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Photochemical Ethoxycarbonylmethylation of Alkylbenzenes with Ethyl Chloroacetate. MO Calculation for Prediction of Orientation[1)]

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Synopsis. Photoreaction of ethyl chloroacetate with cumene gives ethyl cumenylacetates (17.5%) in the ratio $o:m:p=17:46:37$. The same reaction with *t*-butylbenzene gives ethyl *t*-butylphenylacetate (23%) in the ratio $o:m:p=$ trace: 65: 35. Addition of BF_3 increases the total yield of the substitution products. Orientations together with those for toluene and anisole in ethoxycarbonylmethylation were discussed in terms of INDO-type MO calculation of the lowest singlet excitation energies.

Reports were given on the ethoxycarbonylmethylation of aromatic compounds with haloacetate.[2–4)] Irradiation of a 0.3 M ethyl chloroacetate solution in toluene gave ethyl tolylacetate with isomer distribution: ortho, 33%; meta, 61%; and para, 6%; total yields 16%.[4)] Irradiation of a 0.1 M ethyl chloroacetate solution in anisole gave ethyl methoxyphenylacetates with isomer distribution: ortho, 59%; meta, 28%; and para, 13%; total yields 17%.[5)] The mechanism may involve an attack of radical species $\cdot CH_2COOEt$ on the aromatic ring in view of the by-products of dimerized $\cdot CH_2COOEt$, *i.e.*, diethyl succinate, but the yields of meta isomer are higher than those of para isomer. This is abnormal on the basis of the ground state π-electron densities.[6,7)]

We wish to report on the product distribution in the photo-reaction of ethyl chloroacetate and cumene or *t*-butylbenzene, where the yield of meta-substituted product is higher than that of para-substituted one as observed with toluene and anisole. The results including previous ones will be rationalized by the molecular orbital consideration.

Results and Discussion

Irradiation of 0.1 M ethyl chloroacetate in cumene for 60 h gave an isomeric mixture of ethyl cumylacetates. The isomer distribution of produced ethyl cumylacetates was as follows: ortho (Ia), 17%; meta (IIa), 46%; and para (IIIa), 37%, in a total yield of 54% based on the consumed ethyl chloroacetate. Ethyl 2-methyl-2-phenylpropionate (IVa) (7.5%) and dimeric cumene (V) were obtained, no β-ethoxycarbonylmethylation taking place. Addition of $BF_3\cdot Et_2O$ (a Lewis acid) (0.1 M) to the same mixture gave higher yields with an analogous distribution of ethyl cumylacetates: ortho (Ia), 21%; meta (IIa), 45%; para (IIIa), 34%, in a total yield of 65% based on the consumed ethyl chloroacetate along with (IVa) (8.0%). In addition, isomeric bicumenyls were obtained.

Similar irradiation of a 0.1 M ethyl chloroacetate solution in *t*-butylbenzene for 60 h gave ethyl *t*-butylphenylacetates: ortho (Ib), trace; meta (IIb), 65%; and para (IIIb), 35%, in a total yield of 82% based on the consumed ethyl chloroacetate. In this case, the yield of dimeric *t*-butylbenzene was low. Addition of $BF_3\cdot Et_2O$ (0.1 M) to the same mixture gave higher yields of ethyl *t*-butylphenylacetates composed of ortho (Ib), 5%; meta (IIb), 50%; and para (IIIb), 45%, in a total yield of 89% based on the consumed ethyl chloroacetate.

$$R\text{-}C_6H_5 + ClCH_2COOEt \xrightarrow{h\nu} \begin{cases} o\text{-}R\text{-}C_6H_4\text{-}CH_2COOEt & \text{(I)} \\ m\text{-}R\text{-}C_6H_4\text{-}CH_2COOEt & \text{(II)} \\ p\text{-}R\text{-}C_6H_4\text{-}CH_2COOEt & \text{(III)} \\ C_6H_5\text{-}C(CH_3)_2COOEt & \text{(IVa)} \\ C_6H_5\text{-}C(CH_3)_2\text{-}C(CH_3)_2\text{-}C_6H_5 & \text{(V)} \end{cases}$$

$$\text{a: } R=CH(CH_3)_2 \quad \text{b: } R=C(CH_3)_3$$

As apparent from the above data, isopropyl- and *t*-butylbenzenes afford lower yields of ortho isomers than toluene and anisole because of steric hindrance.

The yields of meta isomers, (IIa) and (IIb), are higher than those of the corresponding para isomers, (IIIa) and (IIIb), which are similar to the yield reported for toluene. Since the attacking species $\cdot CH_2COOEt$ would be cationic by the electron-withdrawing effect of carbonyl, it is difficult to explain the results in terms of ground state electron density. In the reactions of proton (H–D exchange), the π-π^* singlet excited aromatics react with the electrophile, giving ortho and meta orientation with toluene and anisole.[7,8)] A similar phenomenon, observed with solvolysis of methoxybenzylacetates is called "meta-transmission".[9)]

Calculations were made on the electronic structures of these alkylbenzenes by the INDO-type method.[10)] The calculated lowest singlet excitation energies and their transition moments are summarized in Table 1 together with the experimental ones. The calculated

TABLE 1. EXCITATION ENERGY AND TRANSITION MOMENT OF ALKYLBENZENES AND ANISOLE

R	Calcd by CI method		Obsd	
	Excitation energy (mm)	Transition moment[a)]	λ_{max} (mm)	log$_{max}$
CH_3	224	−0.011	261	2.25[b)]
OCH_3	226	0.229	277	3.15[c)]
$CH(CH_3)_2$	223	0.037	261	2.31[b)]
$C(CH_3)_3$	224	−0.076	258	2.36[b)]

a) All transition moments are in the direction of short axis. b) A.P.I. Research Project, No. 44, I (1945). c) A.B. Raway and J.T. Chanberlain, *J. Chem. Soc.*, **1952**, 2310.

energy values are somewhat larger than the observed ones, the parallelism between the calculated and the observed values of excitation energy and their moments being fairly good.

Since the lowest excited states of alkylbenzenes are constructed by two important configurations, the frontier electron density of rth position is given by

$$f_r^{\mathrm{R}} = C_1^2[(C_{\mathrm{ir}})^2+(C_{\mathrm{kr}})^2] + C_2^2[(C_{\mathrm{jr}})^2+(C_{\mathrm{lr}})^2],$$

where indices i and j denote the occupied MO's, k and l the vacant MO's in the ground state of alkylbenzene, and C_1 and C_2 are the CI coefficients of the i→k and j→l excited states, respectively.

TABLE 2. THE FRONTIER ELECTRON DENSITIES OF AROMATIC COMPOUNDS CALCULATED BY CI METHOD AND OBSERVED COMPOSITION OF PRODUCTS IN THE PHOTOREACTION OF AROMATIC COMPOUNDS WITH ETHYL CHLOROACETATE

R	Lowest excited state frontier electron density				Ethoxycarbonylmethylation products composition		
	1	2(*o*)	3(*m*)	4(*p*)	2(*o*)	3(*m*)	4(*p*)
CH_3	0.309	0.340	0.321	0.309	33	61	6
OCH_3	0.238	0.350	0.314	0.267	59	28	13
$CH(CH_3)_2$	0.289	0.335	0.311	0.287	17	46	37
$C(CH_3)_3$	0.260	0.327	0.295	0.258	trace	65	35

In all cases, the frontier electron densities of lowest excited states decrease in the order: ortho>meta>para (Table 2). The difference in the calculated frontier electron densities can be used for an examination of the difference in relative reactivities for electrophilic attack. For example, in the case of toluene, the ground state π-electron densities calculated by a similar INDO-type MO calculation are: ortho, 1.012; meta, 1.000; and para, 1.016,[11] and those by the Hückel MO calculation are: ortho, 1.0044; meta, 0.9999; and para, 1.0037,[6] whereas the orientation in the nitration of toluene is: ortho 58; meta 4; para 38. The similar small difference in the ground-state π-electron densities of anisole (*o*, 1.056; *m*, 0.982; *p*, 1.020) gives rise to the observed large difference in *o*, *m*, and *p*-orientations.[11]

The calculated frontier electron densities in the lowest excited states coincide with the observation with anisole but not ground state electron densities. The yields of meta isomers in alkylbenzenes, however, are higher than the yields of ortho isomers. The lower yields of ortho isomers can be ascribed to the steric requirement, since the yields of ortho isomer decrease in the order: toluene>cumene>*t*-butylbenzene in spite of the small difference in the calculated frontier electron densities. As shown in Table 2 the reactivity of para position is higher than that expected from calculation. This might reflect the electrophilic nature of $\cdot CH_2COOEt$ radical which is increased by the presence of BF_3. The isomeric ratio in toluene, at least, (meta: para=10: 1) cannot be explained by statistical attack (2: 1) of neutral molecules on the ground state toluene. In the case of the other aromatic compounds, the isomeric distribution can be explained by the statistical ratio (meta: para=2: 1). However, on the basis of electrophilic nature of $\cdot CH_2COOEt$ the para attack should be preferred to the meta attack, if the attack were to occur on ground states.

Since the lowest energy for excitation of alkyl chloroacetate (4.56 eV) is lower than that of alkylbenzens (5.5—5.6 eV), the dissociation of C–Cl bond would be preferred to the excitation of alkylbenzenes. However, the very low concentration of chloroacetates would result in the simultaneous excitation of both reactants.

The attempted reaction of 0.1 M ethyl chloroacetate with chlorobenzene gave self-condensation products (biphenyl and diethyl succinate) together with ethyl phenylacetate (23%) but no ethoxycarbonylmethylation product. Nitrobenzene did not react with ethyl chloroacetate on irradiation. The results show the electrophilic nature of $\cdot CH_2COOEt$ radical.

Experimental

Materials. Isopropylbenzene (bp 152—153 °C) and *t*-butylbenzene (bp 167—169 °C) of guaranteed grade were used after washing with H_2SO_4 and distillation. Ethyl chloroacetate (bp 51—52 °C/20 Torr) was distilled before use.

A Typical Procedure. A Halos high-pressure 300 W Hg lamp was used as a light source. The sample solution was placed in a cylindrical quartz vessel (25×200 mm). The vessel and the lamp were immersed in a water bath (20 °C) at a distance of 5 cm. The sample solution was irradiated for 60 h.

Identification of the products was carried out by means of GLC using a column (1.2 m×4 mm) packed with Silicone OV-17 (5 wt%) on Shimalite W of 80—100 mesh and a column (1.2 m×4 mm) packed with PEG 20 M (10 wt%) on Chromosorb WAN of 60—80 mesh in comparison with the authentic specimen. The yields of products were determined also by means of GLC using a column (1.2 m×4 mm) packed with Silicone OV-17 (5 wt%) on Shimalite W of 80—100 mesh using N_2 as a carrier gas (20 cm³/min) at 80—270 °C (8 °C/min) using naphthalene as an internal standard.

UV Spectra. Following UV spectra peaks ($\lambda_{\max}$) were observed for reactants: Ia, 262 nm; IIa, 259 nm, ethyl chloroacetate, 236 nm; Ia–BF_3, and IIa–BF_3 mixtures had the same peaks as those of Ia and IIa, respectively. Systems Ia–$ClCH_2CO_2Et$ and IIa–$ClCH_2CO_2Et$ showed no extra peak besides those of the component materials.

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