Photolysis of Diazocarbonyl Compounds in Allylic Alcohols: New Preparation of Bicyclic Lactones

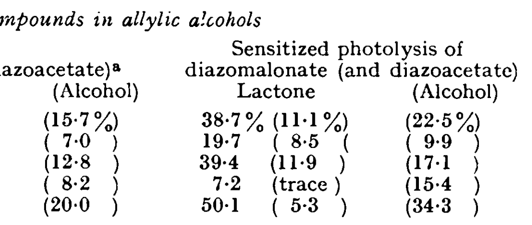
By Wataru Ando,* Isamu Imai, and Toshihiko Migita

(*Department of Chemistry, Gunma University, Kiryu, Gunma, Japan*)

Summary Photolysis of dimethyl diazomalonate and ethyl diazoacetate in allylic alcohols gives the O–H insertion products of the carbene together with bicyclolactones; sensitized photolysis gives only bicyclolactones.

Recent publications have described the preparation of bi- and tri-cyclic lactones from the appropriate diazo-precursor. The intramolecular addition of carbenoids generated by copper catalysed decomposition of allylalkyl diazomalonates and acetates gave a variety of bicyclic lactones.[1–3]

We have found that bicyclic lactones can be prepared conveniently in high yields from the reaction of diazocarbonyl compounds with allylic alcohols.



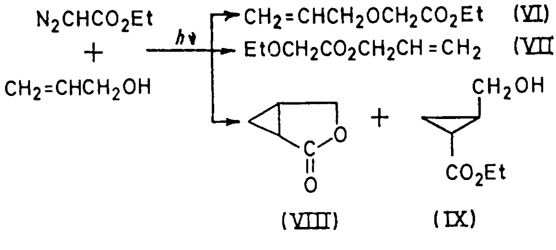
Photolysis of diazocarbonyl compounds in allylic alcohols

Alcohol	Direct photolysis of methyl diazomalonate (and ethyl diazoacetate)[a] O–H Insertion		Lactone		(Alcohol)	Sensitized photolysis of diazomalonate (and diazoacetate) Lactone		(Alcohol)
(I)	31·9%	(11·5%)	24·5%	(10·8%)	(15·7%)	38·7%	(11·1%)	(22·5%)
(II)	33·2	(14·2)	14·9	(8·3)	(7·0)	19·7	(8·5 (	(9·9)
(III)	21·2	(12·0)	34·1	(7·0)	(12·8)	39·4	(11·9)	(17·1)
(IV)	69·2	(10·1)	11·5	(5·5)	(8·2)	7·2	(trace)	(15·4)
(V)	11·8	(0[b])	21·2	(9·8)	(20·0)	50·1	(5·3)	(34·3)

[a] Wolff rearrangement products were also obtained in 15—25% yields, except in the case of (V). [b] The product was not detected by g.c.

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(methoxycarbonyl)carbene produced by direct photolysis of dimethyl diazomalonate afforded two principal products, (Ia) and (Ii) (a = addition, i = insertion), in 25 and 32% yields, respectively. The formation of the latter product may be rationalized by assuming a bis(methoxycarbonyl)methylene intermediate which inserts into the O–H bond to give (Ii). (Ia), which was not an expected product, was shown by i.r., n.m.r., and elemental analysis to be the bicyclic lactone. The formation of this product can be explained in terms of lactonization with elimination of methanol from the initially formed cyclopropenylmethanol.

Photolysis of ethyl diazoacetate in allylic alcohols yields similar adducts in comparable yields together with *trans*-cyclopropenylmethanol. The formation of products (VI) and (VIII) occurs by a mechanism identical to that for the diazomalonate. (VII) is the Wolff-rearrangement product



of the intermediate ethoxycarbonylcarbene. *trans*-Cyclopropenylmethanol (IX) cannot be converted into bicyclic lactone under the conditions of the reaction, because of the steric requirements of the ester and O-H groups. Other allylic alcohols give similar products (Table).

Studies on the reaction of dimethyl diazomalonate showed that the O–H bond of αα-dimethylallyl alcohol is only 0·6 times as reactive as its terminal C=C bond, while the O–H bond of γγ-dimethylallyl alcohol is 6·0 times more reactive than its C=C bond toward the same carbene. Similarly, while the photolysis of ethyl diazoacetate in αα-dimethylallyl alcohol led to C=C bond addition products, the photolysis in γγ-dimethylallyl alcohol gave both O–H insertion and addition products in comparable amounts. Because of the decreasing reactivity of the C=C bond with methyl substitution and of the O–H bond with substitution at the α-carbon, it is to be expected that steric factors are most important in determining at which site in an allylic alcohol—the O–H bond or the C=C bond—the alkoxycarbonylcarbene attack will occur.[4]

It is possible to generate the triplet carbene by selectively activating benzophenone in the presence of diazocarbonyl compounds.[5] The sensitized photodecomposition of diazomalonate and diazoacetate in allylic alcohols produced a species showing little tendency to undergo O–H insertion or Wolff rearrangement, and instead formed the C=C addition product predominantly (see Table).

The photosensitized decomposition of diazocarbonyl compounds in allylic alcohols produced substantial amounts of cyclopropenylmethanol and bicyclic lactones.

(*Received*, 17*th April* 1972; *Com.* 635.)

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