Photo-induced Benzoylation of Anthracene

By Takashi Tamaki
(*Research Institute for Polymers and Textiles, Sawatari 4, Kanagawa-ku, Yokohama 221, Japan*)

Summary The photoreaction of anthracene with benzoyl, *p*-toluoyl, and *p*-anisoyl chlorides give the corresponding 2- and 9-aroylanthracenes.

PHOTO-INDUCED Friedel–Crafts reactions, which include both alkylation and acylation, have been reported.[1–3] The isomer distribution in the methoxyphenylacetamide obtained from the photoreaction of anisole and chloroacetamide suggested a homolytic mechanism,[1] whereas an ionic mechanism was proposed for the benzene–trifluoroacetic acid system.[3] This communication describes the photo-induced aroylation of anthracene (I) with benzoyl (IIa), *p*-toluoyl (IIb), and *p*-anisoyl (IIc) chlorides, and the quenching of anthracene fluorescence by these aroyl chlorides. The order of quenching rate constants suggests charge transfer from the excited molecule to the quencher.

TABLE. Quenching of anthracene singlet state by aroyl chlorides in benzene.

Aroyl chloride	Florescence quenching $k_q\,\tau^a$/l mol^{-1}	k_q l mol^{-1} s^{-1}	Benzoylation $k_q\,\tau$/l mol^{-1}
Benzoyl chloride ..	39	$7{\cdot}9 \times 10^9$	35
p-Toluoyl chloride ..	31	$6{\cdot}3 \times 10^9$	25
p-Anisoyl chloride ..	18	$3{\cdot}7 \times 10^9$	11

[a] τ for anthracene is 4·9 ns (S.L. Murov, 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973, p. 3.)

A benzene solution of (I) (0·01 M) and an aroyl chloride (0·15 M) was exposed to a mercury (3650 Å) lamp which caused photoexcitation of only the former. The major products were identified as 2- and 9-aroylanthracene isomers: 2-benzoylanthracene, 19% (relative to consumed anthracene), m.p. 169—171 °C (lit.[4] 175 °C), yellow needles (MeOH), green coloration in EtOH, purple with H_2SO_4, ν_{max} 1660 cm^{-1} (C=O), τ 1·55 (2H, m, Ar) and 1·6—2·75 (12H, m, Ar); 9-benzoylanthracene, 47%, m.p. 145—146 °C (lit.[5] 148 °C), yellow prisms (MeOH), Prussian blue coloration with H_2SO_4, ν_{max} 1665 cm^{-1} (C=O), τ 1·52 (1H, s, Ar) and 1·9—2·85 (13H, m, Ar); 2-(*p*-toluoyl)anthracene, 23%, m.p. 183—185 °C, yellow needles (MeOH), green coloration in EtOH, purple with H_2SO_4, ν_{max} 2910s (Me) and 1662s (C=O) cm^{-1}, τ 1·58 (2H, m, Ar), 1·7—2·8 (11H, m, Ar), and 7·63 (3H, s, Me); 9-(*p*-toluoyl)anthracene, 53%, m.p. 125—126 °C, yellow prisms (MeOH), Prussian blue coloration with H_2SO_4, ν_{max} 2990s (Me) and 1663s (C=O) cm^{-1}, τ 1·48 (1H, s, Ar), 1·8—3·1 (12H, m, Ar), and 7·12 (3H, s, Me); 2-(*p*-anisoyl)anthracene, 29%, m.p. 189—190 °C, yellow needles (MeOH), green coloration in EtOH, red with H_2SO_4, ν_{max} 2840s (OMe) and 1645s (C=O) cm^{-1}, τ 1·5 (2H, m, Ar), 1·55—3·07 (11H, m, Ar), and 6·1 (3H, s, OMe); and 9-(*p*-anisoyl)anthracene, 30%, m.p. 185—186 °C, yellow prisms (MeOH), purple coloration with H_2SO_4, ν_{max} 2830s (OMe) and 1660s (C=O) cm^{-1}, τ1·5 (1H, s, Ar), 1·9—3·25 (12H, m, Ar), and 6·25 (3H, s, OMe).

The aroyl chlorides (IIa—c) were found to quench the anthracene fluorescence according to linear Stern–Volmer relationships. As shown in the Table, the quenching rate constant, k_q, decreases with increasing electron donating ability of the *para*-substituent on the benzoyl chromophore, *i.e.* $k_q = 7{\cdot}9 \times 10^9$ for (IIa), $6{\cdot}3 \times 10^9$ for (IIb), and $3{\cdot}7 \times 10^9$ l mol^{-1} s^{-1} for (IIc). The results suggest the formation of charge transfer complex (exciplex) between the aromatic molecule in the singlet excited state and the aroyl system in the ground state, though no exciplex emission could be detected. Similar mechanisms have been proposed for quenching of molecular pairs such as naphthalene and benzoic acid[6] and 1,4-dimethoxybenzene and benzyl chloride.[7] It is possible that the photoreaction would provide a ready pathway for the deactivation of a singlet exciplex. A related mechanism was proposed for the benzene–trifluoroacetic acid system, in which charge transfer from S_1 benzene to the acid, followed by the transformation to the zwitterionic intermediate, was involved.[3]

Evidence for the singlet mechanism was obtained from kinetic studies on the quantum yield of aroylation. Increasing the concentration of aroyl chlorides (IIa—c) increased the quantum yield of anthracene consumption ascribed to aroylation by up to 0·1. A linear relationship was observed between the reciprocals of quantum yield and aroyl chloride concentration. The quenching constants as calculated from the data are listed in the Table. These values agree well with those for the fluorescence quenching.

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