Tetrahedron Letters No.36, pp. 2527-2529, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE DIRECT INTRODUCTION OF ETHYL OXALLYL RADICAL INTO CYCLOHEXANE BY A PHOTOCHEMICAL REACTION

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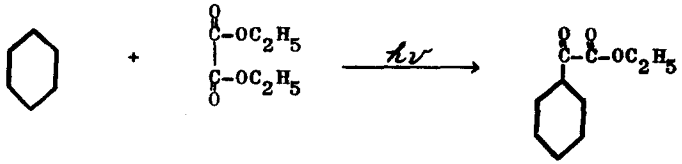
(Received 15 June 1964; in revised form 20 July 1964)

Since Barton et al.[1] prepared 18- and 19-substituted steroids from compounds lacking substituents at these positions by photolysis of suitably constituted organic nitrites and demonstrated its utilization to synthetic organic chemistry, increasing interest has, from the viewpoint of organic synthesis, been shown in the study on the direct introduction of the important functional groups, especially by means of photochemical reaction, and the new photochemical studies on cyanation with cyanogen halide[2], amidation with formamide[3] and ethoxycarbonylation with ethyl chloroformate[4] have been ardently undertaken by several groups of workers. In an earlier paper dealing with the photolysis of ethyl cyanoformate[5], the present anthors reported that the direct and concurrent introduction of cyano and ethoxycarbonyl radicals into cyclohexane was successful.

We wish to report here the result of our study on the direct introduction of ethyl oxallyl radical into cyclohexane by means of photolysis of diethyl oxalate.

Irradiation of a solution of diethyl oxalate (36.5g.) in cyclohexane (420g.), using a 600 w. high pressure mercury arc lamp was carried out under nitrogen for 7 hours at room temperature. During the irradiation, the contineous evolution of gas was observed, and it was shown by gas chromatographic analysis that ca. 400 ml. of gas collected at the end of the reaction consisted of carbon monoxide, carbon dioxide, ethylene, methane and ethane in the ratio of 30.7 : 7 : 3.6 : 2.7 : 1. Besides the above constituents very small amounts of hydrogen and propane were found. In addition, as the liquid products, ethyl cyclohexyl glyoxylate (5.2g.) and ethyl cyclohexyl carbonate (1.0g.) were obtained, along with ethyl alcohol (1.1g.), acetone (1.3g.), ethyl ether (0.6g.) and bicyclohexyl (0.4g.). The conversion percentage of diethyl oxalate was 20.6%. Consequently, the ultimated yield of ethyl cyclohexyl glyoxylate was 54.9%.



In a similar reaction in tetrahydrofuran, we have also observed the formation of ethyl 2-tetrahydrofuryl glyoxylate in a good yield.

The results presented in this paper show a plain demonstration of the possibility of the direct introduction of ethyl oxallyl radical by photolysis of diethyl oxalate.

Details of this and further works will be reported shortly.

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