BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2463—2466 (1966)

The Direct Introduction of an Ethoxycarbonyl Group by the Photolysis of Some Substituted Formates in Solution

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(Received February 22, 1966)

The direct introduction of an ethoxycarbonyl group by the photolysis of various substituted formates ($RCO_2C_2H_5$) was carried out. Both ethyl cyanoformate and ethyl chloroformate effectively underwent ethoxycarbonylation by a hydrogen-donating solvent such as cyclohexane, with the yields of 19% and 15%, respectively. On the other hand, the photolysis of ethyl acetate, diethyl carbonate, and ethyl carbamate gives mainly carbinols and carbon monoxide instead of ethyl carboxylate. On the basis of these results, the effects of the substituent in the formate on the ethoxycarbonylation were considered. First, the electronic effect of the substituent R has an influence on the position of the bond fission of the formate. Cyano and chloro groups, which are the electron-withdrawing substituents, weaken the R-carbon bond in the formates. Second, the ability of the hydrogen abstraction of the radical R produced by the photolysis of the formate is very important in the ethoxycarbonylation. Thus, it is clear that there is a relationship between the electron affinity of the radical R and the yield of the ethyl carboxylate.

Since the chloroformylation of cyclohexane by the photolysis of oxalyl chloride was investigated by Kharasch,[1] photochemical studies of the direct introduction of important functional groups, e. g., the nitroso,[2] cyano,[3] carbamoyl[4] and ethyl oxalyl groups,[5] have been extensively carried out. Little attention, however, has been paid to direct alkoxycarbonylation, though this is very valuable

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[1] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 329 (1942).

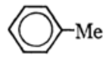
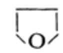
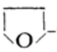
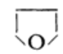
[2] M. A. Naylor and A. W. Anderson, *J. Org. Chem.*, **18**, 115 (1953).

[3] E. Müller, *Chem. Ber.*, **96**, 670, 2319 (1963).

[4] DovElad, *Tetrahedron Letters*, No. **2**, 77 (1963).

[5] Y. Odaira, T. Tominaga, T. Sugihara and S. Tsutsumi, ibid., No. **36**, 2527 (1964).

TABLE I. ETHOXYCARBONYLATION WITH THE PHOTOLYSIS OF FORMATE (RCO_2Et)

R	Electron affinity of R, kcal./mol.	Solvent	Carboxylate, %[a]	Other liquid products,[b] %[a]
Cl	87		15	 -Cl (5)
CN	64		19	 -$COCO_2Et$ (3)
CN	64		37	
H	—		4	 -CH(OH)Me(I) (3),  -CH_2OH(II) (3), EtOH(III) (7),  -OEt(IV) (2)
Me	26		Trace	I (9), II (6), III (8) IV (3), MeCHO (9)
EtO	34		Trace	I (0.5), II (0.1)
EtO	34		Trace	 -CH(OH)Me(V) (18)
NH$_2$	28		None	V (Trace)

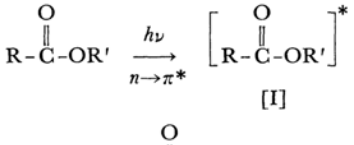
a) Basis on consumed formate.

b) The dimer of the solvent is excluded from this Table. See experimental for the amounts of the dimer.

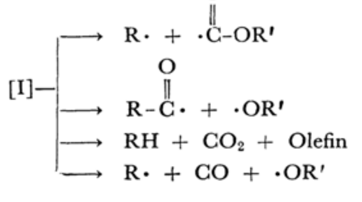
in organic synthesis. In our preliminary report,[6] the possibility of the direct introduction of an ethoxycarbonyl group into cyclohexane by means of the photolysis of ethyl cyanoformate was verified. In this paper, we wish to report on ethoxycarbonylation by the photolysis of various substituted formates, focusing attention on the effect of the substituent in the formate on the ethoxycarbonylation.

Results and Discussion

Although the photochemical reactions of alkyl esters (e. g., RCO_2R') are very complicated, it is generally considered that the following four primary steps proceed through the excitation of the molecule by the $n\rightarrow\pi^*$ transition of the carbonyl group in the esters:

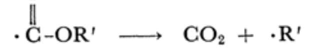


$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[n\rightarrow\pi^*]{h\nu} \left[R-\overset{O}{\overset{\|}{C}}-OR'\right]^* \quad [I]$$



$$[I] \begin{cases} \longrightarrow R\cdot + \cdot\overset{O}{\overset{\|}{C}}-OR' & (1) \\ \longrightarrow R-\overset{O}{\overset{\|}{C}}\cdot + \cdot OR' & (2) \\ \longrightarrow RH + CO_2 + \text{Olefin} & (3) \\ \longrightarrow R\cdot + CO + \cdot OR' & (4) \end{cases}$$

Of the above four steps, step 1, leading to the formation of an alkoxycarbonyl radical, will be most important for the alkoxycarbonylation. It is, however, well known that the alkoxycarbonyl radical produced in step 1 is so unstable that it decomposes exothermically to carbon dioxide and a free alkyl radical with an activation energy of only about 1—2 kcal./mol.[7]:



$$\cdot\overset{O}{\overset{\|}{C}}-OR' \longrightarrow CO_2 + \cdot R' \qquad (5)$$

The results of ethoxycarbonylations by the photolysis of various formates in hydrogen-donating solvents are summarized in Table I. In spite of the above disadvantage, the data shown in Table I indicate that both ethyl cyanoformate and ethyl chloroformate, among others, effectively underwent ethoxycarbonylation by hydrogen-donating solvents. However, contrary to expectation, carbinols and carbon monoxide, not ethyl carboxylate, were mainly obtained in the photolysis of ethyl acetate, diethyl carbonate and ethyl carbamate. From these results, it is found that the R substituent in the formate influences the nature of the product of the photolysis of the formate. Therefore, it seems

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[6] T. Tominaga, Y. Odaira and S. Tsutsumi, This Bulletin, **37**, 596 (1964).

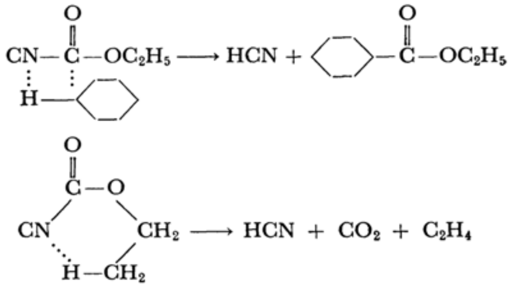
[7] P. Gray and J. C. J. Thynne, *Nature*, **191**, 1357 (1961).

to be more reasonable to assume that the substituent in the formate plays a very important role in the photolytic behavior of the formate; the following two effects of the substituent may then be considered.

First, the electronic effect of the substituent has a considerable influence on the position of the bond fission of the formate. From the fact that the photolysis of ethyl cyanoformate and ethyl chloroformate affords ethyl carboxylate exclusively, it seems that the electron-withdrawing substituents weaken the R-carbon bond in the formates, thus causing this bond to break easily upon photolysis. Consequently, step 1 proceeds predominantly to produce the ethoxycarbonyl radical. The fact that carbon monoxide and carbinols are the major products in the photolyses of the other formates in Table I means that the electron-releasing substituents, e. g., methyl, ethoxy and amino groups, probably make the R-carbon bond fission conversely difficult. Consequently, the photolysis of the formates must proceed through step 2 to produce an acyl radical and an alkoxy radical. The acyl radical may decompose immediately to carbon monoxide and an alkyl radical. There is also a possibility that carbon monoxide may be produced directly by the photolysis of the formates through step 4.

Second, the ethoxycarbonylation is influenced by the ability of the R radical produced by step 1 to produce hydrogen abstraction. As is well-known, the chloro atom and the cyano radical, which have large electron affinities, effectively abstract the hydrogen of the solvent. On the other hand, the hydrogen-abstraction ability of methyl, alkoxy and amino radicals, which have small electron affinities, is not so powerful as that of the above radicals, even if these radicals are generated through step 1. In the case of the photolysis of diethyl carbonate in cyclohexane, the ethyl cyclohexanecarboxylate obtained was only small amount; carbon dioxide was the major product in the gaseous products. Therefore, the ethoxycarbonyl radical decomposes to carbon dioxide and the ethyl radical, as is shown in step 5.

Interestingly, ethyl cyano- and ethyl chloroformate react in a little different manner, as indicated by the composition of their products. Ethylene was a major gaseous product of the photolysis of ethyl cyanoformate. On the contrary, ethyl chloroformate afforded mainly ethane. In addition, the obtainable dimer of the solvent was very little in the photolysis of the former as compared with that of the latter. These results suggest that the transition state of the hydrogen abstraction is different in the cases of the two formate. Presumably, the ethoxycarbonylation with ethyl cyanoformate proceeds through a somewhat four-centered mechanism, or the intramolecular hydrogen abstraction of the formate leads to hydrogen cyanide, carbon dioxide and ethylene through a six-membered transition state, as is shown hereunder:



On the other hand, ethyl chloroformate may dissociate to a chloro atom and an ethoxycarbonyl radical. Then, the chloro atom generated would abstract the hydrogen of the solvent, thus producing a free solvent radical. This solvent radical may combine with the ethoxycarbonyl radical, or it may dimerize by itself.

Furthermore, in order to examine the effect of the substituent R′, the phenoxycarbonylation of cyclohexane by means of the photolysis of phenyl chloroformate was also attempted. In this reaction, phenol was obtained as the major product, together with a small amount of phenyl cyclohexanecarboxylate. This result leads us to assume that a phenoxycarbonyl radical generated through step 1 may be easily decomposed to carbon monoxide and a phenoxy radical because of its large resonance stabilization.

Further studies of ethoxycarbonylation by means of ethyl cyanoformate will be presented elsewhere.

Experimental[8]

Materials.—Ethyl cyanoformate was prepared in a 54% yield from ethyl chloroformate and sodium cyanide according to the procedure of Sheppard,[9] b. p. 116—118°C, n_D^{20} 1.3812: phenyl chloroformate was synthesized in a 54% yield by the method of Raiford and Inman from phenol and phosgene in the presence of dimethylaniline,[10] b. p. 84—87°C/23—24 mmHg, $n_D^{29.5}$ 1.5067, the other formates and solvents were commercial-grade chemicals; they were purified by the usual methods and distilled before use.

The Photolysis of Ethyl Chloroformate.—A mixture of ethyl chloroformate (38 g., 0.35 mol.) and cyclohexane (147 g., 1.75 mol.) was irradiated with a 350 W. high-pressure mercury arc lamp for 25 hr. under nitrogen at room temperature. During the irradiation, the continuous evolution of gas was observed and 450 ml. gas was collected. Hydrogen chloride was identified qualitatively as the precipitate of silver chloride. The other gaseous products were analyzed by gas chromatography using a 2.5-m. active carbon column. The main gaseous products were carbon dioxide, ethane, and carbon monoxide, plus small amounts of methane

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8) Melting points are uncorrected.
9) W. A. Sheppard, *J. Org. Chem.*, **27**, 3756 (1962).
10) L. C. Raiford and G. O. Inman, *J. Am. Chem. Soc.*, **56**, 1586 (1934).

and ethylene. The liquid products were fractionally distilled and analyzed by gas chromatography using a 2.5-m. Si DC-550 column and an Apiezone N column. The conversion percentage of ethyl chloroformate was about 6%. The high-boiling products (1.7 g.) were ethyl cyclohexanecarboxylate (15%, based on the ethyl chloroformate consumed), cyclohexyl chloride (4.5%), and bicyclohexyl, plus small amounts of methyl cyclohexylcarbinol, diethyl oxalate, and ethyl cyclohexane.

The Photolysis of Ethyl Cyanoformate.—The irradiation of a solution of ethyl cyanoformate (39.6 g., 0.4 mol.) in cyclohexane (168 g., 2.0 ml.) was carried out under the same conditions as above for 50 hr. The gas evolved amounted to about 300 ml., consisting of carbon dioxide, carbon monoxide, ethylene, and small amounts of methane. Hydrogen cyanide was determined qualitatively as silver cyanide. The conversion percentage of ethyl cyanoformate was about 33%. The main liquid products were ethyl cyclohexanecarboxylate (3.9 g, 19%) and ethyl cyclohexaneglyoxylate (0.7 g., 3%). The above α-ketoester was isolated by preparative gas chromatography using a 3-m. Si DC-550 column. 2, 4-Dinitrophenylhydrozone was recrystallized from ethyl alcohol to yield yellow needles, m. p. 158—160°C. A mixed-melting-point determination with an authentic sample of ethyl cyclohexaneglyoxylate 2, 4-dinitrophenylhydrazone showed no depression. Small amounts of ethyl alcohol, cyclohexyl cyanide, propionitrile, and bicyclohexyl were identified by gas chromatography. The photolysis of ethyl cyanoformate in toluene was also carried out using a 1-KW. high-pressure mercury arc lamp for 40 hr. The ultimate yield of ethyl phenylacetate was about 37%. The photolysis of ethyl cyanoformate at the wave length of 3660 Å did not occur to any appreciable extent. The effective wave length in the photolysis of the formates seemed to be shorter than 3660 Å.

The Photolysis of Ethyl Formate.—A mixture of ethyl formate (148 g., 2.0 mol.) and cyclohexane (420 g., 5.0 mol.) was irradiated with a 350-W. high-pressure mercury arc lamp for 68 hr. About 2800 ml. of gas was evolved, consisting largely of carbon monoxide. The other gaseous products were carbon dioxide and ethane, plus small amounts of methane and ethylene. The conversion of ethyl formate was about 32%. The main liquid products were bicyclohexyl (4.8 g.), ethyl cyclohexanecarboxylate (3.8 g., 3.8%), methyl cyclohexylcarbinol (3.2 g.), cyclohexylcarbinol (2.2 g.), ethyl alcohol (2.2 g.), and acetone (2.2 g.). Small amounts of acetaldehyde, diethyl oxalate, and ethoxycyclohexane were also obtained.

The Photolysis of Ethyl Acetate.—A mixture of ethyl acetate (105.6 g., 1.2 mol.) and cyclohexane (252 g., 3.0 mol.) was irradiated for 50 hr. The conversion of ethyl acetate was about 37%. The gaseous products (2500 ml.) were carbon monoxide, ethylene, carbon dioxide, methane, and ethane. The liquid products were methyl cyclohexylcarbinol (5.5 g.), cyclohexylcarbinol (4.6 g.), bicyclohexyl (16 g.), ethoxycyclohexane (1.6 g.), ethyl alcohol (1.6 g.), and acetaldehyde (1.7 g.). Ethyl cyclohexanecarboxylate, however, was present in only a very small amount.

The Photolysis of Diethyl Carbonate.—A mixture of diethyl carbonate (59 g., 0.5 mol.) and cyclohexane (336 g., 4.0 mol.) was irradiated for 30 hr. The conversion rate of diethyl carbonate was about 21%. The gaseous products (300 ml.) were carbon dioxide, carbon monoxide, ethane, ethylene, methane, n-butane, and hydrogen. Almost the only liquid product was a polymeric substance (5.8 g.). Small amounts of bicyclohexyl (0.8 g.) and methyl cyclohexylcarbinol (0.1 g.) were also obtained. Ethyl cyclohexanecarboxylate, cyclohexylcarbinol, and ethyl alcohol were present only in trace amounts.

The photolysis of diethyl carbonate in tetrahydrofuran was also carried out. A mixture of diethyl carbonate (47.2 g., 0.4 mol.) and tetrahydrofuran (144 g., 2.0 mol.) was irradiated for 75 hr. under the same conditions. The gaseous products (1100 ml.) were almost the same as those of the above case, except that carbon monoxide instead of carbon dioxide was the main product. The main liquid products obtained were methyl-2-tetrahydrofurylcarbinol (1.7 g.) and 2, 2′-ditetrahydrofuryl (2.8 g.). Small amounts of ethyl 2-tetrahydrofurancarboxylate and 2-tetrahydrofurylcarbinol were also obtained.

The Photolysis of Ethyl Carbamate.—A mixture of ethyl carbamate (44.5 g., 0.5 mol.) and tetrahydrofuran (144 g., 2.0 mol.) was irradiated for 110 hr. The total volume of gas evolved was about 850 ml. The main gaseous product was carbon monoxide. Carbon dioxide, ethane, ethylene, methane, and hydrogen were also identified. After the tetrahydrofuran had been removed, the residue was cooled overnight and then filtered. Hydrochloric acid (1.5 N) was added to the filtrate, and the solution was extracted with ether. The ethereal solution was washed by 5% aqueous sodium bicarbonate and water successively, and dried over sodium sulfate. After the ether had been removed, the residue was fractionally distilled under reduced pressure. 2, 2′-Ditetrahydrofuryl (0.5 g.) and small amounts of methyl-2-tetrahydrofurylcarbinol were obtained. However, ethyl 2-tetrahydrofurancarboxylate was not obtained.

The Photolysis of Phenyl Chloroformate.—A mixture of phenyl chloroformate (109.6 g., 0.7 mol.) and cyclohexane (343 g., 4.2 mol.) was irradiated with a 1-KW. high-pressure mercury arc lamp for 7.2 hr. The gaseous products were hydrogen chloride and carbon monoxide. The conversion of phenyl chloroformate was about 27%. The main liquid product was phenol (12.6 g.). Phenyl cyclohexanecarboxylate was obtained only in trace amounts.

We are indebted to Mr. Koichi Matsumoto and Mr. Takeshi Fujimoto for their excellent assistance.