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PHOTOCHEMICAL REACTION OF N-METHYLPHENANTHRENE-9,10-DICARBOXIMIDE WITH SECONDARY AMINES. AMINOLYSIS FROM N-H ABSTRACTION

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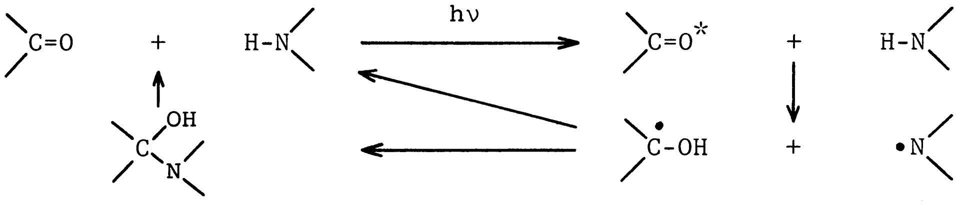
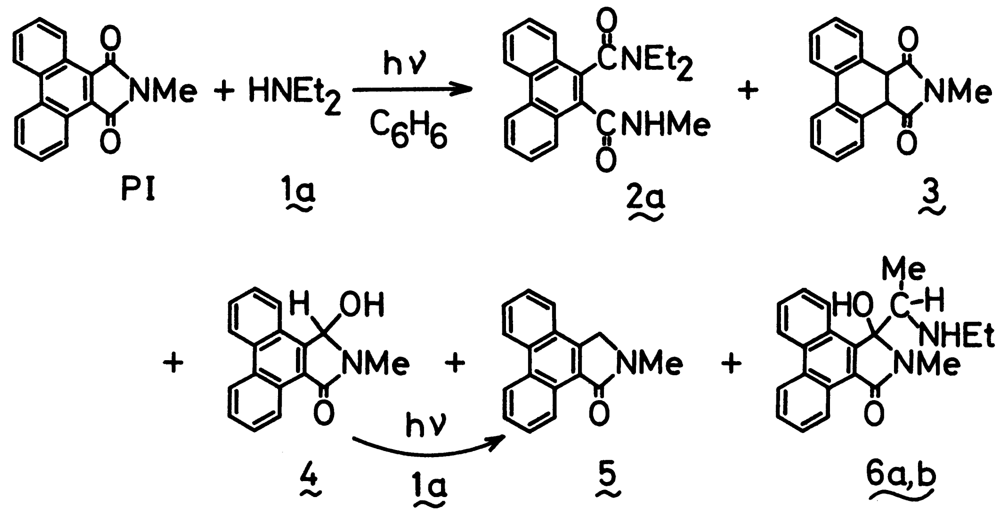
Photolysis of N-methylphenanthrene-9,10-dicarboximide (PI) with diethylamine (1a) in benzene gave an aminolysis product together with reduction-products and other coupling products. Effects of addition of 1-propanethiol and concentration of 1a indicate that the aminolysis appears to arise from N-H abstraction mainly by excited triplet state of PI.

The interaction of electronically excited organic molecules with amines has provided much of the basis for understanding of exciplex and radical ion pair phenomena.[1)] The results of interaction with aliphatic secondary amines are: (a) hydrogen abstraction to give an aminyl (N-H abstraction) or α-aminoalkyl radical intermediate (C-H abstraction),[2)] and (b) adduct formation from the aminyl radical.[3)] In the reaction with carbonyl compounds the N-H abstraction process has been known only to regenerate the starting materials directly from the adduct of ketyl and aminyl radicals or via disproportionation of the two radicals (Scheme 1).[4)] However, we hypothesize that if formation of the ketyl radical is associated with alteration of the nature of neighboring chemical bond, the N-H abstraction process would result in some reaction products other than regeneration to the starting materials. Here we wish to report the first example of this hypothesis, which is photo-aminolysis of N-methylphenanthrene-9,10-dicarboximide (PI) with aliphatic secondary amines.



Scheme 1.

The photo-reaction of PI and diethylamine (1a) in N_2-purged benzene gave aminolysis product (2a), C=C reduction product (3), C=O reduction product (4), 2-methyl-1H-dibenzo[e,g]isoindol-3(2H)-one (5), and a diastereomeric pair of coupling products of ketyl and α-aminoalkyl radicals (6a,b) (Eq. 1). The structures of 2a, 5, and 6a,b were characterized by elemental analyses and their spectroscopic properties.[5)] The structure of unsymmetric diamide (2a) was further supported by the observation that 2a alone gave PI by heating at 120 °C. The possibility that 2a was produced by thermal reaction of PI with 1a was excluded by a control experiment: reflux of a benzene solution containing PI and a large excess of 1a in



(1)

dark resulted in quantitative recovery of PI. The ^{1}H-NMR and IR spectra of 3 and 4 were identical with those of the samples synthesized separately: 3 was prepared by the reaction of 9,10-dihydrophenanthrene-9,10-dicarboxylic anhydride$^{6)}$ and methylamine, and 4 by reduction of PI with sodium borohydride.$^{7)}$ It was confirmed that 5 is a secondary photo-product of 4, since irradiation of 4 and 1a in benzene gives rise to 5 quantitatively, possibly by the photochemical electron transfer reduction. Other products were photostable even under prolonged irradiation.

The yields of the photo-products depended largely on the concentration of the amine (1a) as shown in Fig. 1. In the figure the sum of the yields of 4 and 5 together with those of 2a, 3, and 6a,b are plotted against concentration of 1a. With decreasing the concentration of 1a the yields of 2a increase markedly but those of 4+5 increase slightly and those of 3 and 6a,b decrease.

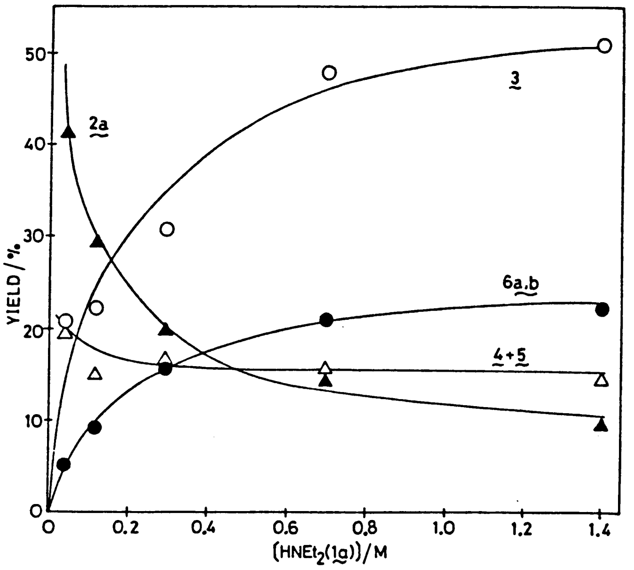
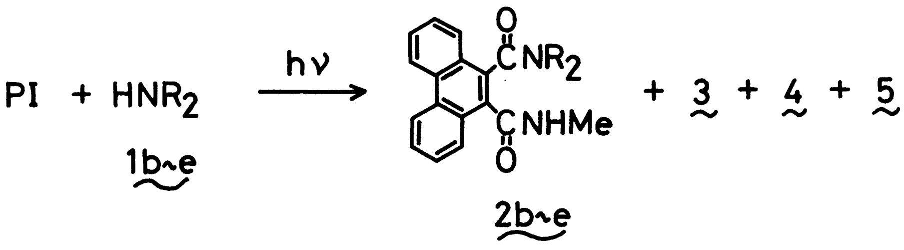


Fig. 1. Effect of concentration of 1a on the yields of products in the photoreaction of PI (7.7 mM, 1 mM =1X10^{-3} mol dm^{-3}) and 1a in benzene. The yields were based on consumed PI (conversion: >80%).

This concentration effects can be related to the multiplicity in the excited states of PI. The triplet excited state ($\pi\pi^*$, E_T= 218 kJ mol^{-1}) of PI can possess a longer lifetime relative to the singlet excited state ($\pi\pi^*$, E_S= 309 kJ mol^{-1}).$^{8)}$ Then, reactions due to the excited triplet state of PI would predominate at a lower concentration of the amine. Thus, the aminolysis which predominates at a lower concentration of amine may arise from the excited triplet state of PI at

Table 1. Yields of Products from PI and Secondary Amines (1b-e) in Benzene



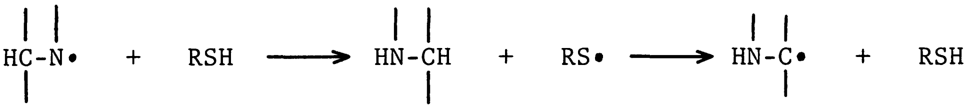
R	1	[1] mM	Yield$^{a)}$ /% 2		3	4+5
$CH_3CH_2CH_2CH_2$	1b	63	2b	29	15	<7
$(CH_3)_2CHCH_2$	1c	66	2c	46	10	<3
$CH_3CH_2CH_2$	1d	81	2d	53	14	<8
$(CH_3)_2CH$	1e	40	2e	0	61	—
$(CH_3)_2CH$	1e	795	2e	0	78	—

a) Yields were based on consumed PI.

least for the most part.

The results of the photo-reaction of PI with other aliphatic secondary amines are shown in Table 1. Predominant formation of unsymmetric diamides (2b-d) was generally observed in the photolyses at a low amine concentration. In case of using α-branched diisopropylamine (1e), however, the C=C reduction was an exclusive reaction.

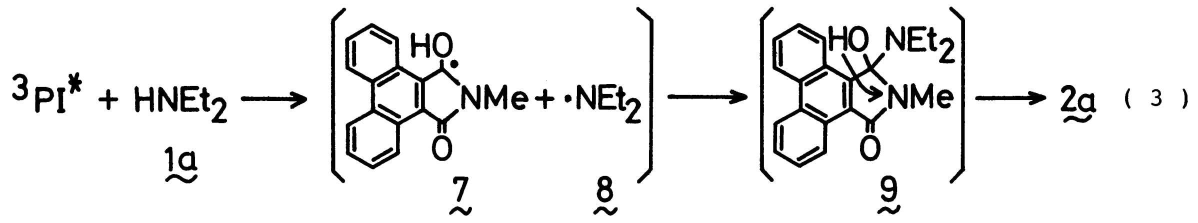
Aliphatic thiols are known to catalytically convert alkylaminyl radicals to α-aminoalkyl radicals according to Eq. 2.[4a)]



$$\text{HC-N}\bullet + \text{RSH} \longrightarrow \text{HN-CH} + \text{RS}\bullet \longrightarrow \text{HN-C}\bullet + \text{RSH} \quad (2)$$

Thus, when the aminyl radical is involved as an intermediate in the aminolysis reaction, addition of a thiol would inhibit the reaction. After confirmed that no reaction was observed in the photolysis of PI in benzene in the presence of 1-propanethiol, photolysis of a benzene solution containing PI (9.6 mM), 1a (358 mM), and 1-propanethiol (148 mM) was undertaken. The products were 2a (<8%), 3 (45%), 4+5 (29%), and 6a,b (14%). This result is a significant contrast to that obtained in the absence of the thiol: 2a (20%), 3 (35%), 4+5 (7%), and 6a,b (23%). Hence, an aminyl radical intermediate appears to be involved at least in the aminolysis to form 2a.

A plausible reaction mechanism postulated from above experiments concerning the formation of 2a is shown in Eq. 3. The ππ* triplet state of PI abstracts hydrogen from N of diethylamine (1a), followed by formation of the radical pair (7 and 8), adduct formation (9), and then intramolecular 1,3-hydrogen transfer within



(3)

9 affords the stable product (2a). Similar intramolecular hydrogen transfer reactions are familiar in the photo-hydrogen abstraction of imides.[9] In addition, stability of the final product (2a) seems to facilitate the intramolecular hydrogen transfer stage.

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5) 2a: ^{13}C NMR (CDCl$_3$, 400 MHz) δ 12.7 (q), 13.6 (q), 26.4 (q), 39.0 (t), 43.7 (t), 122.4-130.7 (Arom 13C), 168.1 (s, amide), 168.9 (s, amide); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.86 (t, 3H), 1.27 (t, 3H), 2.96 (d, 3H, NHMe), 3.00-3.08 (m, 1H), 3.17-3.22 (m, 1H), 3.32-3.38 (m, 1H), 3.83-3.89 (m, 1H), 6.90 (br s, 1H, NH), 7.53-7.63 (m, 4H), 7.72 (d, 1H), 8.01 (d, 1H), 8.56 (t, 1H); IR (KBr) 3250 (NH), 1645, 1615 (amide), 1455, 1278, 762, 725 cm^{-1}.
   5: ^{1}H NMR (CDCl$_3$, 100 MHz) δ 3.26 (s, 3H, NMe), 4.59 (s, 2H, CH$_2$), 7.1-7.2 (m, 1H), 7.5-8.0 (m, 4H), 8.6-8.8 (m, 2H), 9.3-9.6 (m, 1H); IR (KBr) 1675 (amide), 1450, 750, 720 cm^{-1}.
   6a,b: ^{1}H NMR (CDCl$_3$, 100 MHz) δ 0.62 (d, 3H, CHMe-isomer a), 0.82 (t, 3H, CH$_2$Me-isomer b), 1.08 (t, 3H, CH$_2$Me-a), 1.21 (d, 3H, CHMe-b), 1.60 (br s, NH), 2.1-3.1 (m), 2.94 (s, NMe-a,b), 3.64 (q, 1H, CHMe-a), 4.56 (br s, 1H, OH-a), 4.63 (br s, 1H, OH-b), 7.2-8.1 (m, Arom H); IR (KBr, a+b) 3450 (OH), 1705 (amide), 1455, 1438, 747 cm^{-1}.
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