November, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *55*, *3659—3660* (1982) 3659

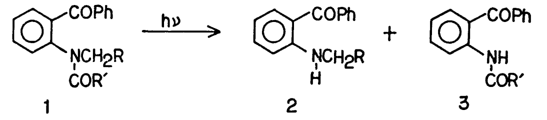
# Photolysis of *o*-(*N*-Alkylacylamino)benzophenones

Tadashi HASEGAWA,* Satomi KOSAKU, Junko UENO, and Shōshichi OGUCHI
*Department of Chemistry, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184*

(Received March 15, 1982)

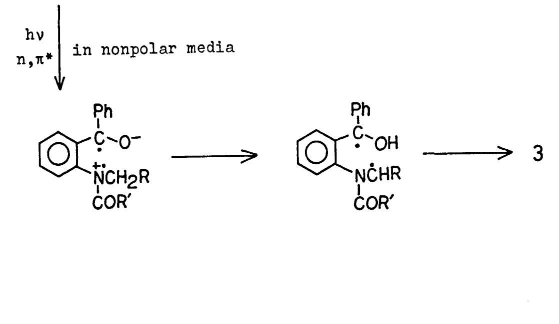
**Synopsis.** The photochemical reactions of *o*-(*N*-alkylacylamino)benzophenones have been studied. Photochemical behavior of the (acylamino)benzophenones was dependent on the solvent polarity. The (acylamino)benzophenones underwent photodeacylation in polar solvents and photodealkylation in nonpolar solvents.

Hydrogen abstraction by benzophenone and its derivatives is one of the most extensively studied primary photochemical processes. It is now well established that the n,π* triplet state of the benzophenones undergo hydrogen abstraction and that the π,π* states are generally inert toward the primary photochemical process.[1] We previously reported photocyclization of *o*-(dialkylamino)benzophenones to indoles *via* intramolecular δ-hydrogen abstraction by the excited carbonyl oxygen.[2] We report here that *o*-(*N*-alkylacylamino)benzophenones undergo unusual photoreactions depending on the solvent polarity.



| | R | R′ | Solvent | **2**(%) | **3**(%) |
|---|---|---|---|---|---|
| a : | H | Ph | MeOH | 57 | — |
| b : | Ph | Ph | MeOH | 70 | — |
| | | | $C_6H_6$ | 5 | 28 |
| c : | H | Me | MeOH | 88 | — |
| d : | Ph | Me | MeOH | 89 | — |
| | | | $C_6H_6$ | — | Trace |

A methanol solution of *o*-(*N*-methylbenzoylamino)benzophenone (**1a**) was irradiated under nitrogen with a 450 W high-pressure mercury lamp through a Pyrex filter. After removal of the solvent, the residue was chromatographed on silica gel to yield *o*-(methylamino)benzophenone (**2a**) and benzoic acid in 57 and 38% yield, respectively. Similarly, irradiation of the (acylamino)benzophenone **1b**—**d** under the same conditions gave the corresponding (alkylamino)benzophenone **2**. A trace of *o*-aminobenzophenone (**4**) was also obtained in the cases of photolyses of **1b** and **1d**.[3] No indoles, which were expected to form *via* δ-hydrogen abstraction by the excited carbonyl group, and no methyl esters were detected in all cases. The isolation of benzoic acid in the photolysis of **1a** and the absence of methyl esters suggest that the deacylation proceeds *via* homolytic cleavage of CO–N bond. Photodeacylation is well known in the photochemistry of imides.[4] The (acylamino)benzophenone **1** is considered to be the aromatic vinylog of imides.



The quantum yield for production of **2c** from **1c** in methanol was taken as 0.05. The quantum yield was dependent on the solvent polarity. Polar solvents appreciably enhance the quantum efficiency with which the acylamino ketone **1c** undergoes photodeacylation in solution. (Fig. 1) The acylamino ketone **1c** in hexane showed an ultraviolet-absorption peak at 334 nm (ε 140) attributable to the n,π* transition. This peak underwent blue shift in ethanol and was discerned at 330 nm as a shoulder. These results indicate that the relative disposition of the n,π* and the π,π* states of the ketone **1c** is reversed in polar media compared to that in nonpolar media and that photodeacylation occurs from the π,π* excited state of the acylamino ketone **1c**.

In the case of photolysis of **1b** in benzene *o*-(benzoylamino)benzophenone (**3b**, 28%) was obtained as the main photoproduct, together with **2b** (5%) and a trace of **4**. Similarly, irradiation of *N*-benzylamide **1d** under the same conditions gave a trace of dealkylated photoproduct **3d**. On the other hand, no dealkylated photoproducts could be detected in the cases of *N*-methylamide **1a** and **1c** in benzene. Gold suggested that the Type II cyclization predominated over the Type II elimination in photochemistry of acylamino ketones;[5] however, no indoles could be detected in photolysis of **1** in benzene. The dealkylation

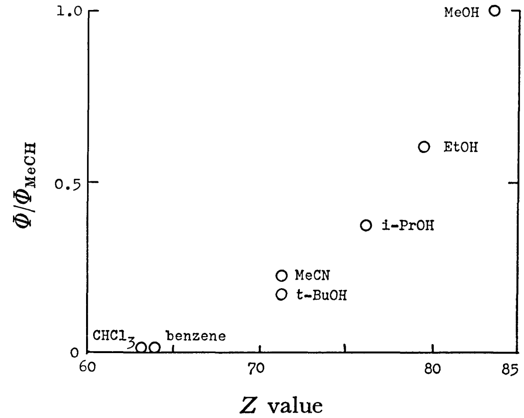


Fig. 1. Relative quantum yields for production of **2c**[a] as a function of solvent polarity (*Z* value[b]).
a) The (acylamino)benzophenone **1c** was irradiated at 313 nm. Production of **2c** was measured by UV spectroscopy. b) [E. M. Kosower, *J. Am. Chem. Soc. Soc.*, **80**, 3253 (1958).

product **3b** formed in benzene could not be detected in the photolysis of **1b** in methanol. We have already reported that a smilar photochemical dealkylation occurred in *o*-(dialkylamino)benzophenones.[2] Production of acylamino ketone **3** can be explained in terms of photodealkylation via intramolecular $\delta$-hydrogen abstraction by the excited carbonyl group. A similar photochemical dealkylation of *o*-methoxybenzophenone via intramolecular $\delta$-hydrogen abstraction by the carbonyl group has been reported by Leary and Oliver.[6] The solvent effect described above also suggests that dealkylation takes place from the n,$\pi^*$ state of the acylamino ketone **1**.

Quenching of the photodealkylation of the acylamino ketone **1b** by 0.1 M 1,3-pentadiene ($E_T$=57 kcal)[7] was not observed. The photodealkylation may be considered to proceed from the n,$\pi^*$ singlet state of the (acylamino)benzophenone **1b**. However, it is quite improbable that $\delta$-hydrogen abstraction from the n,$\pi^*$ singlet state can compete with intersystem crossing because the rate of intersystem crossing of benzophenone is very rapid (*ca.* $10^{11}$ s$^{-1}$).[1] Therefore, the photodealkylation seems to be reasonably explained in terms of the charge-transfer mechanism from the n,$\pi^*$ state. The charge-transfer interaction is considered to contribute in the excited state of aminobenzophenone,[8] and the interaction between amide nitrogen and carbonyl oxygen was reported in photochemistry of $\beta$-oxo amides.[9]

## Experimental

*Chemicals.* The (acylamino)benzophenones **1a—d** were prepared by the usual methods from (alkylamino)-benzophenone, and benzoyl chloride or acetic anhydride.[10]

*General Procedure for Photolysis of (Acylamino)benzophenone **1**.* An (acylamino)benzophenone **1** (500 mg) in solvent (70 ml) was irradiated under nitrogen with a 450 W high-pressure mercury lamp (Ushio Elect. Co.) through a Pyrex filter. After removal of the solvent, the residue was chromatographed on silica gel. Elution with a mixture of benzene–ethyl acetate gave an amino ketone **2** and/or an acylamino ketone **3**. The structure of **2** and **3** were determined by direct comparison with authentic samples.[10]

*Quantun Yield Determinations.* The degassed solution of (acylamino)benzophenone **1** was irradiated on a merry-go-round apparatus using a 100 W high-pressure mercury lamp (Taika Elect. Co.) and a potassium chromate filter solution to isolate 313 nm irradiation. Production of **2** was measured by a Hitachi EPS-033 UV spectroscopy. Valerophenone was used as a chemical actinometer.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 56740205 from the Ministry of Education, Science and Culture.

## References

1) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Interscience Publishers, New York (1969).

2) H. Aoyama, T. Nishio, Y. Hirabayashi, T. Hasegawa, H. Noda, and N. Sugiyama, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 298.

3) Prolonged irradiation of **1b** changed the yield of **2b** and **4**. The yield of **4** was increased and that of **2b** was decreased. When the amino ketone **2b**, which was prepared independently, was irradiated in methanol under the same conditions, **4** was obtained. These results indicate that **4** was produced from **2b** as a secondary photoproduct.

4) P. H. Mazzocchi, W. Jameson, T. Nishiyama, and A. DeCamp, *Tetrahedron Lett.*, **1980**, 989; Y. Kanaoka, T. Tsuji, K. Itoh, and K. Koyama, *Chem. Pharm. Bull.*, **21**, 453 (1973); R. O. Kan and R. C. Furey, *Tetrahedron Lett.*, **1966**, 2537.

5) E. H. Gold, *J. Am. Chem. Soc.*, **93**, 2793 (1971).

6) G. Leary and J. A. Oliver, *Tetrahedron Lett.*, **1968**, 299.

7) S. L. Murov, "Handbook of Photochemistry," Mercel Dekker, New York (1973).

8) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

9) T. Hasegawa, H. Aoyama, and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 963.

10) P. Grammatikis, *Bull. Soc. Chim. Fr.*, **1953**, 93.