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PHOTOCHEMICAL DIRECT ALKYLAMINATION OF 1-BENZAMIDOANTHRAQUINONE

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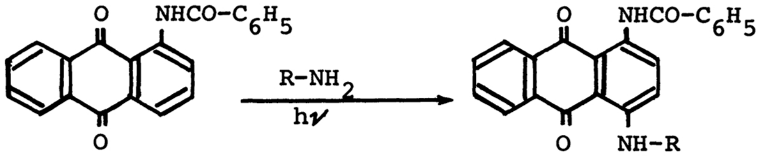
The photochemical reaction of 1-benzamidoanthraquinone with primary aliphatic amines in aerated benzene leads to the formation of 1-benzamido-4-(alkylamino)anthraquinones in 58-64% yields.

Recently, the photochemical substitution of anthraquinone derivatives have attracted considerable attention. Many reports have been written on the replacement of the methoxy,[1,2] halogeno,[3,4] and SO_3Na[5,6] groups, attached to the anthraquinone nucleus, by the amino groups or electronegative groups. The replacement of aromatic hydrogen of anthraquinone nucleus by nucleophiles has also been reported.[2,7]

We now report that 1-benzamidoanthraquinone(1) undergoes photochemical substitution with primary aliphatic amines to give 1-benzamido-4-(alkylamino)anthraquinones(2).



1

2

2a R= $n\text{-}C_4H_9$
b R= $s\text{-}C_4H_9$
c R= $n\text{-}C_8H_{17}$
d R= C_6H_{11} (cyclohexyl)
e R= $C_6H_5\text{-}CH_2$

For example, when an aerated benzene solution of 1 and n-butylamine was externally irradiated with a high-pressure mercury lamp, 1 was thoroughly consumed after 3.5h (Table 1, Run 1). The color of the solution turned from the initial pale yellow to a deep blue. After removal of the solvent, the residue was extracted with benzene and separated by column chromatography. A blue crystalline compound was obtained and identified as 1-benzamido-4-(butylamino)anthraquinone(2a) by comparison with the authentic sample; 2a: mp 216.5-217°C(from ethanol); UVmax(benzene) 575(ε 11100), 612nm (ε 9700); PMR($CDCl_3$) δ=0.99(3H, t), 1.62(4H, m), 3.31(2H, q), 7.07(1H, d J=10.0 Hz), 7.4-8.3(9H, m), 9.05(1H, d J=10.0 Hz), 10.24(1H, broad), 13.40(1H, broad); Found: C, 75.15; H, 5.47; N, 6.83%. Calcd for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03%.

The reaction proceeded equally well under air or oxygen, but was very slow under nitrogen. This suggests that dissolved oxygen plays an important role in the photo-amination. Similar photo-amination of 1 by other alkylamines such as s-butylamine, n-octylamine, cyclohexylamine and benzylamine was also observed and produced the corresponding 2. However, photo-amination of 1 with aqueous ammonia, aniline, and diethylamine was unsuccessful. These results suggest that both the basicity and the size of the amine significantly affected the reactivity. The results obtained from the photo-amination of 1 by alkylamines are summarized in Table 1. In the photo-amination, it was also found that acylation of amino group is essential, because 1-amino-, 2-amino-, and 1,5-diamino-anthraquinones could not undergo the similar photo-amination, but the corresponding acylamino-anthraquinones could undergo the similar photo-aminations by alkylamines.

Table 1. Photo-amination of 1-benzamidoanthraquinone(1) by alkylamines[a)]

Run	Amine	Atmosphere	Time/h	Product No	Product Yield/%
1	n-$C_4H_9NH_2$	air	3.5	2a	61
2	"	N_2	3.5	"	11
3	"	O_2	3.5	"	64
4	s-$C_4H_9NH_2$	air	5.5	2b	61
5	n-$C_8H_{17}NH_2$	air	3.5	2c	62
6	$C_6H_{11}NH_2$	air	7.0	2d	58
7	C_6H_5-CH_2NH_2	air	3.5	2e	58

a) A benzene solution of 1(7.5×10^{-4} mol/ l) and alkylamine(3.0×10^{-1} mol/ l) in a Pyrex tube was externally irradiated at 30°C with a 400 W high-pressure mercury lamp.

References

1) M. Ahmed, A. K. Davies, G. O. Phillips, and J. T. Richards, J. Chem. Soc., Perkin II, 1973, 1386.

2) J. Griffiths and C. Hawkins, J. Chem. Soc., Perkin I, 1974, 2383.

3) O. P. Studzinskii, O. P. Rtishchev, N. L. Rtishchev, and A. V. El'tsov, Zh. Org. Khim., 11, 1133 (1975).

4) H. Inoue, M. Hida, T. D. Tuong, and T. Murata, Bull. Chem. Soc. Jpn., 46, 1759 (1973); H. Inoue, K. Nakamura, S. Kato, and M. Hida, ibid., 48, 2872 (1975); H. Inoue and M. Hida, ibid., 51, 1793 (1978); H. Inoue, T. Shinoda, and M. Hida, ibid., 53, 154 (1980).

5) O. P. Studzinskii, A. V. El'tsov, and N. I. Rtishchev, Zh. Org. Khim., 7, 1272 (1971); N. I. Rtishchev, O. P. Studzinskii, and A. V. El'tsov, Zh. Org. Khim., 8, 349 and 774 (1972).

6) G. G. Wubbels, D. M. Tollefsen, R. S. Meredith, and L. A. Herwaldt, J. Amer. Chem. Soc., 95, 3820 (1973).

7) J. O. Morley, J. Chem. Soc., Chem. Comm., 1976, 88.

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