Direct Introduction of Ethoxycarbonyl Radical into Hydrocarbons by Photochemical Reactions

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Recently, it has been reported that methoxycarbonyl radical is produced by the abstraction of chlorine atom in methyl chloroformate with methyl radical[1].

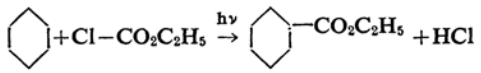
It would also be expected that alkoxycarbonyl radical might be produced from alkyl chloroformate by light in the same manner as the photolysis of phosgene[2] and of oxalylchloride[3],

$$Cl-CO_2R \xrightarrow{h\nu} \cdot Cl + \cdot CO_2R$$

being accompanied by the direct introduction of the radical into hydrocarbons.

Therefore, the photochemical reactions of ethyl chloroformate with hydrocarbons were studied, and it was found that the ethoxycarbonyl radical produced by a high pressure mercury arc (600 W) from ethyl chloroformate was introduced into hydrocarbons, such as cyclohexane, benzene and cyclohexene.

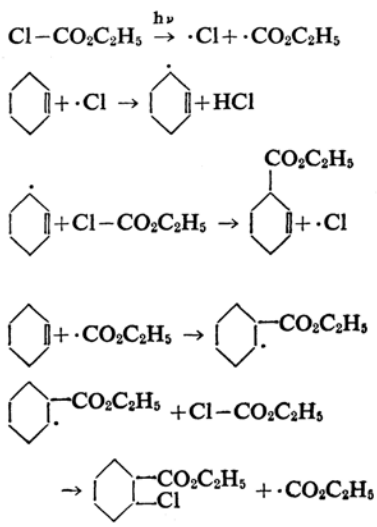
The over-all reaction with respect to cyclohexane is shown as follows;



The irradiation of a mixture of cyclohexane (168 g.) and ethyl chloroformate (83 g.) (mole ratio; 3 : 1) gave the following liquid products at room temperature for 6 hr. in the atmosphere of nitrogen; 1 g. of an ester (b. p. 93~96°C/35 mmHg, n_D^{26} 1.4510) and 1.5 g. of bicyclohexyl (b. p. 65~70°C/3 mmHg, n_D^{26} 1.4743). The above ester was identified as ethyl cyclohexanecarboxylate by infrared absorption spectra, gas chromatographic analyses and the mixed-melting point test of its anilide with an authentic sample (m. p. 143~143.5°C, recrystallized from ligroin). During the irradiation, gases were evolved and analyzed by gas chromatography, which consisted of large amounts of carbon dioxide and ethane, small amounts of ethylene and a trace of ethyl chloride.

In a similar way, a mixture of benzene and ethyl chloroformate afforded only a small amount of ethyl benzoate, without the formation of gaseous products. Ethyl benzoate was confirmed by gas chromatographic analyses.

In the case of cyclohexene, ethyl cyclohexanecarboxylate and 3, 3'-bicyclohexenyl were obtained as major products, although we expected 3-ethoxycarbonylcyclohexene or 1-ethoxycarbonyl-2-chlorocyclohexane as a major product, taking into account the previous experimental results which are shown as bellow;



In spite of irradiation for a longer time, the amounts of gaseous products were very small compared with those found in the case of cyclohexane. Details of this reaction are now under investigation.

The method of direct carboxylation into hydrocarbons with ethyl chloroformate has never been reported, thus we are intending to carry out further researches in this field.

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1) J. C. J. Thynne and P. Gray, *Proc. Chem. Soc.*, **1962**, 141.
2) Bodenstein et al., *Z. physik. Chem.*, **B3**, 459 (1929).
3) Rollefson et al., *J. Am. Chem. Soc.*, **56**, 1089 (1934); **58**, 443 (1935).