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PHOTOCHEMICAL ETHOXYCARBONYLMETHYLATION OF BENZENE WITH ETHYL HALOACETATE IN THE PRESENCE OF METALLIC HALIDES*

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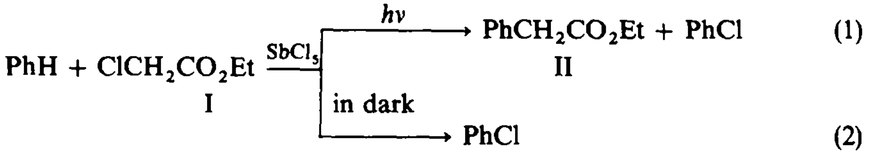
Abstract—Photochemical ethoxycarbonylmethylation of benzene with ethyl haloacetate has been studied in the presence of $SbCl_5$, $AlCl_3$, $ZnCl_2$ or $FeCl_3$. In all cases, ethyl phenylacetate (2·3–24·4%) was obtained as a sole photoproduct and diethyl succinate, which suggests the formation of an ethoxycarbonylmethyl radical, could not be detected. The similar reaction of toluene in the presence of $ZnCl_2$ gives ethyl *p*-tolylacetate (12·8%) without *o*- and *m*-isomers. A probable reaction pathway involving photochemical electrophilic substitution is discussed.

IN OUR previous paper[1] we reported that a photochemical reaction of ethyl chloroacetate with an excess of benzene gave ethyl phenylacetate (1·7%) and diethyl succinate (1·6%), while in the presence of $AlCl_3$ only ethyl phenylacetate was produced as a sole photoproduct (11·5%). On the basis of our data and available postulates[2,3] of similar radical substitution in the benzene ring, the observed photo-products without $AlCl_3$ could be explained by a photochemical homolytic fission of the C-Cl bond in chloroacetate followed by radical reactions. On the other hand, ethyl phenylacetate as a sole photo-product in the presence of $AlCl_3$ may be explained by either a coordination of $AlCl_3$ with a chlorine atom of the excited chloroacetate *via* n,π^* excitation of the carbonyl group which makes the chlorinated carbon atom the reactive site or an excitation of C-T complex of ethyl chloroacetate and $AlCl_3$ followed by the similar electrophilic substitution.

The purpose of this paper is to show that the excitation in the presence of metallic halides is probably a n,π^* type of the carbonyl group in chloroacetate and hence the reactive species may be such a C-T exciplex as $(MCl_{n+1}^{-}\ {}^{+}CH_2CO_2Et)^*$ in the photo-Friedel–Crafts reaction, and that the yield of ethyl phenylacetate may depend on the relative acceptor-strength[4] of the metallic halides for the donor-acceptor complex ($EtO_2CCH_2Cl: Cl_nM$).

RESULTS AND DISCUSSION

UV irradiation of a mixture of ethyl chloroacetate (I) and $SbCl_5$ in C_6H_6 with an unfiltered high-pressure Hg lamp at room temperature gave ethyl phenylacetate (II) (24·4%) together with a small amount of chlorobenzene. Although chlorobenzene was obtained even without light at room temperature, no formation of II was observed in the dark.



A series of experiments was carried out in the presence of other metallic halides, i.e., $ZnCl_2$, $FeCl_3$ and $AlCl_3$ with the molar ratio of I to halide 1:1. The results are shown in Table 1. In the cases of $FeCl_3$ and $SbCl_5$, the yield of II decreases as the concentration of the metallic halide increases. The lowering of yield may be due to cutting off the incident light by black photoproducts containing Fe^{2+} or Sb^{3+} deposited on the wall of reaction vessel. Interestingly, the formation of diethyl succinate (III), which suggests the formation of ethoxycarbonylmethyl radical ($EtO_2CCH_2\cdot$), could not be detected in all cases with chloroacetate and metallic halides. Thus, as suggested in our previous paper,[1] the formation of II via a photochemical ionic reaction rather than a radical reaction seems to be favourable. Only ethoxycarbonylmethylation of ring carbon to give ethyl *p*-tolylacetate (12·2%) took place on irradiation of a toluene solution of I with $ZnCl_2$, but no side-chain substitution was observed. This result may support the ionic formation of II as mentioned above. In addition, no detection of *o*-isomer suggests that the attacking species in the present ethoxycarbonylmethylation are considerably bulky and thus hinder sterically ortho substitution.

TABLE 1. EFFECTS OF METALLIC CHLORIDES (MCl_n) ON THE YIELDS OF PRODUCTS, II AND III

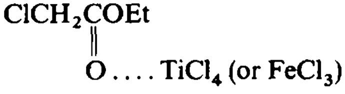
Substrate and solvent	XCH_2CO_2Et(I) (M)	MCl_n^a (M)	Yields of product, %[b] II	III
	X:Cl			
C_6H_6	0·1	none	1·7	1·6
C_6H_6	0·1	$AlCl_3$	11·5	none
C_6H_6	0·1	$SbCl_5$	trace	none
C_6H_6	0·02	$SbCl_5$	24·4	none
C_6H_6	0·1	$ZnCl_2$	4·9	none
C_6H_6	0·01	$ZnCl_2$	5·1	none
C_6H_6	0·1	$FeCl_3$	0·6	none
C_6H_6	0·01	$FeCl_3$	2·3	none
	X:Br			
C_6H_6	0·1	$ZnCl_2$	4·6	trace
Toluene	0·1	$ZnCl_2$	12·8[c]	none

[a] Molar ratio $[XCH_2CO_2Et]/[MCl_n] = 1$
[b] Based on I added
[c] Ethyl *p*-tolylacetate

o-and *p*-Chlorotoluenes and bibenzyl (only a trace) were detected in the reaction of toluene. The chlorotoluenes were produced even without light, which has been previously postulated by Kovacic and his co-workers.[5]

With ethyl bromoacetate instead of I, a similar yield of II and a trace of III were obtained.

Prior to discussing the excited state of I in the presence of metallic halides, the IR spectra of mixtures of I and metallic halides with molar ratio of 1 : 1 were measured. As shown in Table 2, the shifts ($\Delta\nu_{C=O}$) in the carbonyl stretching frequency between free I and its complexes with $TiCl_4$ or $FeCl_3$ are 115–135 cm^{-1}. These values are comparable to those[4] of 1:1 addition compounds of EtOAc with various metallic (group III or IV) halides. IR data for $TiCl_4$ or $FeCl_3$ may require the complex structure IV, where the acyl oxygen is the electron donor.



$$\underset{\substack{\| \\ O \cdots\cdots TiCl_4\ (\text{or } FeCl_3)}}{ClCH_2COEt}$$

IV

In contrast, the shifts with the other metallic halides are smaller. Characteristic IR absorptions due to $AlCl_4^-$ at 490 cm^{-1} and to $SbCl_6^-$ at 665 cm^{-1} are observed in the corresponding complexes.[6] Consequently, the donor atom seems to be chlorine rather than acyl oxygen atom.

TABLE 2. INFRARED AND ULTRAVIOLET SPECTRA OF ($ClCH_2CO_2Et \cdot MCl_n$)

	IR			UV[c]
MCl_n	$\Delta\nu_{C=O}$[a] (cm^{-1})	ν_{C-Cl}[b] (cm^{-1})	MCl_{n+1}^- (cm^{-1})	(new band) (nm)
$TiCl_4$	135	560	620	—[d]
$FeCl_3$	115	570	none	none
$AlCl_3$	105	570	490	365[e]
$SbCl_5$	85	560	665	none
$ZnCl_2$	15	570	none	370

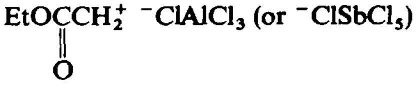
[a] Shift to shorter carbonyl stretching frequency as between free I ($\nu_{C=O}$ 1760 and 1735 cm^{-1}) and its complex

[b] 570 cm^{-1} for free I

[c] In C_6H_6

[d] Measurement was impossible because of sombrely coloured solution

[e] In diethyl ether

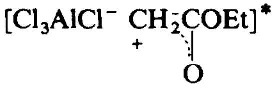


$$\underset{\substack{\| \\ O}}{EtOCCH_2^+}\ ^-ClAlCl_3\ (\text{or } ^-ClSbCl_5)$$

V

However, the electrostatic attraction between ions in the ion pair V may be strong on account of the electron-withdrawing carbonyl group so that no ordinary Friedel–

Crafts reaction takes place in the dark. When the carbonyl group in V is excited through n, π^*, the carbonium ion may be stabilized by the participation of a reversal of ordinary carbonyl π-electron polarization.



$$[\mathrm{Cl_3AlCl^-}\ \overset{+}{\mathrm{C}}\mathrm{H_2}\underset{\substack{\vdots|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{OEt}]^*$$

VI

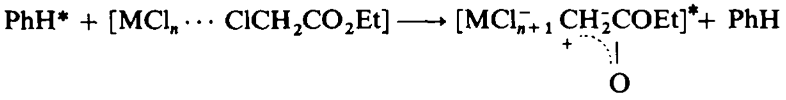
The electrostatic attraction in the excited state may be lowered and hence an electrophilic attack of carbonium ion on the aromatic ring is expected. In fact, the higher yield in the presence of $AlCl_3$ or $SbCl_5$ may meet this expectation (see Table 1).

The IR spectral data for a mixture of I and $ZnCl_2$ suggest a weak interaction between them at the ground state.

The UV spectra for $I \cdot AlCl_3$ and $I \cdot ZnCl_2$ showed new absorptions at 3650 and 3700 Å, respectively, but not for other metallic halides. Hence, the new absorptions do not contribute to the present photochemical ethoxycarbonylmethylation.

On the basis of these facts, the photochemical ethoxycarbonylmethylation of C_6H_6 in the presence of metallic halides may proceed as shown in the following reaction pathways.

$$\mathrm{PhH} \overset{h\nu}{\rightleftharpoons} \mathrm{PhH^*} \tag{3}$$



$$\mathrm{PhH^*} + [\mathrm{MCl}_n \cdots \mathrm{ClCH_2CO_2Et}] \longrightarrow [\mathrm{MCl}_{n+1}^-\ \overset{+}{\mathrm{C}}\mathrm{H_2}\underset{\substack{\vdots|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{OEt}]^* + \mathrm{PhH} \tag{4}$$

VI

$$\mathrm{VI} + \mathrm{PhH} \longrightarrow \mathrm{PhCH_2CO_2Et} + \mathrm{MCl}_n + \mathrm{HCl} \tag{5}$$

$$\mathrm{I} + \mathrm{PhH^*} \longrightarrow \mathrm{I^*} + \mathrm{PhH} \tag{6}$$

$$\mathrm{I^*} + \mathrm{MCl}_n \longrightarrow \mathrm{VI} \tag{7}$$

For $AlCl_3$ and $SbCl_5$ the main reaction may proceed by way of Eqs 4 and 5, while for other metallic halides by Eqs 6, 7 and 5. The ineffective formation of an exciplex VI through Eq 7 may explain the poor yield of II. The properties of excited I, *e.g.*, its lowest triplet or singlet energy and the extent of coupling[7] between n,π^* and π,π states, are uncertain except the quenching [8a] of the fluorescence of toluene with I, but it is probable that the lowest singlet and triplet energies of I may be lower than those of C_6H_6 (E_S 115 kcal/mole, ϕ_{ST} 0·25, E_T 85 kcal/mole[9a]) or toluene (E_T 83 kcal/mole[9b]). Energy levels of exciplex VI may lie lower than those of the excited I[8b]. Thus the energy transfers shown by Eqs 4 and 6 may be possible.

EXPERIMENTAL

UV spectra were measured by a Hitachi Model 124 double-beam spectrophotometer, IR spectra by Perkin–Elmer 337 grating spectrophotometer. GLC was carried out by employing a Yanagimoto Model GCG-500F with a flame ionization detector using a 1 m × 3 mm column of 2% PEG 20M on 40–60 mesh Camelite CK at 60–170° (6°/min between 60° and 80°, 16°/min between 80° and 170°).

Ethyl bromoacetate, bp 158·5–159°, ethyl chloroacetate (I), bp 143·6–144·2°, authentic ethyl phenylacetate (II), bp 115–116°/22 mm, and authentic diethyl succinate (III), bp 108–108·5°/19 mm, were prepared as previously described.[1] Authentic ethyl *p*-tolylacetate, bp 144°/45 mm, was prepared by the conventional esterification of *p*-tolyacetic acid with ethanol.[10] *p*-Tolylacetic acid was prepared[11] by hydrolysis of *p*-methylbenzyl cyanide[12] obtained by cyanation of ω-monobromo-*p*-xylene.[13] Commercial benzene and toluene were purified by rectification. Anhydrous $FeCl_3$ was prepared by dehydration of hydrated $FeCl_3$ with $SOCl_2$.[14] Other anhydrous metallic halides were guaranteed and used without further purification.

Measurements of IR spectra of the mixtures of I *and metallic chlorides.* The mixtures with the molar ratio of 1:1 were prepared in the absence of solvent under N_2 atmosphere in a gloved box. Mixing was exothermal. Their spectra were measured between KBr plates without spacers.

Irriadiation of solutions of I *and metallic halides in benzene.* All experiments were carried out in a cylindrical quartz vessel (30 × 300 mm) equipped with a silicone rubber stopper. A solution of 0·01–0·1 M I and equimolar metallic chloride in C_6H_6 (100 ml) was placed in the vessel, and it was sealed after bubbling a slow stream of dry N_2 through the solution. A Halos high-pressure 400 W Hg lamp with a water cooling quartz jacket was used. The vessel was placed at the distance of 10 cm from the light source in a water bath and irradiation was carried out at 25° for 20 hr. After irradiation, the mixture was carefully condensed to identify and determine the products by means of GLC. The similarity of the retention times of the peaks of authentic materials with those of the samples established their identity. The yield of II was estimated by GLC using *n*-butyl benzoate as an internal standard.

Irradiation of solution of ethyl bromoacetate and $ZnCl_2$ *in toluene.* A solution of 0·1 M ethyl bromoacetate and 0·1 M $ZnCl_2$ in toluene was irradiated. The yield of ethyl *p*-tolylacetate was estimated by means of GLC using benzyl chloride as an internal standard.

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