CHEMISTRY LETTERS, pp.641-642, 1976. Published by the Chemical Society of Japan

METALLOPORPHYRINS. I. PHOTOINDUCED meso-ACYLAMINATION OF PORPHYRIN RING USING ACYL AZIDES

Kunihiro ICHIMURA
Research Institute for Polymers and Textiles
Sawatari 4, Kanagawa-ku, Yokohama 221

Zinc octaethylporphin sensitizes the photodecomposition of acyl azide to yield zinc complex of 5-acylamino-2,3,7,8,12,13-17,18-octaethylporphin.

Little have been known about the photochemical transformation of metalloporphyrins except photoreduction and photooxidation, although photochemical works on the pigments are attracting intensive interest in relation to the biological significances.[1] We now wish to report the photoacylamination on the meso-position of zinc octaethylporphin (ZnOEP) which seems to be a first example of the photochemical substitution on the porphyrin ring, while Grigg have described the meso-ethoxycarbonylation of some porphyrins with use of ethoxycarbonylnitrene generated in the dark reaction.[2]

When a solution of ZnOEP (100 mg) and benzoyl azide (43 mg) in dichloromethane (120 mg) was irradiated with light of >450 nm under argon stream, the color of the solution turned immediately in dark violet. The reaction was followed by tlc. Red violet needles (70 mg) was separated by preparative tlc on silica gel.[3] The visible absorption bands at 413, 544 and 582 nm in dichloromethane suggested that the product is a metal complex. The nmr spectrum in $CDCl_3$ revealed the presence of a meso-substituent since the ethyl protons of the porphyrin are no longer equivalent[4,5] and only three meso-protons were observed. The appearance of five protons due to phenyl ring derived from the azide and the presence of the ir absorption band of amide group at 1655 cm^{-1} as well as the elemental analyses supported that the photolysis product is a zinc complex of octaethylporphin substituted by PhCONH- or PhNHCO- group at the meso-position. The structure for the product was unequivocally confirmed by the synthesis of the authentic sample, which was obtained by the benzoylation of meso-amino-octaethylporphin,[5] followed by the metallation, and identified with the photoproduct (ir, visible, tlc). Using various acyl azides, meso-acylaminated ZnOEP's were prepared in a similar manner (Table 1).

The photoreaction was quenched by oxygen[6] and nitrobenzene.[7] The photolysis occured even in a highly diluted solution (ca. 10^{-5} M/l in both ZnOEP and azide). These results suggest that the triplet ZnOEP plays a key role in the photolysis. The mechanistic studies will be described in detail in near future.

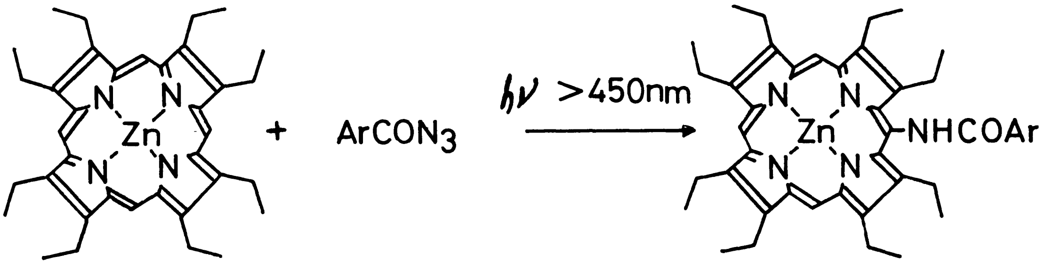

Table 1. Zinc complexes of 5-acylamino-2,3,7,8,12,13,17,18-octaethylporphin.

acyl	mp(decomp.)(°C)	yield(%)	irrad. period(hr)*)
benzoyl	307-309	58	4
p-anisoyl	295-301	50	6
p-chlorobenzoyl	324-325	61	2
p-cyanobenzoyl	298-299	59	0.2
p-nitrobenzoyl	305-307	35	14
m-nitrobenzoyl	277-279	65	15
α-naphthoyl	283-286	47	2
cinnamoyl	296-301	43	1

*) with a high pressure Hg lamp filtered by a Corning No. 3-72 filter.

References

1) J.-H. Fuhrhop, Angew. Chem., 86, 363 (1974).

2) R. Grigg, J. Chem. Soc. (C), 1971, 3664.

3) The chromatogram was complex, and the studies on the structure elucidation of the minor products are now in progress.

4) H.-H. Inhoffen, J.-H. Fuhrhop, H. Voigt, and H. Brockmann Jr., Liebigs Ann. Chem., 695, 133 (1966).

5) R. Bonnett and G. F. Stephenson, J. Org. Chem., 30, 2791 (1965).

6) J.-H. Fuhrhop, Ann. N. Y. Acad. Sci., 206, 533 (1973).

7) J. K. Roy, F. A. Carroll, and D. G. Whitten, J. Amer. Chem. Soc., 96, 6349 (1974).

(Received April 13, 1976)