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Photochemical Ethoxycarbonylmethylation of Benzene with Ethyl Haloacetates[1]

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The ultraviolet light-induced reaction of ethyl haloacetate with an excess benzene gives ethyl phenylacetate (1.7%) and diethyl succinate (1.6%) as main products, while the same reaction of excess chloroacetate with benzene gives ethyl phenylacetate higher yield (optimum 78.4%). Addition of aluminum chloride to the reaction mixture using an excess benzene gives ethyl phenylacetate as a sole product (11.5%). The effect of reaction conditions on the yield is examined.

In the Friedel-Crafts reactions of ordinary carboxylic acids and esters with aromatic compounds, the carbon atom of carbonyl group is the main electrophilic site. In general, the substitution of aromatic rings by $-CH_2COOH$ (carboxymethylation) and by $-CH_2COOR$ (alkoxycarbonylmethylation) are difficult and the papers on these reactions are few.[2] For example, the condensation of naphthalene with chloroacetic acid affording α-naphthaleneacetic acid in the presence of ferric oxide needs *ca.* 20 hrs' refluxing at 218°C.[2a] The photo-induced reaction of this type has been

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[1] Contribution No. 113.

[2] a) Y. Ogata and J. Ishiguro, *J. Am. Chem. Soc.*, **72**, 4302 (1950). b) Y. Ogata, J. Ishiguro and Y. Kitamura, *J. Org. Chem.*, **16**, 239 (1951). c) R. L. Lehmann and J. Linter, U. S. Patent 2617822 (1952); *Chem. Abstr.*, **48**, 725 (1954). d) N. K. Bhattacharyya, S. Singh, O. P. Vig and S. M. Mukherji, *Science and Culture (India)*, **18**, 341 (1953); *Chem. Abstr.*, **48**, 2019 (1954).

reported by Kharasch,[3] who succeeded in the carboxymethylation of benzene and cyclohexene with iodoacetic acid, but he provided no detail discussions.

The present paper describes our results on the photochemical ethoxycarbonylmethylation of benzene with ethyl chloroacetate or ethyl bromoacetate in the presence and absence of aluminum chloride.

$$C_6H_6 + ClCH_2COOC_2H_5 \xrightarrow{h\nu} C_6H_5CH_2COOC_2H_5 + HCl$$

Results and Discussion

The ultraviolet irradiation of a solution containing ethyl haloacetate and benzene gave ethyl phenylacetate (I), diethyl succinate (II) and a trace of biphenyl. These products were identified by means of GLC. The results are shown in Table 1 and Fig. 1.

TABLE 1. THE YIELD OF ETHYL PHENYLACETATE AND DIETHYL SUCCINATE IN THE PHOTOCHEMICAL REACTION OF ETHYL HALOACETATE WITH BENZENE IN EXCESS AT 30°C[a]

$[ClCH_2CO_2Et]$ M	$[C_6H_6]$ M	Yield, %[b] I	Yield, %[b] II	Recovery, %[b] $ClCH_2CO_2Et$
0.1	Solvent	1.7	1.6	—
0.1[c]	Solvent	1.8	0.4	96
0.1[d]	Solvent	2.5	Trace	93
0.1[e]	Solvent	3.0	1.3	69
0.1[f]	0.1	0	0	—
0.1[g]	0.1	0	0	—

a) Irradiation by immersion-type high-pressure Hg lamp for 30 hr.
b) On the basis of added ethyl chloroacetate.
c) Low-pressure Hg lamp was used.
d) Temperature was 65°C.
e) $BrCH_2CO_2Et$ was used.
f) Acetone solution.
g) Methanol solution.

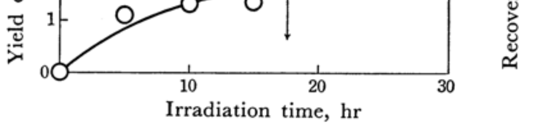

Fig. 1. Typical conversion curves for the reaction of ethyl chloroacetate with benzene.

Irradiation of a benzene solution of 0.1 M ethyl chloroacetate with high-pressure Hg lamp gave I, but in a poor yield (1.7%), while the reaction did not take place in the dark even at refluxing temperature. Almost no further photochemical reactions of I and II occurred.

Since both ethyl chloroacetate and benzene show an absorption band below 2600 Å, a low-pressure Hg lamp which emits almost exclusively 2537 Å light was used under similar conditions, but there was no appreciable effect on the yield of ethyl phenylacetate.

Irradiation at higher temperature (65°C) slightly increased the yield of ethyl phenylacetate. A slight increase in the yield of I was observed, when bromoacetate was used in place of chloroacetate probably because of the lower bond energy of C–Br than that of C–Cl, but the yield was still poor. Generally, the reaction in a solution of an excess benzene gave I in a poor yield, which may be due to the inner filter behavior of solvent benzene.

Further, the irradiation of an acetone or methanol solution of 0.1 M ethyl chloroacetate and 0.1 M benzene gave neither I nor II.

On the other hand, it was of interest to note that the irradiation of 0.1 M benzene in ethyl chloroacetate as solvent gave considerable yields of I and II as main products. In contrast to the reaction in a benzene solution, the yield of I is increased to 78.4%, while that of biphenyl also increases (Table 2). In addition, two other products were detected, neither of which has yet been identified.

TABLE 2. THE YIELD OF ETHYL PHENYLACETATE IN THE PHOTOCHEMICAL REACTION OF EXCESS ETHYL CHLOROACETATE WITH BENZENE AT 25°C[a]

$[ClCH_2CO_2Et]$ M	$[C_6H_6]$ M	Yield, %[b] I	Yield, %[b] II[d]
Solvent[c]	0.1	78.4	1.1
Solvent	0.1	39.5[e]	0.9
		48.2[f]	1.6
		45.4	1.1

a) External irradiation by high-pressure Hg lamp for 30 hr.
b) On the basis of added benzene.
c) Immersion-type lamp.
d) Molar ratio of II to I.
e) Oxygen was added.
f) Iodine was added.

A probable primary process of this light-induced reaction may be the bond fission of excited ethyl haloacetate. The following types of bond cleavage have been considered to occur in the photolysis

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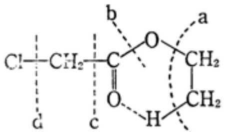
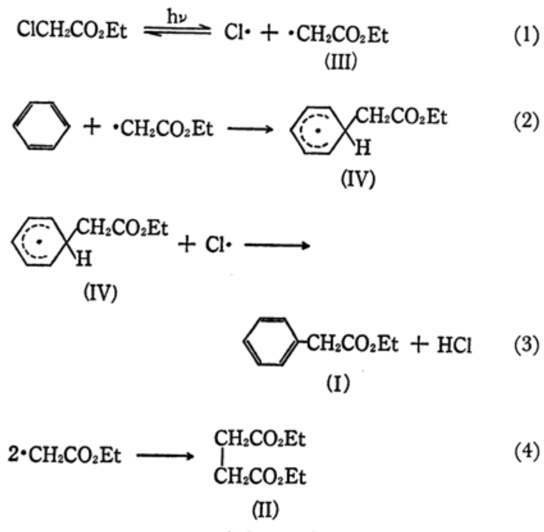
[3] a) N. Kharasch and L. Göthlich, *Angew. Chem.*, **74**, 651 (1962). b) N. Kharasch, P. Lewis and R. K. Sharma, *Chem. Commun.*, 435 (1967).

of alkyl esters[4]; (a) γ-H abstraction by an oxygen atom of carbonyl group and concerted alkyl-oxygen bond fission, (b) acyl-oxygen bond fission and (c) carbonyl-carbon fission. Fission of type (b) occurs mostly at shorter wavelengths (2380 Å and 1870 Å), while fissions of the types (a) and (c) take place at longer wavelength.



Since a high-pressure Hg lamp was used as the light source in the present reaction, fissions of the types (a) and (c) seem to be more probable. The formation of phenylacetate indicates the occurrence of another type of fission (d) (halogen-carbon bond fission).

The formation of diethyl succinate indicates the formation of ethoxycarbonylmethyl radical (III). In addition, hydrogen chloride was detected in the reaction products by the silver nitrate test. On the basis of these data and available postulates[3,5] of similar radical substitutions on benzene ring, probable reaction pathways to account for the observed products can be presented as follows.



Scheme 1

This scheme involves a σ-complex IV as an unstable intermediate. If the hydrogen atom abstraction from IV (Eq. (3)) would be the rate-determining step, addition of oxygen or iodine as an oxidizing agent to the system should tend to increase the yield of I, but this tendency was virtually not observed; *i. e.*, the addition of oxygen, which may quench the excited chloroacetate, somewhat decreased the yield of I, while the addition of iodine slightly increased the yield.

Interestingly, the mixture of 0.1 M aluminum chloride with a benzene solution of 0.1 M ethyl chloroacetate gave on irradiation ethyl phenylacetate as a sole product (Table 3). The yield of I was made better than that without aluminum chloride. These improvements in selectivity and yield of I seem to indicate the participation of an ionic mechanism similar to the ordinary Friedel-Crafts reaction.

TABLE 3. THE YIELDS OF ETHYL PHENYLACETATE IN THE PHOTOCHEMICAL REACTION OF ETHYL CHLOROACETATE WITH EXCESS BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE AT 25°C[a)]

$[ClCH_2CO_2Et]$ M	$[C_6H_6]$	$[AlCl_3]$ M	Yield of $PhCH_2CO_2Et$ %[b)]
0.1[c)]	Solvent	0.1	11.5
0.2	Solvent	0.1	1.7
0.1	Solvent	0.1	3.2
0.1	Solvent	0.2	3.2

a) Irradiation by high-pressure Hg lamp for 30 hr.
b) On the basis of added ethyl chloroacetate.
c) Deposit on the wall of reaction vessel was cleaned at appropriate interval of time.

The ordinary Friedel-Crafts reaction of benzene with ethyl acetate in the dark gives acetophenone, ethylbenzene and *p*-ethylacetophenone.[6] In the similar dark reaction of benzene with ethyl chloroacetate, the formation of ethylbenzene, diethylbenzene and triethylbenzene has been reported.[7] It has been shown that the activity of halogen atom in ethyl chloroacetate was suppressed by the presence of carbonyl group. The closer the carbonyl group is located to the halogen atom, the more effective is the suppression; *e. g.*, ethyl ω-chloropropionate and ω-chlorobutyrate can react at the halogenated carbon atom in the Friedel-Crafts reaction.[7] However, the halogenated carbon atom is the reaction site in our photo-Friedel-Crafts reaction. This difference may be explained by the photo-excitation of the carbonyl group. If the carbonyl oxygen atom of the ester would gain a positive formal charge through its *n*-π* excitation by irradiation, a coordination of aluminum

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[4] a) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958). b) P. Ausloos, *J. Am. Chem. Soc.*, **80**, 1310 (1958).

[5] a) J. M. Blair, B. Bryce-Smith and B. W. Pengilly, *J. Chem. Soc.*, **1959**, 3174. b) G. E. Corbett and G. H. Williams, *ibid.*, **1964**, 3437.

[6] a) L. I. Kashtanov, *Zh. Obsch. Khim.*, **2**, 515 (1932). b) I. G. Farbensindustrie A.-G. Geran Patent 637384 (1936); *Chem. Abstr.*, **31**, 703 (1937). c) J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, **61**, 1413 (1939). d) J. F. Norris and P. Arthur, Jr., *ibid.* **62**, 874 (1940).

[7] I. P. Tsukervanik and I. V. Terenteva, *Dokl. Akad. Nauk SSSR,* **50**, 257 (1945); *Chem. Abstr.*, **43**, 4638 (1949).

chloride to halogen rather than carbonyl should occur, hence the halogenated carbon atom should become the attacking site.

No spectral evidence for a coordination compound between ethyl chloroacetate and aluminum chloride has been reported, while aluminum chloride is shown to coordinate to the carbonyl oxygen atom of ethyl acetate in view of the shift of the carbonyl stretching absorption from 1741 cm^{-1} in ethyl acetate to 1622 cm^{-1} in the complex.[8] Characteristic IR absorption bands of a mixture of aluminum chloride and ethyl chloroacetate are listed in Table 4. Observed shift of ν_{C-Cl} and $\nu_{C=O}$ suggests that aluminum chloride coordinates with both halogen and carbonyl in the ground state, but the halogenated carbon atom can be the more reactive site in the n–π^* excited state of the carbonyl because of its reverse π-electron polarization to that in the ground state.

$$AlCl_3 + ClCH_2CO_2Et \xrightarrow[n\text{-}\pi^*]{h\nu} \left[\overset{\delta-}{A}lCl_3\cdots Cl\overset{\delta+}{C}H_2CO_2Et\right]$$

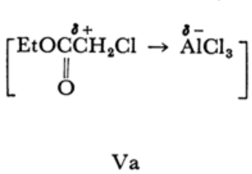
These speculations are rationalized by the photochemical formation of ethyl phenylacetate alone in the presence of aluminum chloride.

TABLE 4. INFRARED SPECTRA (cm^{-1}) OF ETHYL CHLOROACETATE AND ITS COMPLEX WITH ALUMINUM CHLORIDE AT 20°C

$ClCH_2CO_2Et$ (liquid)	$ClCH_2CO_2Et\cdot AlCl_3$	Assignment
1770	1740	$\nu_{C=O}$
1195	1215	ν_{CO-O}
1030	1025	ν_{O-Et}
570	490	ν_{C-Cl}

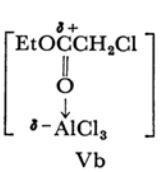
The participation of 1 : 1 complex between ethyl chloroacetate and aluminum chloride in this reaction is suggested by the following experiments. When the molar ratio of chloroacetate to aluminum chloride was varied, the yield of I reached to a maximum value at 1 : 1 of the molar ratio (Table 3).

On mixing ethyl chloroacetate with aluminum chloride, new absorption bands appear at 2750 Å and 3650 Å. These bands may be assigned to the complexes (Va and Vb) of ethyl chloroacetate and aluminum chloride, *i. e.*,



$$\left[\begin{array}{l}EtO\overset{\delta+}{C}CH_2Cl \rightarrow \overset{\delta-}{A}lCl_3\\ \quad\;\; \| \\ \quad\;\; O\end{array}\right]$$

and



$$\left[\begin{array}{l}EtO\overset{\delta+}{C}CH_2Cl\\ \quad\;\; \| \\ \quad\;\; O\\ \quad\;\; \downarrow\\ \;\;\delta\text{-}AlCl_3\end{array}\right]$$

Va Vb

Therefore, the excitation of these complexes (perhaps C-T complex) also might play an important role as well as the n–π^* excitation of carbonyl in this light-induced primary process, *i. e.*,

$$\rangle C{=}O \xrightarrow{h\nu} \rangle \underset{\cdot}{\overset{\delta-}{C}}\text{-}\underset{\cdot}{\overset{\delta+}{O}}$$

But the excitation of the C-T complexes cannot explain the selective formation of I. Therefore, it is probable that the n–π^* excitation of carbonyl group participates more than that of C-T complexes.

Experimental

Materials. Ethyl bromacetate[9] was prepared by the conventional esterification of bromoacetic acid with ethanol catalyzed by concentrated sulfuric acid, bp 158.5—159°C, ν_{max} 1730, 1185 and 1028 cm^{-1}. Ethyl chloroacetate, bp 52—53°C/21 mmHg, ν_{max} 1770, 1195, 1030 and 570 cm^{-1}, authentic ethyl phenylactate, bp 115—116°C/22 mmHg, ν_{max} 1740, 1605, 1500, 1155 and 1030 cm^{-1}, and authentic diethyl succinate, bp 108—108.5°C/19 mmHg, ν_{max} 1740, 1160 and 1030 cm^{-1}, were also prepared by the similar esterification of the corresponding acids. The IR spectra were measured by a Perkin-Elmer Model 337 spectrophotometer.

General Procedure. A Halos high-pressure 300 W Hg lamp and a low-pressure 30 W Hg lamp with a water-cooling quartz jacket were used as light sources. The reaction mixture was placed in a cylindrical quartz vessel (30×300 mm), N_2 gas being bubbled into the mixture. The vessel together with the lamp was immersed into a water bath at a distance of 5 cm.

For the immersion type irradiation, the light source was immersed in a reaction mixture in a reactor equipped with a N_2 gas inlet, a thermometer and a condenser.

The reaction mixture was irradiated for 30hr. At appropriate intervals of time, aliquots were taken out, each yield being estimated by means of GLC.

Analysis of Products. The identification of products was done by means of GLC employing a Yanagimoto Model GCG-220 operated with a column (1 m×4 mm) packed with Silicone DC 550 (30 wt %) on Celite 545 of 80—100 mesh using H_2 as a carrier gas (40 m*l*/min) at 180°C or a Yanagimoto Model GCG-550 F equipped with a hydrogen-flame ionization detector, operated with a column (0.75 m×3 mm) packed with DEGS (13 wt %) on Celite 545 of 80—100 mesh using N_2 as a carrier gas (30 m*l*/min) at 60—180°C (6°C/min). The yields of products I and II were also estimated by means of GLC under the same conditions using *n*-butyl benzoate as an internal standard. The recovery of the ethyl chloroacetate was estimated by means of GLC operated with a column (2 m×4 mm) packed with Apiezon Grease L (3 wt %) on Celite 545 of 80—100 mesh with H_2 as a carrier gas (40 m*l*/min) at 80°C using anisole as an internal standard.

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[8] M. F. Lappert, *J. Chem. Soc.*, **1961**, 817.

[9] S. Natelson and S. Gottfried, "Organic Syntheses," Coll. Vol. II, p. 381 (1955).