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THE PHOTOCHEMICAL REACTIONS OF ETHYL CHLOROGLYOXYLATE WITH OLEFINS

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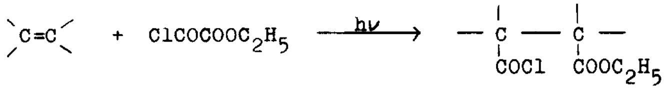
Although the direct introduction of carboxyl groups, such as chloroformyl, alkoxycarbonyl, and carbamoyl groups, into paraffins and olefins by means of radical reactions has been received attention recently (1 - 6), no attempts to introduce two carboxyl groups into the 1,2-positions of an olefin have yet been made. The present paper deals with the direct and concurrent introduction of ethoxycarbonyl and chloroformyl groups into the double bond of an olefin by the photochemical reaction of ethyl chloroglyoxylate (ECG) with the olefin.



$$>C=C< \; + \; ClCOCOOC_2H_5 \xrightarrow{h\nu} -\underset{COCl}{\overset{|}{\underset{|}{C}}}-\underset{COOC_2H_5}{\overset{|}{\underset{|}{C}}}- \qquad (1)$$

I

A mixture of ECG (37 g., 0.27 mole) and norbornene (19 g., 0.2 mole) placed in a quartz tube was irradiated for 27 hours with an unfiltered high pressure mercury arc (600 watt) at room temperature in the atmosphere of nitrogen. The gases evolved during the irradiation were analyzed by gas chromatography, and found to consist of carbon monoxide, carbon dioxide, ethane, and ethylene. The liquid products isolated were diethyl oxalate (a 16% yield)[*], ethyl norbornane-*exo*-2-carboxylate (27%), and the derivative of norbornane-*trans*-2,3-dicarboxylic acid II (32%). The last product exhibited strong infrared absorption bands at 1800 (the carbonyl group of an acid chloride), 1740, and 1180 cm.$^{-1}$ (an ester of an aliphatic carboxylic acid), and gave norbornane-*trans*-2,3-dicarboxylic acid after hydrolysis with an ethanolic potassium hydroxide. In addition, the treatment of II with an absolute ethanol afforded the diethyl ester, showing a single peak with the same retention time as that of diethyl norbornane-*trans*-2,3-dicarboxylate in its gas chromatogram.[**] The photochemical reactions of ECG with 1-hexene and 1-octene led to the formation of the derivatives of *n*-butylsuccinic and *n*-hexylsuccinic

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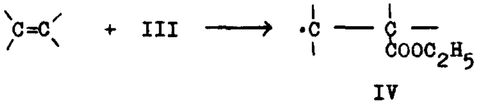
[*] Noted otherwise, yields were based on ECG not recovered.

[**] *Exo*- and *endo*-cis isomers displayed shorter and longer retention times than *trans* isomer, respectively (a 1/4" × 10 column packed with silicone grease on Chromosorb).

acids (10 - 15%), respectively, though no efforts were made to establish the optimum conditions.

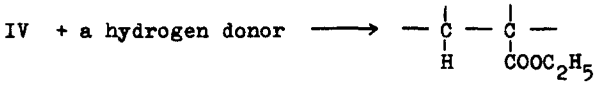
The result obtained with norbornene shows that a chain reaction mechanism might be operative for the formation of I, and a four-center mechanism is unlikely, since exo- and endo-cis isomers were not detected. Taking together with the other results (7), the species wthich initially attacks to an olefin might be an ethoxycarbonyl radical generated by the photolytic decomposition of ECG, and the addend radical IV might attack to the acid chloride function of ECG (8) to give I, or might terminate by the hydrogen abstraction:

$$ClCOCOOC_2H_5 \xrightarrow{h\nu} \cdot COCl + \underset{III}{\cdot COOC_2H_5} \qquad (2)$$



$$>C=C< + III \longrightarrow \underset{IV}{\cdot\overset{|}{\underset{|}{C}} - \overset{|}{\underset{COOC_2H_5}{C}} -} \qquad (3)$$

$$IV + ClCOCOOC_2H_5 \longrightarrow I + III \qquad (4)$$



$$IV + \text{a hydrogen donor} \longrightarrow -\overset{|}{\underset{H}{C}} - \overset{|}{\underset{COOC_2H_5}{C}} - \qquad (5)$$

Judging from the results descrived above, this reaction will provide a convenient method for the direct synthesis of the derivative of 1,2-dicarboxylic acid. Further studies are now in progress.

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7) Our unpublished results show that an ethoxycarbonyl radical adds to olefins without significant decomposition. On the other hand, the attack of a chloroformyl radical to olefins has been appeared in no literature. In fact, we were unable to detect an acid chloride in the products from the photolysis of oxalyl chloride (9) in cyclohexene.

8) The dibenzoyl peroxide-catalyzed reaction of ECG with cyclohexane gave a 60% yield of cyclohexanecarbonyl chloride along with only a small amount of ethyl cyclohexylglyoxylate, while ethyl cyclohexanecarboxylate could not be detected. It is evident from the above result that a cyclohexyl radical (probably the species IV) attacks to the carbonyl group of the acid chloride function of ECG.

9) It has been suggested that oxalyl chloride is photolyzed by the light quantum at 2537 A region to generate chloroformyl radicals (Rollefson *et al.*, *J. Amer. Chem. Soc.*, *58*, 443 (1936).), and hence a low pressure mercury arc was used as the light source.