Photo-ethoxycarbonylation of Anisole, Dimethylaniline and Thiophene in Carbon Tetrachloride-Ethanol Solutions*

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UV-Irradiation of anisole, dimethylaniline and thiophene with carbon tetrachloride in ethanol produced ethoxycarbonylated compounds. In general, this photo-ethoxycarbonylation proceeds effectively when a charge transfer complex between aromatic compound and carbon tetrachloride is excited. Attack of trichloromethyl radicals formed by the sensitized decomposition of carbon tetrachloride also occurs in parallel with the charge transfer mechanism.

The authors have reported that ferrocene undergoes photo-ethoxycarbonylation, formylation and ethoxymethylation in carbon tetrachloride–, chloroform–, and dichloromethane–ethanol solutions, respectively.[1a] These photoreactions result from the excitation of the charge transfer complexes of ferrocene with halogenated hydrocarbons.[1b]

Recently, Hirao and Yonemitsu reported the photochemical introduction of formyl group into phenol and diethylaniline during UV-irradiation in chloroform–methanol solutions.[2] They also described the formation of methyl hydroxybenzoates during UV-irradiation of phenol and carbon tetrachloride in aqueous methanol solution.

This paper deals with the photo-ethoxycarbonylation of anisole, dimethylaniline and thiophene in carbon tetrachloride–ethanol solutions.

Experimental

Materials. Commercially available anisole and *N,N*-dimethylaniline (Wako Junyaku E. P. grade reagents) were purified by distillation under reduced pressure and checked by thin layer chromatography after the distillation. Thiophene (Wako Junyaku E. P. grade reagent) was purified by distillation under atmospheric pressure. Carbon tetrachloride was purified as described previously.[1a] Spectrograde cyclohexane (Wako Junyaku Dotite Spectrosol) was used for the measurement of UV-spectra.

Irradiation. The irradiation procedure was similar to that described previously.[1a]

Separation of the Photoproducts (General Procedure). The irradiated solution was washed with aqueous sodium hydrogen carbonate solution and water after which the organic layer was extracted with ether. The ether solution was dried and then the ether was removed under reduced pressure by a rotary evaporator. The residue was chromatographed on a silica gel column. The eluate was further purified by successive thin layer chromatography on silica gel (Merck, GF-254).

Identification of the Photoproducts. The photoproducts were identified by comparing their IR and NMR spectra, and gas chromatograph retention times with those of authentic samples.

Quantitative Analysis. The products were analyzed with a Yanagimoto GC-550F gas chromatograph equipped with a 1.5 m glass column of Carbowax 20 M on Diasolid L (20%, 60—80 mesh), at 150—184 °C. The analyses listed in Table 1 are the averages of at least three separate experiments.

Measurements. IR spectra were recorded with a Hitachi 215 grating infrared spectrophotometer. UV spectra were recorded with a Hitachi 124 spectrophotometer. NMR spectra were measured with a Hitachi R-24 (60 MHz) or a Hitachi R-22 (90 MHz) spectrometer.

Results and Discussion

The UV-spectra of dimethylaniline, anisole and thiophene in cyclohexane and in carbon tetrachloride are shown in Figs. 1, 2, and 3.

In dimethylaniline, the enhancement of the UV-absorption near 300 nm in the presence of carbon tetrachloride is attributed to the formation of a charge

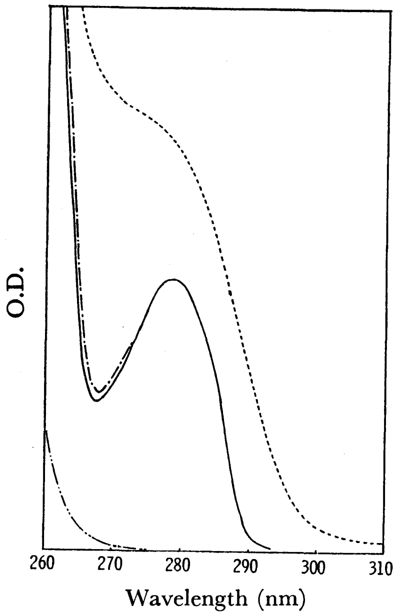

Fig. 1. UV-Spectra of dimethylaniline in cyclohexane and in carbon tetrachloride. (Path length, 1 mm)
(——): Dimethylaniline (3.456×10^{-3}mol·l^{-1}) in cyclohexane.
(-----): Dimethylaniline (3.456×10^{-3}mol·l^{-1}) in carbon tetrachloride.
(········): Carbon tetrachloride.
(—·—): The sum of the absorption of dimethylaniline in cyclohexane (3.456×10^{-3}mol·l^{-1}) and that of carbon tetrachloride.

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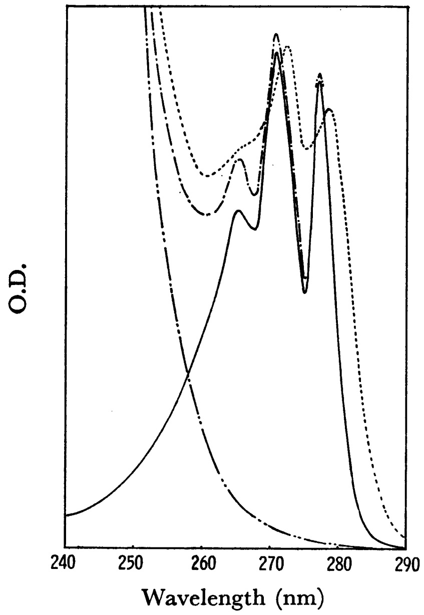


Fig. 2. UV-Spectra of anisole in cyclohexane and in carbon tetrachloride. (Path length, 1 mm)
(——): Anisole $(3.456\times 10^{-3}\,\mathrm{mol\cdot l^{-1}})$ in cyclohexane.
(----): Anisole $(3.456\times 10^{-3}\,\mathrm{mol\cdot l^{-1}})$ in carbon tetrachloride.
(—·—): Carbon tetrachloride.
(—··—): The sum of the absorption of anisole in cyclohexane $(3.456\times 10^{-3}\,\mathrm{mol\cdot l^{-1}})$ and that of carbon tetrachloride.

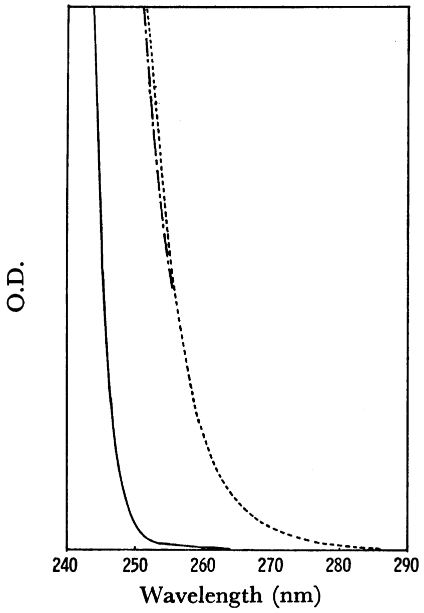


Fig. 3. UV-Spectra of thiophene in cyclohexane and in carbon tetrachloride. (Path length, lmm)
(——): Thiophene $(3.456\times 10^{-3}\,\mathrm{mol\cdot l^{-1}})$ in cyclohexane.
(----): Thiophene $(3.456\times 10^{-3}\,\mathrm{mol\cdot l^{-1}})$ in carbon tetrachloride.
(—·—): Carbon tetrachloride.
The sum of the absorption of thiophene in cyclohexane $(3.456\times 10^{-3}\,\mathrm{mol\cdot l^{-1}})$ and that of carbon tetrachloride is smaller than that of thiophene in carbon tetrachloride $(3.456\times 10^{-3}\,\mathrm{mol\cdot l^{-1}})$.

transfer complex of dimethylaniline with carbon tetrachloride, as was proposed by Davis and Farmer.[3]

Anisole also shows a slight enhancement of UV-absorption at 250—260 nm and at 270—290 nm. Thiophene also shows a slight enhancement near 250 nm. The linear correlation between ionization potential and wavelength of absorption maximum of the charge transfer band was reported for alkylbenzene-carbon tetrachloride systems.[4,5] Since the ionization potentials of anisole (8.20 eV)[6] and thiophene (8.86 eV)[6] are close to those of hexamethylbenzene (8.15 eV,[7] $h\nu_{\mathrm{CT}}$ 240—246 nm[5]) and *m*-xylene (8.9 eV,[7] $h\nu_{\mathrm{CT}}$ 232—238 nm[5]), respectively, the enhancement of the UV-absorption of anisole in carbon tetrachloride near 250 nm or that of thiophene in this region can be ascribed to the formation of charge transfer complexes with carbon tetrachloride.

The UV-irradiation of anisole, dimethylaniline and thiophene with carbon tetrachloride in ethanol solution gave the corresponding ethoxycarbonylated compounds, as in the irradiation of the ferrocene–carbon tetrachloride–ethanol system. In the case of anisole and dimethylaniline, the yields of photoproducts and the ratios of isomers obtained are changed significantly by changing the wavelength of irradiating light. The results are summarized in Table 1.

Photoreaction of Dimethylaniline. Irradiation with 254, 313, and 365 nm light gave both *o*- and *p*-dimethylaminobenzoates. Irradiation with 254 nm light resulted in an *o*/*p* ratio of 3.7. An irradiation with 254 nm light, the incident light was mostly absorbed by uncomplexed dimethylaniline. The addition of cyclohexene, a radical scavenger, markedly suppressed the formation of ethyl dimethylaminobenzoates, especially the *ortho* isomer: the *o*/*p* ratio in the presence of cyclohexene was 0.47. Irradiation with light of longer wavelength gave different results: lower *o*/*p* ratio (1.31 and 1.78) were obtained on irradiation with 313 and 365 nm light. The *o*/*p* ratios in the presence of cyclohexene are similar on irradiation with 254 and 313 nm light (0.47 and 0.39). The photo-ethoxycarbonylation of dimethylaniline with 313 nm light, which was not affected by added cyclohexene, can be considered to proceed in the solvent cage. The value of the *o*/*p* ratio, 1.31, obtained on irradiation with 313 nm light is closer to 0.47 and 0.39 than to the 3.7 obtained on irradiation with 254 nm light. In the photo-ethoxycarbonylation of dimethylaniline with 313 nm light, the charge transfer complex between dimethylaniline and carbon tetrachloride contributes greatly to the photo-substitution. Irradiation with 365 nm light also gave an *o*/*p* ratio, 1.78, which is close to that obtained on irradiation with 313 nm light.[8]

Higher yields of the ethoxycarbonylated products were obtained in the presence of cyclohexene than in its absence on irradiation with 313 nm light. The reason for this effect of cyclohexene is still not clear.

The formation of hydrogen chloride during the reaction may cause the decomposition of dimethylaniline to give *N*-methylaniline and an anilinum cation which reacts with dimethylaniline photochemically to give biphenyl derivatives.[9] Although a quantitative analy-

Table 1. Photo-ethoxycarbonylation of aromatic compounds in carbon tetrachloride–ethanol solutions[a]

Aromatic compound (20 mmol)	CCl_4 (mmol)	Cyclohexene (mmol)	hν/Time (nm)/(hr)	Conversion (%)	Products and Yields[b]					
					Ethyl methoxybenzoates[c]				*p*-Chloroanisole	Ethyl salicylate
					o-	*m*-	*p*-	*o*/*p*		
Anisole	40	—	254/48	8.5	4.6	0.6	7.8	[0.59]	18.7	trace
Anisole	40	20	254/48	24.4	3.9	1.1	4.4	[0.88]	24.9	trace
Anisole	40	—	265/48	16.7	8.9	2.2	10.7	[1.71][d]	5.8	9.4
Anisole	40	20	265/48	13.6	1.3	0.2	2.7	[0.50]	0.1	trace
					Ethyl *N*,*N*-dimethylaminobenzoates[e]					
					o-	*m*-	*p*-			
Dimethylaniline	40	—	254/48	9.2	14.5 (1.3)	0	3.9 (0.3)	[3.7]		
Dimethylaniline	40	20	254/48	1.3	7.9 (0.1)	0	16.6 (0.2)	[0.47]		
Dimethylaniline	40	—	313/48	4.9	8.4 (0.4)	trace	6.4 (0.3)	[1.31]		
Dimethylaniline	40	20	313/48	14.2	4.9 (0.7)	trace	12.4 (1.7)	[0.39]		
Dimethylaniline	40	—	365/48	3.0	17.8 (0.5)	trace	10.0 (0.3)	[1.78]		
					Ethyl 2-thiophenecarboxylate[f]					
Thiophene	100	—	254/18		0.8					
Thiophene	100	20	254/18		0.8					
Thiophene	100	—	365/45		0.0					

a) The total volume of the sample solution was 50 ml. b) The values listed in this table are averages of at least three separate experiments. The yields were calculated from glpc data on the basis of starting materials consumed. c) The isomer distributions are as follows: 254 nm, *o*-: *m*-: *p*- =34.8: 5.3: 59.8, 254 nm with cyclohexene, *o*-: *m*-: *p*- =41.4: 11.7: 46.8, 265 nm, *o*-: *m*-: *p*- = 58.4: 7.1: 34.3, 265 nm with cyclohexene, *o*-: *m*-: *p*- =31.7: 4.0: 64.1. d) Ethyl salicylate was taken as an *ortho*-isomer. e) The values in parentheses are the yields on the basis of starting material. f) The yield based on starting material used.

sis was not made, *N*-methylaniline was detected by gas chromatography, but no biphenyl derivatives were detected.

Photoreaction of Anisole. For anisole, the ratio of the photoproducts also changed with the wavelength of the irradiating light; irradiation with 254 nm light gave *p*-chloroanisole and ethyl methoxybenzoates (*o*-: *m*-: *p*-=34.8: 5.3: 59.8) as the main products, whereas irradiation with 265 nm light gave ethyl methoxybenzoates and ethyl salicylate (*o*-: *m*-: *p*-=58.4: 7.1: 34.3, ethyl salicylate was considered as an *ortho*-substituted product) as the main products. The yield of *p*-chloroanisole on irradiation with 265 nm light was nearly one third of that on irradiation with 254 nm light. Cyclohexene was observed to have a marked effect on product formation as in the case of dimethylaniline. The addition of cyclohexene diminished the yields of ethyl methoxybenzoates and *p*-chloroanisole upon irradiation with 265 nm light, whereas the ethoxycarbonylation with 254 nm light was retarded to a lesser extent. In general, the *o*/*p* ratio of the isomers in the free radical substitution of anisole is greater than 1.[10] The *o*/*p* ratio on irradiation with 265 nm light was 1.71 and the addition of cyclohexene lowered the *o*/*p* ratio to 0.50. This indicates that the photoethoxycarbonylation with 265 nm light proceeds mainly *via* a free radical mechanism. On the other hand, the *o*/*p* ratio on irradiation with 254 nm light is less than 1 and the value was affected by cyclohexene to a lesser extent. These results indicate that on irradiation with 254 nm light the ethoxycarbonylated products are not formed *via* free radical attack on anisole but are probably formed by the combination of radical cations of anisole and trichloromethyl radicals produced by the excitation of the charge transfer complex in the solvent cage. This was considered to be the case for dimethylaniline irradiated with 313 nm light which excites mainly charge transfer complexes.

The formation of *p*-chloroanisole on irradiation with 254 nm light can be explained by the attack on anisole by a chlorine atom which is produced either by sensitized decomposition[11] of carbon tetrachloride or by electron transfer between a cation radical and a chloride anion.[12] The possible reaction mechanisms of the

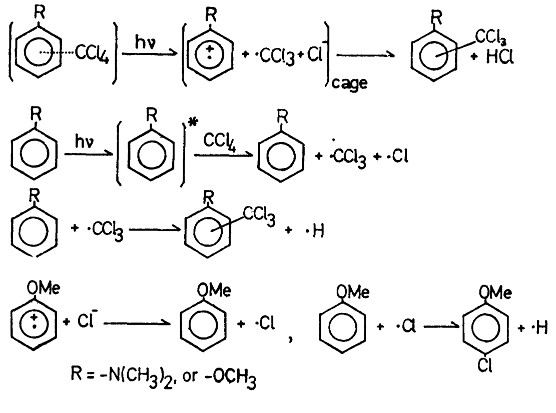
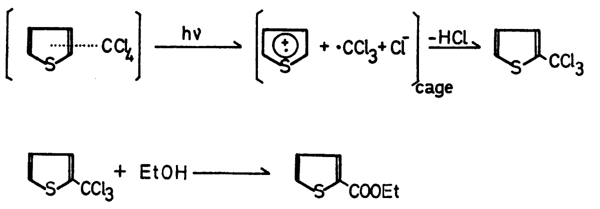


photo-ethoxycarbonylation of dimethylaniline and anisole are shown in the following schemes.

Photoreaction of Thiophene. Thiophene undergoes a similar photo-ethoxycarbonylation upon irradiation with 254 nm light giving ethyl 2-thiophenecarboxylate. In this case, the substitution at the 2-position occurred selectively and no chlorothiophene was detectable. Polymeric substances were also obtained. The addition of cyclohexene did not reduce the yield of ethyl 2-thiophenecarboxylate. The UV-spectrum of thiophene and carbon tetrachloride in ethanol solution showed a slight enhancement of absorption near 254 nm. These results and the effect of cyclohexene on the photoproduct suggest that the trichloromethyl radicals which are formed by the dissociation of the charge transfer complex between thiophene and carbon tetrachloride attack the radical cation of thiophene in the solvent cage.

An attempt to isolate the intermediate trichloromethylthiophene was unsuccessful, but when thiophene was irradiated in carbon tetrachloride and ethanol was then added to the reaction mixture after the irradiation, ethyl 2-thiophenecarboxylate was detected by gas chromatography. As reported,[13] the trichloromethyl group is solvolyzed rapidly during UV-irradiation. The isolation of trichloromethylated compounds may thus be quite difficult. The possible reaction processes for the photo-ethoxycarbonylation of thiophene is shown in the following schemes.



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