

Yoshio Ueno\*, Jinya Koshitani and Takatoshi Yoshida

Department of Industrial Chemistry, Nagoya Institute of Technology,  
Gokiso-cho, Showa-ku, Nagoya-shi 466, Japan

Received December 16, 1980

Photochemical reactions of 6-alkylamino- and 6-alkylanilino-5*H*-benzo[*a*]phenothiazin-5-ones have been investigated. 6-Ethylamino- and 6-isopropylamino-5*H*-benzo[*a*]phenothiazin-5-ones and 6-methylanilino- and 6-ethyl-anilino-5*H*-benzo[*a*]phenothiazin-5-ones gave 6-amino-5*H*-benzo[*a*]phenothiazin-5-one and 6-anilino-5*H*-benzo[*a*]phenothiazin-5-one, respectively, on irradiation.

*J. Heterocyclic Chem.*, **18**, 1245 (1981).

In a previous paper, the reactions of imino quinone with aldehydes (1) and alkylthiols (2) were investigated and structures were assigned to the reaction products. As part of the general problem of the study of the photochemical reaction of iminoquinone, we have extended the investigation to the photochemical reaction of 6-alkylamino- and 6-alkylanilino-5*H*-benzo[*a*]phenothiazin-5-ones.

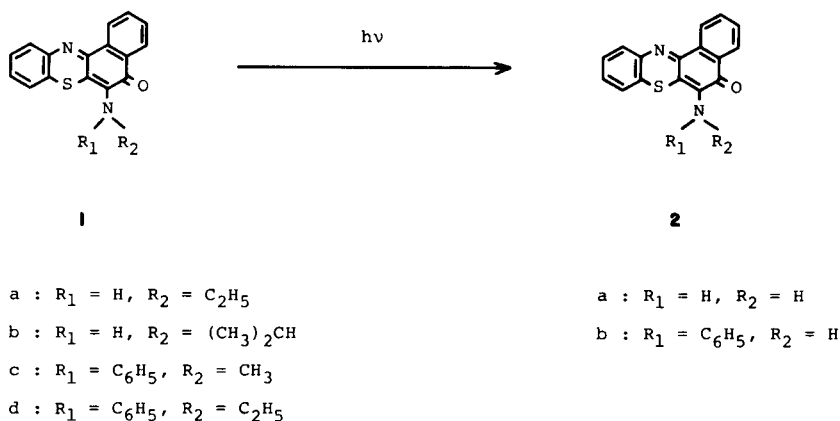
It has been reported that 3-substituted 2-alkylanilino-1,4-naphthoquinones and *N*-methylactinomycin C<sub>2</sub> undergo photochemical dealkylation leading to the formation of the corresponding 2-anilino-1,4-naphthoquinone compounds (3-6) and actinomycin C<sub>2</sub> (7). However, 2-alkylamino-3*H*-phenoxazin-3-ones gave either the corresponding cyclization compounds, oxazolophenoxazines or mixtures of the cyclized oxazolinphenoxazines and the dealkylated 2-amino-3*H*-phenoxazin-3-ones as minor products on irradiation (8). It is of interest to investigate what type of reaction occurs on irradiation of benzophenothiazone derivatives. We report here the photochemical reactions of 6-alkylamino- and 6-alkylanilino-5*H*-benzo[*a*]phenothiazin-5-ones.

When 6-ethylamino- and 6-isopropylamino-5*H*-benzo[*a*]phenothiazin-5-ones (**1a,b**) were irradiated in a Pyrex

vessel for 60 hours with a high-pressure mercury lamp in 20% methanol in benzene, 6-amino-5*H*-benzo[*a*]phenothiazin-5-one (**2a**) was obtained in 20 and 13% yields, respectively. The ir absorption of the amino group was at 3460 and 3340 cm<sup>-1</sup> in the photoproduct **2a**, while singly raising at 3335 and 3305 cm<sup>-1</sup> in compounds **1a,b**, respectively. Furthermore, photo product **2a** was identified by direct comparison with a sample prepared by an alternate route. This route involves the condensation of 2-aminothiophenol with 2-amino-3-chloro-1,4-naphthoquinone (9). However, the photochemical dealkylations of 6-methylamino- and 6-*t*-butylamino-5*H*-benzo[*a*]phenothiazin-5-ones (**1e,f**) did not occur under the same condition. Irradiation of 6-methylanilino- and 6-ethyl-anilino-5*H*-benzo[*a*]phenothiazin-5-ones (**1c,d**) also gave 6-anilino-5*H*-benzo[*a*]phenothiazin-5-one (**2b**) in 28 and 51% yields, respectively. This compound was identified by direct comparison with an authentic sample (10). Significantly, the ir spectra of **1c,d** did not show an absorption in the region 3300-3500 cm<sup>-1</sup>, but those of the photoproducts of **1c,d** exhibited an absorption at 3247 cm<sup>-1</sup> due to the amino group.

It can be summarized that with the exception of **1e,f**, all

SCHEME I



the compounds examined undergo photochemical dealkylation on irradiation, but none of them give the corresponding cyclization products.

### EXPERIMENTAL

Melting points were determined on a Yanagimoto micromelting apparatus and are uncorrected. The infrared spectra were recorded on a Jasco DS 701G spectrometer. Absorption frequencies are quoted in reciprocal centimeters. Nuclear magnetic resonance spectra were determined on a Hitachi R-20B spectrometer using tetramethylsilane as an internal reference. Chemical shifts are quoted in parts per million ( $s$  = singlet,  $d$  = doublet,  $t$  = triplet,  $q$  = quartet,  $m$  = multiplet). Mass spectra were determined on a Hitachi M-52 spectrometer.

#### Materials.

6-methylamino-, 6-ethylamino-, 6-isopropylamino-, 6-*t*-butylamino-, and 6-methylanilino-5*H*-benzo[*a*]phenothiazin-5-ones were prepared by the method of Ueno (9).

#### 6-Ethylanilino-5*H*-benzo[*a*]phenothiazin-5-one (1d).

A solution of 2-ethylanilino-3-chloro-1,4-naphthoquinone (3.11 g, 0.01 mole) and 2-aminothiophenol (1.25 g, 0.01 mole) in pyridine (60 ml) was stirred for 0.5 hour at room temperature and then heated under reflux for 2 hours. After cooling, an equal volume of methanol was added. The precipitate was collected and washed with dilute hydrochloric acid. The crude product (3.4 g, 64%) was purified by chromatography on a silica gel column (benzene as eluent), mp 250-251.5°; ms:  $m/e$  382 ( $M^+$ ); ir (potassium bromide): 1635  $cm^{-1}$  (C=O); nmr (deuteriochloroform):  $\delta$  1.27 ( $t$ , 3H),  $\delta$  3.75 ( $q$ , 2H),  $\delta$  6.50-9.10 ( $m$ , 13H, arom.).

Anal. Calcd. for  $C_{22}H_{18}N_2OS$ : C, 75.37; H, 4.75; N, 7.32; Found: C, 75.64; H, 4.63; N, 7.32.

Irradiation of 6-Alkylamino- and 6-Alkylanilino-5*H*-benzo[*a*]phenothiazin-5-ones (1a-f).

A solution of 6-alkylamino- and 6-alkylanilino-5*H*-benzo[*a*]phenothiazin-5-ones (1a-f) (100 mg) in 40 ml of dry benzene and 10 ml of absolute methanol was irradiated in a Pyrex glass tube from outside by means of 100 Watt high-pressure mercury arc lamp in a nitrogen atmosphere through a 7 cm-thick layer of cold water (0-5°). After the removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column using benzene as an eluent. In the case of 1d, the residue was chromatographed on a silica gel column using benzene-acetate (40:1) as an eluent.

The structure of the products 2a,b was identified by direct comparison of their ir and mass spectra with those of their authentic materials (9,10).

### REFERENCES AND NOTES

- (1) Y. Ueno, H. Shiraki, J. Koshitani and T. Yoshida, *Synthesis*, 313 (1980).
- (2) Y. Ueno, Y. Takeuchi, J. Koshitani and T. Yoshida, *J. Heterocyclic Chem.*, in press.
- (3) I. Ya. Postovskii and I. F. Vladimirtsev, *Dokl. Akad. Nauk SSSR*, **84**, 74 (1952).
- (4) I. F. Vladimirtsev, I. Ya. Postovskii and L. F. Trefilova, *Zh. Obshch. Khim.*, **24**, 181 (1954).
- (5) I. F. Vladimirtsev, I. Ya. Postovskii and L. F. Trefilova, *J. Gen. Chem. USSR*, **24**, 183 (1954).
- (6) E. P. Fokin and E. P. Prudchenko, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 98 (1966).
- (7) H. Brockmann, G. Pampus and R. Mecke, *Chem. Ber.*, **92**, 3082 (1959).
- (8) S. G. Levine and M. C. Wani, *J. Org. Chem.*, **30**, 3185 (1965).
- (9) Y. Ueno, J. Koshitani and T. Yoshida, *Aromatikkus*, **32**, 199 (1980).
- (10) N. L. Agarwall and R. L. Mital, *Appl. Sci. Bull.*, **27**, 83 (1975).