.10 (q, 2 H)	60.74	8.92	60.42	8.75
III	3420, 1730 (35621-63-7)	0.80–1.75 (m, 3 H), 1.20 (s, 3 H), 1.25 (t, 3 H), 2.93 (s, 1 H), 3.38 (d, 2 H), 4.10 (q, 2 H)	60.74	8.92	60.56	8.69
IV	3420, 1730 (35621-64-8)	0.78–1.71 (br m + s, 11 H), 3.20–3.71 (m, 3 H), 4.10 (q, 2 H)	62.76	9.36	62.41	9.33
V	3420, 1730 (35621-65-9)	0.81–1.76 (m + br s, 14 H), 4.10 (q, 2 H)	62.76	9.36	62.74	9.29

[a] W. Kirmse and H. Dietrich, *Chem. Ber.*, **98,** 4027 (1965). [b] H. O. House and C. J. Blankley, *J. Org. Chem.*, **33,** 53 (1968).

yields, respectively. The Wolff rearrangement and the O–H insertion products were not isolated by glpc.

The spectral properties of resulting products are shown in Table V.

Photolysis of Dimethyl Diazomalonate in Allylic Ethers.—In 1 ml of γ,γ-dimethylallyl methyl ether was dissolved 0.38 mmol of dimethyl diazomalonate. The solution was then irradiated for 20 hr using the high pressure mercury lamp as described before. From the analysis by glpc, the two main products were found; one of them was identified as the product of insertion of the carbene into C—O bond involving the allylic rearrangement and the other as a product of addition of the carbene to C=C bond. The structures were assigned by comparison of the ir and nmr spectra with those of authentic samples.

A similar reaction on the same scale was carried out in allyl methyl ether, γ-methylallyl methyl ether, β-methylallyl methyl ether, and α,α-dimethylallyl methyl ether. The reaction mixture was examined by glpc. Two principal products were present in each case. These are found to be "insertion" and addition products from the comparison of the ir and nmr spectra with authentic samples.

Registry No.—I, 107-18-6; Ia, 13353-12-3; Ii, 35621-67-1; II, 6117-91-5; IIa, 35589-62-9; IIi, 35589-63-0; III, 513-42-8; IIIa, 13353-14-5; IIIi, 35621-69-3; IV, 556-82-1; IVa, 35621-70-6; IVi, 35621-71-7; V, 115-18-4; Va, 13353-17-8; Vi, 35621-73-9; dimethyl diazomalonate, 6773-29-1; ethyl diazoacetate, 623-73-4.