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Photo-acylamination on Anthracene with Use of Acyl Azides

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Synopsis. Irradiation of anthracene in the presence of acyl azide gives isocyanate and 9-acylaminoanthracene. The photolysis of aromatic hydrocarbon-acyl azide was followed by UV spectrophotometry and analyzed by the EDQ (quotients of extinction differences) diagram method.

Although direct photolysis of acyl azide has been extensively investigated,[1] its sensitized decomposition is scarcely known. In relation to the photolysis of acyl azide–zinc porphyrin system,[2] studies have been extended to the interaction of excited aromatic hydrocarbons with the ground state of acyl azides. In this paper a report is given on the decomposition of benzoyl azides sensitized by anthracene affording isocyanates and 9-acylaminoanthracenes. This seems to be the first example of sensitized photo-Curtius rearrangement;[3] benzophenon-sensitization has been reported to involve the free radical chain reaction initiated by benzophenone triplet which affords no isocyanate.[4]

A solution of anthracene (**1**) and excess benzoyl azide (**2a**) was irradiated in dichloromethane under nitrogen with light of >320 nm absorbed specifically by the hydrocarbon. The IR spectral change indicated the formation of phenyl isocyanate accompanied by the disappearance of **2a**. TLC revealed the formation of a non-fluorescent product. The pale yellow crystals of mp 250—251 °C were separated by means of column chromatography. The IR bands at 3250 and 1648 cm^{-1} are assignable to the amide band. The structure of the product was unequivocally confirmed by identification with 9-benzoylaminoanthracene (**3a**). In a similar way, 9-(*p*-chlorobenzoylamino)- (**3b**) and 9-(*p*-cyanobenzoylamino)anthracene (**3c**) were obtained. The formation of the corresponding isocyanates was confirmed by the presence of the characteristic IR band. The results are summarized in Tables 1 and 2.

TABLE 1. 9-ACYLAMINOANTHRACENES (**3**)

Acyl	Mp (°C)	Yield (%)	Elementary analyses					
			Found			Calcd		
			C	H	N	C	H	N
C_6H_5	250—251	37	84.34	4.83	4.69	84.81	5.09	4.72
p-ClC_6H_4	266—268	30	75.82	4.18	4.34	76.02	4.25	4.23
p-CNC_6H_4	297—300	20	81.21	4.32	8.50	81.99	4.38	8.70

TABLE 2. ULTRAVIOLET AND INFRARED SPECTRA OF 9-ACYLAMINOANTHRACENES

Acyl	λ_{max} nm ($\times 10^{-3}$)$^{a)}$	$\tilde{\nu}_{max}$ cm^{-1} $^{b)}$
C_6H_5	258 (117), 335 (3.04), 350 (5.91), 367 (8.50), 386 (7.74).	3250, 1648
p-ClC_6H_4	258.5 (124), 335 (3.10), 351 (5.94), 368 (8.05), 387 (7.68).	3250, 1648
p-CNC_6H_4	258.5 (103), 335 (3.01), 351 (5.54), 368 (8.05), 387 (7.68).	3250, 2225, 1646

a) In chloroform. b) In KBr.

In order to extend the sensitization to the other aromatics, the photolysis of aromatic hydrocarbon–benzoyl azide was followed UV-spectrophotometrically and analyzed by the ED (extinction differences)- and EDQ (quotients of extinction differences)-diagram methods.[5] As shown in Fig. 1-a, the family of absorption curves of **1**–**2a** system irradiated with light of wavelength >320 nm intersect at the early stage of photolysis, the absorption spectrum of the photoproduct being almost the same as that of **3a**. Linearity was observed in the EDQ-diagram, but not in the ED-diagram. This implies that the photolysis contains two successive reactions: the formation and subsequent slower disappearance of **3a**. It was confirmed that the irradiation of **3a** in the presence of **2a** causes the disappearance of **3a** and that the rate of photolysis of the **3a**–**2a** system is much slower than that of the **1**–**2a** system. The

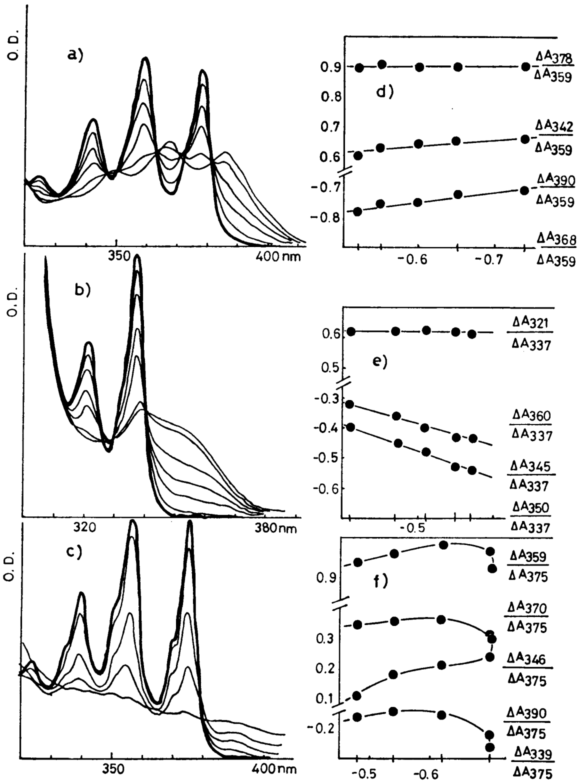


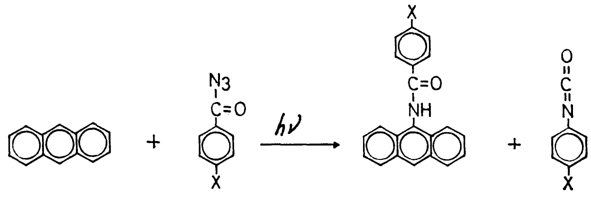
Fig. 1. The electronic absorption spectra recorded at intervals for the UV irradiation of aromatic hydrocarbon-acyl azide system ((a): anthracene-benzoyl azide in toluene, (b): pyrene-benzoyl azide in toluene, (c): anthracene-*p*-toluenesulfonyl azide in methylcyclohexane) and the corresponding EDQ diagrams ((d)—(f)).

spectral change of **3a**–**2a** shows a linear ED-diagram, in line with the linearity of EDQ-diagram for the photolysis of **1**–**2a**.

When a solution containing pyrene and **2a** was irradiated with light of wavelength >320 nm, the peaks due to the hydrocarbon decreased in intensity along with the increase of peaks at 338 nm (Fig. 1-b). The EDQ-diagram was linear in this case (Fig. 1-e). Although the photoproducts are yet to be isolated because of the difficulty of product separation, the appearance of the absorption maxima at greater wavelengths suggests that the photo-induced acylamination may take place on pyrene nucleus as in the case of **1**.

In the cases of 9,10-dimethyl- and 9,10-diphenylanthracene, the absorption peaks decreased on UV irradiation. No new absorption maximum was observed, while the linear EDQ-diagram was obtained.

It was found that anthracene is photolysed in the presence of *p*-toluenesulfonyl azide (**4**). The spectral change during the course of irradiation, however, differs from that of the **1**–**2a** system (Fig. 1–c). A weak absorption maximum appeared at *ca.* 390 nm at an early stage of photolysis and disappeared completely on prolonged irradiation. The absorption may be due to 9-(*p*-tolylsulfonylamino)anthracene (**5**) having $\lambda_{\max}$ at 337.5, 354, 371, and 391.5 nm. In contrast to the **1**–**2a** system, linear EDQ-diagram was no longer observed in this case (Fig. 1-f), indicating the involvement of more than three elementary photoreactions. 9-Sulfonylaminoanthracene (**5**) was found to be photolysed in the presence of acyl azide including **4**, the EDQ-diagram for the photolysis being non-linear, which demonstrates the difference in photolytic behavior between **3a** and **5**. The photolysis rate of **5** was found to be *ca.* 15 times greater than that of **3a** when benzoyl azide coexists. The difference in the mode of spectral change between **1**–**2a** and **1**–**4** systems reflects the difference in the photoreactivity of the products initially formed, *i.e.*, **3** and possibly **5**. As for the effect of acylamino group on the photoreactivity of anthracene nucleus toward acyl azide, it should be mentioned that 9-acylaminoanthracenes are non-fluorescent whilst 9-sulfonylamino derivative (**5**) gives the blue fluorescence. This implies that the introduction of the acylamino group to anthracene shortens the singlet lifetime so that the photoreactivity may be reduced, whereas the sulfonylamino group shows no remarkable influence on the fluorescence behavior and the photoreactivity of anthracene nucleus.



1 *2* *3*

The photoinduced acylamination on anthracene using acyl azide appears to closely resemble that of zinc octaethylporphin.²⁾ A distinct difference between both reactions should be stressed: the photolysis of acyl azide-zinc porphyrin affords no isocyanate. This suggests that the sensitization mechanism is quite different from each other.

Experimental

All melting points were not corrected. Ultraviolet and infrared spectra were recorded on a Hitachi type 323 spectrophotometer and a Hitachi EPI-3G spectrophotometer, respectively.

Photolysis of Anthracene in the Presence of Benzoyl Azide. A solution of anthracene (180 mg) and benzoyl azide (1.42 g) in dichloromethane (20 ml) was irradiated under nitrogen gas with a 450 W high pressure mercury arc passed through a Corning 0-54 filter (>320 nm). The photolysis was followed by TLC and IR- and UV-spectrophotometry. The IR band assignable to phenyl isocyanate appeared in proportion to the disappearance of anthracene. After removal of the solvent, the residue was dissolved in dichloromethane and chromatographed on a silica gel column with use of dichloromethane as an eluent. After eluting the fluorescent fraction of anthracene, a pale yellow fraction was collected and evaporated to dryness. The residue was recrystallized from acetonitrile to give 67.4 mg yellow needles of 250—251 °C which was identified with 9-benzoylaminoanthracene by the mixture melting point and IR spectra. The amount of recovered anthracene was estimated to be 72.4 mg with the aid of UV spectroscopy. The yield of 9-benzoylaminoanthracene was therefore 37% based on consumed anthracene.

In a similar way, 9-(*p*-chlorobenzoylamino)- and 9-(*p*-cyanobenzoylamino)anthracene were obtained, starting from *p*-chlorobenzoyl azide and *p*-cyanobenzoyl azide, respectively. The results are summarized in Tables 1 and 2.

*EDQ-Diagram Examination of Photolysis.*⁵⁾ A three ml solution of anthracene (*ca.* 10^{-5} M/l) and benzoyl azide (*ca.* 10^{-2} M/l) in toluene was irradiated with light of wavelength >320 nm, and the UV spectra were recorded at intervals. The final spectrum was essentially the same as that of 9-benzoylaminoanthracene, the yield being estimated to be 56% (Fig. 1-a).

Similarly, the photolysis of the following combinations were determined by the EDQ-diagrams; pyrene-benzoyl azide in toluene, anthracene-*p*-toluenesulfonyl azide in methyl-cyclohexane, 9,10-dimethylanthracene-benzoyl azide in toluene, and 9,10-diphenylanthracene-benzoyl azide in toluene. Typical examples are shown in Fig. 1.

References

1) a) G. L'abbe, *Chem. Rev.*, **68**, 345 (1968); b) G. R. Felt and W. Lwowski, *J. Org. Chem.*, **41**, 96 (1976), and references cited therein.

2) K. Ichimura, *Chem. Lett.*, **1976**, 641.

3) Horner and coworkers have described the slow evolution of nitrogen gas on irradiation of a solution of naphthalene or triphenylene in the presence of benzoyl azide,⁴ᵃ⁾ but no product was characterized.

4) a) L. Horner, G. Bauer, and J. Doerges, *Chem. Ber.*, **98**, 2631 (1965); b) M. Sukigara, Y. Ito, K. Honda, and S. Kikuchi, *Nippon Shashin Gakukaishi*, **35**, 94 (1972).

5) G. Quinkert, *Angew. Chem.*, **84**, 1157 (1972).