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Photochemical Ethoxycarbonylmethylation of Toluene with Ethyl Chloroacetate[1)]

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Synopsis. UV irradiation of a toluene solution of ethyl chloroacetate under N_2 gave an isomeric mixture of ethyl tolylacetates: ortho, 5.2%, meta, 9.6%, para, 0.9% and a trace of diethyl succinate. The reaction under air increased the yields of all the products. Addition of $AlCl_3$ also increased the yields, especially that of ortho; *i. e.*; 17.9%; meta, 26.5%; para, 10.6%.

In the ordinary aromatic Friedel-Crafts reaction of carboxylic acids and esters, the site of electrophilic reagents is a carbonyl carbon atom because of the addition of $AlCl_3$ to carbonyl; thus the aromatic substitution by CH_2COOH or CH_2COOR is usually difficult and only a few reports are available on this sort of reaction.[2)] However, UV irradiation can overcome this difficulty, the following examples being reported; ethoxycarbonylmethylation of benzene (PhH) giving $PhCH_2COOEt$[3)] and carbamolymethylation of phenols (ArH) giving $ArCH_2CONH_2$.[4)] The present note deals with the ethoxycarbonylmethylation of toluene with ethyl chloroacetate and a disccussion on its orientation.

Results and Discussion

Irradiation of 0.3 M ethyl chloroacetate solution in toluene under N_2 atmosphere for 40 h gave ethyl tolylacetates, the yields being ortho (I), 5.2%; meta (II), 9.6% and para (III), 0.9%. A trace of diethyl succinate (IV) and an unidentified product were also observed by GLC. Consumption of the chloroacetate was 25%.

$$\underset{\text{excess}}{C_6H_5CH_3} + ClCH_2CO_2Et \xrightarrow{h\nu}$$

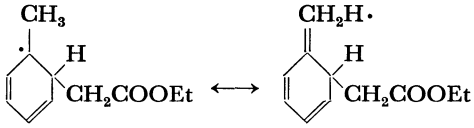
$$\underset{\text{(I)}}{o\text{-}CH_3C_6H_4CH_2COOEt}, \quad \underset{\text{(II)}}{m\text{-}CH_3C_6H_4CH_2COOEt},$$

$$\underset{\text{(III)}}{p\text{-}CH_3C_6H_4CH_2COOEt}, \quad \underset{\text{(IV)}}{\begin{matrix} CH_2COOEt \\ | \\ CH_2COOEt \end{matrix}} \quad \textit{etc.}$$

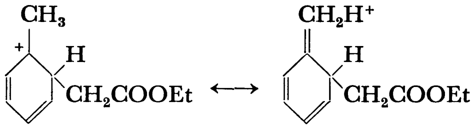
The same reaction under air gave higher yields; I, 16.5%; II, 18.8%; III, 13.8%; IV, 4.5%. Consumption of $ClCH_2COOEt$ was 35%. This effect of oxygen suggests the acceleration of the radical fission of $ClCH_2$-COOEt to Cl· and ·CH_2COOEt radicals by Cl· atom abstraction by molecular oxygen or other radicals. This indicates that molecular oxygen itself and/or radicals derived from the photo-oxidation of organic materials can induce the radical abstraction of Cl atom as suggested from the alkyl-halogen fission of some alkyl halides[5)] and from the behavior in the SO_2Cl_2 chlorination in the presence of these radicals.[6)]

Addition of $AlCl_3$ (3.0 g) to the same mixture of $ClCH_2COOEt$ (5.5 g) and toluene (150 ml) under N_2 for 40 h increased the yields of tolylacetates, especially ortho and para: I, 17.9%; II, 26.5%; III, 10.6%; IV, trace, where 72% of $ClCH_2COOEt$ was photolyzed. Unidentified products in these cases seem to be the same one in view of its GLC peak. Hydrogen chloride was detected in all cases by silver nitrate test.

The yields with toluene were much higher than the reported yield with benzene affording $PhCH_2COOEt$ (2.5% without $AlCl_3$ and 11.5% with $AlCl_3$).[3)] In a previous paper[3)] it was postulated that the attacking species may be a radical ·CH_2COOEt in the absence of $AlCl_3$ and a cation-like species $Al^{\delta-}Cl_3\cdots Cl\cdots C^{\delta+}H_2$-COOEt in the presence of $AlCl_3$ for this type of reaction. The observed effect of CH_3 may imply the stabilization of the transition state by hyperconjugation, which can delocalize both odd electron (V) and positive charge (VI).



(V)



(VI)

However, the yield of III (para) is much lower, and the yield of II (meta) much higher than that expected from the hyperconjugation. This suggests the different charge distribution in the π-π^* singlet excited aromatics as evidenced in the H-D exchange reaction of aromatics,[7)] which prefers ortho and meta substitution of radical and electrophilic reagents to para substitution; The negative charge is more localized at ortho and meta position to CH_3. The observed increase of contents of III and IV under oxygen can be explained in terms of the tendency to statistical orientation due to higher concentration of radical ·CH_2COOEt, while the increase of III by addition of $AlCl_3$ can be ascribed to the leveling of isomer distribution to the thermodynamic equilibrium in the presence of $AlCl_3$ as observed in ordinary Friedel-Crafts alkylation.[8)]

Experimental

Materials. Ethyl *o*-, *m*- and *p*-tolylacetates were prepared by H_2SO_4-catalyzed esterification of the corresponding tolylacetic acids. Boiling points: *o*, 103—104 °C/5 Torr (lit,[9)] bp 236—238 °C); *m*, 104—105 °C/6 Torr (lit,[9)] bp 228—229 °C); *p*, 98—99 °C/4 Torr (lit,[9)] bp 240 °C). Diethyl succinate, bp 104—105 °C/15 Torr (lit,[3)] bp 108 °C/19 Torr). Commercial ethyl chloroacetate of guaranteed grade was used, bp 52—53 °C/21 Torr.

A Typical Procedure. A mixture of ethyl chloroacetate (5.5 g) and toluene (150 ml) was irradiated with a 300 W high pressure Hg lamp in a quartz tube (3 × 30 cm) for 40 h at 20 °C. The tube and the lamp were immersed in a water bath at a distance of 5 cm.

Identification of the products was carried out by comparison of GLC peaks with those of the authentic samples. GLC analysis was carried out with a column (4 mm × 1.2 m) packed with Apiezon Grease L (15 wt%) on Celite 545 of 80—100 mesh and a column (4 mm × 1.5 m) packed with PEG (10 wt%) on Chromosorb WAN using N_2 as a carrier gas (40 ml/min) at 80—250 °C (8 °C/min). Ethyl acetate was used as an internal standard.

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