Selective Photoalkylamination and Photohydroxylation of Aminoanthraquinones and their *N*-Acylated Derivatives

Katsuhira Yoshida,* Masahiro Hikasa, Katsutoshi Ishii, Hisa Kadota, and Yoshio Yamashita

Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780, Japan

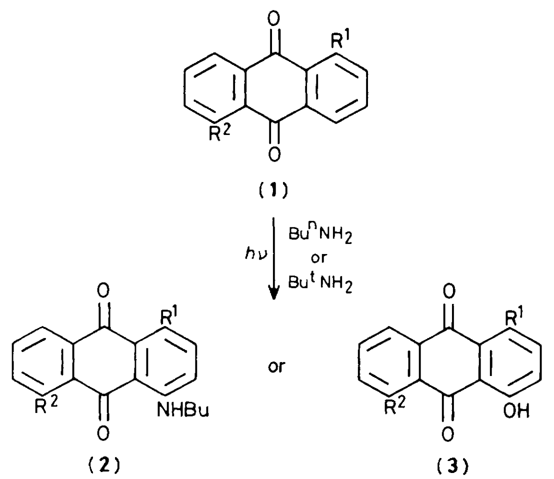
The selective introduction of hydroxy and alkylamino groups into the anthraquinone nucleus was achieved by the photochemical reaction of some aminoanthraquinones and their *N*-acylated derivatives with alkylamines under aerobic conditions.

Photochemical substitution of methoxy, halogeno, and sulpho groups, attached to the anthraquinone nucleus, by amines or other nucleophiles has been studied extensively. Recently, the direct introduction of amino[1] and hydroxy[2] groups into the anthraquinone nucleus has been found to occur in various photochemical reaction systems. We now report a convenient method to introduce hydroxy and alkylamino groups directly into the anthraquinone nucleus of some aminoanthraquinones

Table 1. Photochemical reaction of aminoanthraquinones (**1a**), (**1c**), and (**4a**) and their *N*-acylated derivatives (**1b**), (**1d**), and (**4b**) in the presence of alkylamines under various conditions.

Run	Substrate	Amine	Solvent[a]	Atmosphere	Time/h[b]	Product (yield,[c] %)	
1[d]	(**1a**)	Bu^nNH_2	B–E	Air	4.5	(**2a**) 0	(**3a**) 62
2[d]	(**1a**)	Bu^tNH_2	B–E	Bubbling O_2	4.5	(**2a**) 0	(**3a**) 79
3[e]	(**1b**)	Bu^nNH_2	B	Air	3.5	(**2b**) 61	(**3b**) 0
4[f]	(**1c**)	Bu^tNH_2	B–E	Air	0.3	(**2c**) 0	(**3c**) 65
5[d]	(**1d**)	Bu^nNH_2	B	Air	3.0	(**2d**) 71	(**3d**) 0
6[d]	(**4a**)	Bu^tNH_2	B	Bubbling O_2	4.0	(**5a**) 0	(**6a**) 66
7[d]	(**4b**)	Bu^nNH_2	B	Bubbling air	2.0	(**5b**) 50	(**6b**) 0
8[d]	(**4b**)	Bu^nNH_2	E	Bubbling air	3.5	(**5b**) 58	(**6b**) 0

[a] B–E: benzene–ethanol (1 : 1 v/v), B: benzene, E: ethanol. [b] Irradiation time for the maximum yield obtained by use of a 400 W high-pressure mercury lamp ($\lambda \geqslant 300$ nm) at 30 °C. [c] Determined by spectrophotometry. [d] [Substrate] 7.5×10^{-4} mol/l, [amine] 0.3 mol/l. [e] Cited from ref. 3b. [f] [Substrate] 1×10^{-4} mol/l, [amine] 0.04 mol/l.

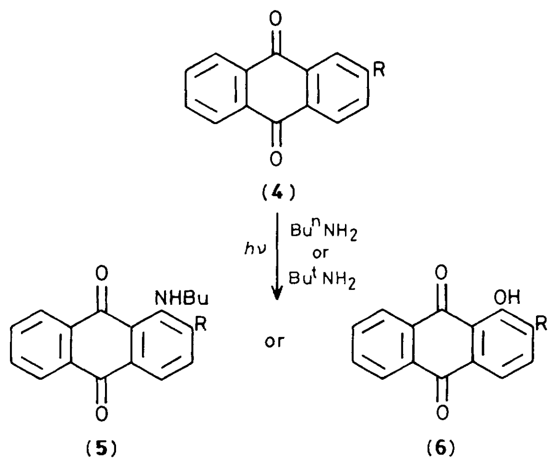


a; R^1 = NH$_2$, R^2 = H
b; R^1 = NHCOPh, R^2 = H
c; R^1 = R^2 = NH$_2$
d; R^1 = R^2 = NHCOMe

and their *N*-acylated derivatives. The results obtained are summarized in Table 1.[†]

In previous papers,[3] we found that the photochemical reaction of 1-acylaminoanthraquinones with alkylamines in benzene gave selectively the 4-alkylamino derivatives in good yields (*cf.* run 3). Other acylaminoanthraquinones were also found to undergo a similar direct photoalkylamination: the reaction of 1,5-diacetamido- (**1d**) and 2-acetamido-anthraquinones (**4b**) with n-butylamine under aerated conditions gave selectively the 4-butylaminated product (**2d**) and the 1-butylaminated product (**5b**) in 71 and 50—58% yields, respectively (runs 5 and 7,8).

Furthermore, we found that hydroxylation took place when 1-amino- (**1a**), 1,5-diamino- (**1c**), and 2-amino-anthraquinones (**4a**) were irradiated with alkylamines under aerobic conditions (runs 1, 2, 4, and 6). In these cases the competitive photoalkylamination was not observed. The photohydroxylation was also observed when other alkylamines, from primary to tertiary, were used instead of the butylamine.



a; R = NH$_2$
b; R = NHCOMe

However, the photohydroxylation did not proceed when the reaction was conducted without either alkylamine or atmospheric oxygen. Therefore, both dissolved O$_2$ and the alkylamine are considered to be essential for the occurrence of the direct photohydroxylation. The mechanism of the photohydroxylation is not not yet clarified and is under investigation; however, the results of Table 1 demonstrate that the selective photoalkylamination and photohydroxylation of aminoanthraquinones is possible. The anthraquinones containing a free amino group can undergo the photohydroxylation, whereas *N*-acylated amino groups facilitate the photoalkylamination, probably as a consequence of a change of energy levels in the excited states of the aminoanthraquinones.[3b]

These reactions are useful for synthesizing a variety of amino- and hydroxy-anthraquinone derivatives which are difficult to obtain by thermal reactions.

Received, 30th December 1985; Com. 1824

[†] Satisfactory spectral and analytical data were obtained for all the products. The properties of (**2b**) have already been described.[3] Selected data for the other products are as follows; (**2d**): ^{1}H n.m.r. δ(CDCl$_3$) 1.02 (3H, t), 1.2—1.9 (4H, m), 2.28 (3H, s), 2.31 (3H, s), 3.37 (2H, q), 7.0—8.1 (3H, m), 8.85—9.2 (2H, m), 10.10 (1H, br.), and 12.55 (1H, br.); (**3a**): ^{1}H n.m.r. δ(CDCl$_3$) 6.97 (1H, d, *J* 9.6 Hz), 7.0 (2H, br.), 7.19 (1H, d, *J* 9.6 Hz), 7.6—8.0 (2H, m), 8.1—8.5 (2H, m), and 13.50 (1H, s); (**3b**): *m/z* 343 (M^+); hydrolysis of (**3b**) in hot 75% H$_2$SO$_4$ gave 1-amino-4-hydroxyanthraquinone; (**3c**): ^{1}H n.m.r. δ (CD$_3$SOCD$_3$) 7.0—7.7 (5H, m), 7.88 (2H, br.), 8.11 (2H, br.), and 13.76 (1H, s); (**5b**): ^{1}H n.m.r. δ (CDCl$_3$ + CD$_3$SOCD$_3$) 0.95 (3H, t), 1.2—1.9 (4H, m), 2.20 (3H, s), 3.38 (2H, q), 7.5—8.0 (4H, m), 8.0—8.4 (2H, m), and 9.0—9.4 (2H, br.); (**6a**): ^{1}H n.m.r. δ(CDCl$_3$ + CD$_3$SOCD$_3$) 6.00 (2H, br.), 6.96 (1H, d, *J* 8.4 Hz), 7.64 (1H, d, *J* 8.4 Hz), 7.7—8.0 (2H, m), 8.1—8.4 (2H, m), and 12.94 (1H, s).

References

1 N. I. Rtishchev, O. P. Studzinskii, and A. V. El'tsov, *Zh. Org. Khim.*, 1972, **8**, 349; N. A. Zvenigorodskaya, E. R. Zakhs, L. S. Efros, and A. V. El'tsov, *ibid.*, 1972, **8**, 1054; J. Griffiths and C. Hawkins, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2283; O. P. Studzinskii, A. V. El'tsov, and Yu. K. Evental, *Zh. Obshch. Khim.*, 1980, **50**, 435; V. A. Loskutov, S. M. Lukonina, A. V. Konstantinova, and E. P. Fokin, *J. Org. Chem. USSR*, 1981, **17**, 500.

2 A. V. El'tsov and O. P. Studzinskii, *Zh. Org. Khim.*, 1979, **15**, 2219; O. P. Studzinskii and A. V. El'tsov, *ibid.*, 1980, **16**, 1101, 2117; 1982, **18**, 1904; A. D. Broadbent and J. M. Stewart, *J. Chem. Soc., Chem. Commun.*, 1980, 676.

3 K. Yoshida, T. Okugawa, and Y. Yamashita, *Chem. Lett.*, 1981, 335; (b) K. Yoshida, T. Okugawa, E. Nagamatsu, Y. Yamashita, and M. Matsuoka, *J. Chem. Soc., Perkin Trans. 1*, 1984, 529.