CHEMISTRY LETTERS, pp. 149-152, 1974. Published by the Chemical Society of Japan

THE PHOTO-INDUCED ALCOHOLYSIS OF BENZOTRICHLORIDE

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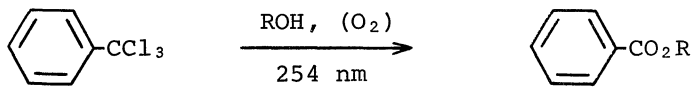
Benzotrichloride undergoes a photochemical solvolysis reaction in alcohol forming alkyl benzoate. The reaction is greatly accelerated in the presence of oxygen. It is suspected the involvement of the normally forbidden $S_0 \rightarrow T_1$ transition in the course of the reaction.

Photo-induced solvolysis, which was first reported by Havinga, De Jongh and Dorst,[1] is an interesting and important branch of photochemistry. Recently the photochemical hydrolysis of monosubstituted benzotrifluorides[2] and trifluoromethyl naphthols[3] has been reported. We wish now to report that benzotrichloride also undergoes the photochemical alcoholysis forming alkyl benzoate, especially in the presence of oxygen. As exemplified in Table I, this photolysis is applicable to a wide variety of alcohols[4] including tert-butyl alcohol, which is unreactive toward the thermal alcoholysis of benzotrihalides in concentrated sulfuric acid.[5] The general execution of the present alcoholysis is illustrated for the conversion of benzotrichloride to ethyl benzoate. An aerated or oxygenated solution of benzotrichloride (1) (1.0 mmol) in ethanol (40 ml) was irradiated with a 16 watt low-pressure mercury lamp through a water cooled quartz probe. After irradiation



(1) (2)

Table I. Photo-induced alcoholysis of benzotrichloride in the presence of oxygen[a]

Alcohol[b]	Ester[c] Ph-CO_2R	Yield, %[d]
Methyl alcohol[e]	R = Methyl	58
Ethyl alcohol[e]	R = Ethyl	52
n-Propyl alcohol	R = n-Propyl	19
iso-Propyl alcohol	R = iso-Propyl	24
n-Butyl alcohol	R = n-Butyl	37
iso-Butyl alcohol	R = iso-Butyl	33
sec-Butyl alcohol	R = sec-Butyl	42
tert-Butyl alcohol	R = tert-Butyl	10
Cyclohexyl alcohol	R = Cyclohexyl	10

[a] All irradiations were carried out in a quartz tube at 25 °C for 18 hr. [b] Unless otherwise stated, non-degassed mixtures of alcohol and ethyl acetate (1:3 v/v) were used. [c] The remainder consisted mainly of the starting material. [d] Determined by glpc. [e] Absolute alcohol was used as solvent.

for 18 hr ethyl benzoate (2) was obtained in 52% yield. The identity of 2 was confirmed by comparison with an authentic specimen.[6] But when a carefully degassed solution of 1 in ethanol was irradiated, the solvolysis of 1 was greatly suppressed and 2 was obtained in only 10% yield. The remainder of the reaction mixture mainly consisted of unreacted starting material.[7] When the irradiation was carried out in 0.03 mol/l ethanolic sodium hydroxide in the presence of oxygen for 3 hr, 2 was obtained in 45% yield, whilst a nonalkaline solution afforded 27% of 2 in 3 hr.

The photo-induced alcoholysis reaction described above possesses the following three characteristics: (1) the formation of 2 from 1 is proportional to the concentration of ethanol, and a mixture of ethanol and ethyl acetate (1:3 v/v) can be used instead of absolute ethanol; (2) the photoreaction can be sensitized by acetone or triphenylene in the degassed solution by a factor of at least three; (3) the addition of a radical scavenger such as cyclohexene

or hydroquinone has no effect on the reaction.

In connection with the acceleration of the reaction by oxygen, we have examined the uv absorption spectra of benzotrichloride in the presence and the absence of oxygen. Oxygen-saturated benzotrichloride shows a contact charge transfer spectrum[8] with oxygen in uv region (<360 nm), which disappears on degassing (Fig I). This suggests the involvement of the normally forbidden $S_0 \rightarrow T_1$ transition due to the benzotrichloride-oxygen charge transfer complex.[9] Hence, it is possible to excite benzotrichloride to triplet state directly.

Careful examination by glpc revealed that ethyl chloride and intermediary benzoyl chloride was produced during the reaction of 1 both in the presence and the absence of oxygen. No trace of diethyl ether could be detected in this reaction. From these observations, the formation of alkyl benzoate is rationalized in terms of nucleophilic attack of alcohol onto the excited trichloromethyl carbon (triplet state)[10] followed by the thermal alcoholysis of intermediary benzoyl chloride (Scheme I).

An analogous reaction occurred in the irradiation of benzal chloride in ethanol for 3 hr, the major product being benzaldehyde in 14% yield. The irradiation of benzyl chloride gave benzyl ethyl ether in 8% yield under similar conditions. But no reactions were observed when benzotrifluoride was used as substrate. The reactivity toward the alcoholysis reaction seems to be in accordance with the order of electrophilicity of the benzylic carbon.

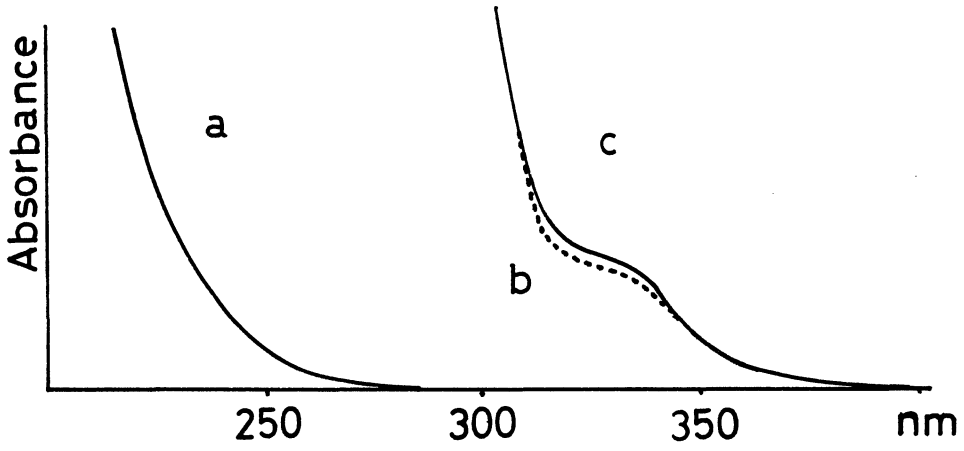
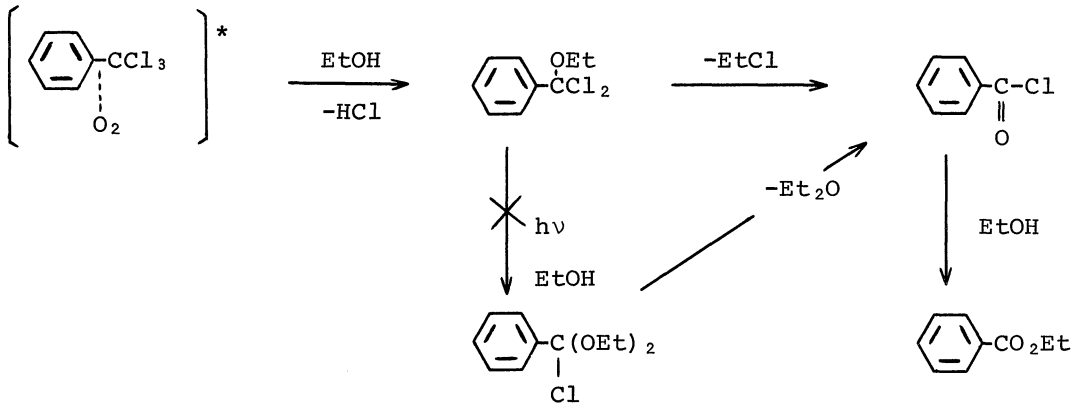


Fig I. Absorption bands induced by saturation with oxygen.
a) ethanol saturated with oxygen; b) benzotrichloride saturated with nitrogen; c) benzotrichloride saturated with oxygen.

Scheme I



NOTES AND REFERENCES

1) E. Havinga, R. O. de Jongh, and W. Dorst, Rec. Trav. Chim., 75, 378 (1956).

2) R. Grinter, E. Heilbronner, T. Petrzilka, and P. Seiler, Tetrahedron Lett., 3845 (1968).

3) P. Seiler and J. Wirz, ibid., 1683 (1971).

4) Irradiation of 1 in a mixture of water and tetrahydrofuran (1:1 v/v) afforded benzoic acid in 30% yield.

5) C. M. Le Fave and P. G. Scheurer, J. Amer. Chem. Soc., 72, 2464 (1950).

6) S. R. Sandler and W. Karo, "Organic Functional Group Preparations", Vol. 1, Academic Press, New York, N. Y., 1968, p. 245.

7) For the other photochemical reactions of benzotrichloride, see R. D. Giles and E. Whittle, Trans. Faraday Soc., 62, 128 (1966); N. Mitsuo, T. Kunieda, and T. Takizawa, J. Org. Chem., 38, 2255 (1973).

8) H. Tsubomura and R. S. Mulliken, J. Amer. Chem. Soc., 82, 5966 (1960): H. Ishida, H. Takahashi, H. Sato, and H. Tsubomura, ibid., 92, 275 (1970).

9) From the result obtained in the degassed solution, the acceleration of an intersystem crossing $S_1 \rightarrow T_1$ by oxygen can be considered as well.

10) Photochemical hydrolysis of trifluoromethyl group stated in the reference 2 and 3, proceed via singlet states and alcohols are ineffective toward the reaction.

(Received October 30, 1973)