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# IRRADIATION OF AROMATIC AMINE OXIDES IN DICHLOROMETHANE IN PRESENCE OF TRIPHENYLPHOSPHINE: A FACILE DEOXYGENATION PROCEDURE OF AROMATIC AMINE N-OXIDES[1]

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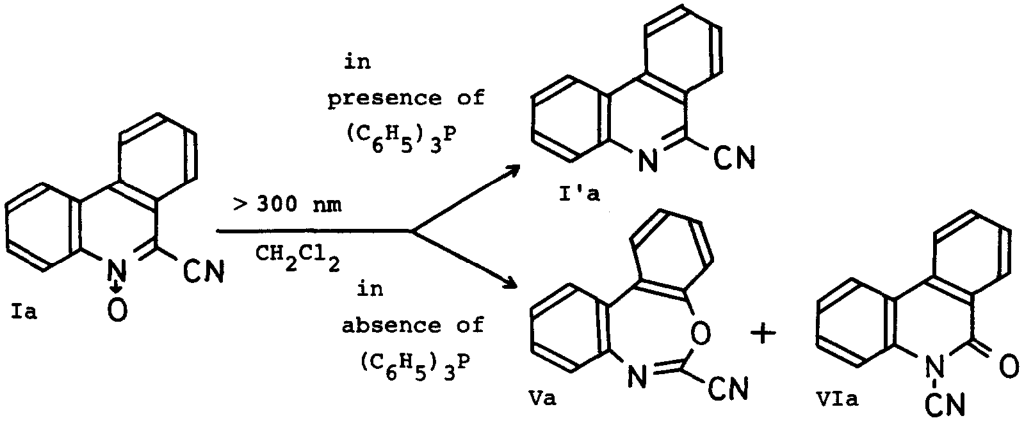
In our continuing studies on the photolysis of aromatic amine N-oxides, we have found that irradiation of these N-oxides in dichloromethane in presence of triphenylphosphine (1.2-5.0 mol equivalent to an N-oxide) under nitrogen atmosphere resulted in the formation of the deoxygenated products in high yields and the formation of the photo-rearrangement products depressed from none to a small amount.[2]

In a typical experiment, 2.5 mmol (550 mg) of 6-cyanophenanthridine 5-oxide (Ia) in 450 ml of dichloromethane containing 3.0 mmol (786 mg) of triphenylphosphine was irradiated by 400 W high-pressure mercury lamp (Toshiba-400P) with a Pyrex filter for 30 min under nitrogen atmosphere. Evaporation of the solvent followed by column chromatography over silica gel afforded 6-cyanophenanthridine (I'a: 485 mg; 94.8%). The other products isolated were triphenylphosphine oxide (657 mg: approximately 1 mol equivalent to the deoxygenated product) and a small amount of the recovered phosphine. Whereas the use of the phosphine in a larger amount gave the same result except for an increasement of recovery of the phosphine, use of the phosphine in a lesser amount (0.6 mol equivalent to Ia) reduced the yield of I'a to 61% with a complete conversion of the phosphine to its oxide and increased the yields of the photo-rearrangement products (total yield: 31%; the ratio of Va to VIa was ca. 12:1). As reported previously,[1] the photolysis of Ia in absence of the phosphine resulted in the formation of two rearrangement products: 6-cyanodibenz[d,f][1,3]-oxazepine (Va; 78%) and 5-cyano-

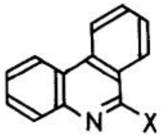


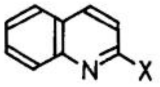
phenanthridin-6(5H)-one (VIa; 13%) together with 3% of the deoxygenated product (I'a).

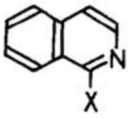
This new deoxygenation method of the N-oxides with triphenylphosphine under irradiation ( > 300 nm) was applied with success to several bicyclic and tricyclic amine N-oxides and the results are shown in Table I.

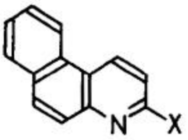
As well known, the photo-isomerization occurs through the lowest singlet state ($S_1$) of the N-oxide, whereas the deoxygenation occurs from the lowest triplet state ($T_1$),[6] and the irradiation of these N-oxides in the absence of a reducing reagent gave the former in predominance (80-90%) and the latter in a few % yield. Though an enhancement of the intersystem crossing from the $S_1$ state to the $T_1$ state seems to be attractive to the present case, such a mechanism may be ruled out, because the amounts of the phosphine necessary to prevent the formation of the photo-rearrangement products differed in each N-oxide.

Though at present a possibility of a direct abstraction of oxygen atom from the excited N-oxide ($S_1$) is not regally excluded, the most reasonable mechanism is the direct abstraction of oxygen atom from an oxaziridine species (this species is believed to be formed as a primary photo-product from the excited N-oxide ($S_1$) and assumed as the precursor of the photo-rearrangement products).[6] In accordance with this mechanism, an oxaziridine derived from a nitrone exhibits a strong oxidizing ability[7] and can be reduced to the parent imine with the phosphine quite readily.[8] Furthermore, the amounts of the amines formed in the present reductions seem to be in parallel with the estimated life time of each









| | | | | |
|---|---|---|---|---|
| N-oxide | I | II | III | IV |
| amine | I' | II' | III' | IV' |

| | X |
|---|---|
| a | CN |
| b | H |
| c | $C_6H_5$ |

Table I. Photochemical Deoxygenation of N-Oxides in Dichloromethane in Presence of Triphenylphosphine[a)]

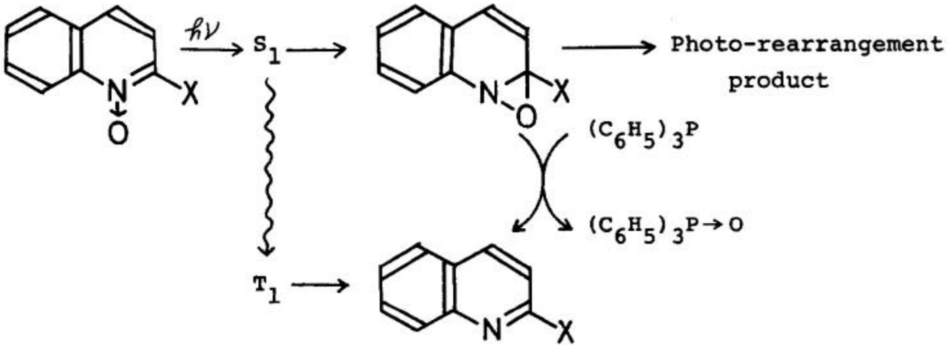
| N-oxide[d)] | triphenylphosphine | yield of product (%) | |
|---|---|---|---|
| | mol equiv. to N-oxide | deoxygenation | rearrangement |
| Ia | 1.2 | 95 | 0 |
| | 3.0 | 95 | 0 |
| | 0.6 | 61 | 31 |
| IIa | 1.2 | 88 | trace[b)] |
| IIIa | 1.2 | 43 | 30[b)] |
| | 3.0 | 78 | 5 |
| IVa | 1.2 | 42 | 32[b)] |
| | 5.0 | 63 | 7 |
| Ib | 1.2 | 88 | trace[c)] |
| IVb | 1.2 | 22 | 59[c)] |
| IIc | 3.0 | 29 | 66[b)] |

a) The solution of 2.5 mmol of the N-oxide in 450 ml of the solvent containing the phosphine was irradiated until the N-oxide was consumed (irrespective of the amounts of the phosphine, 20-30 min-irradiation was required). Triphenylphosphine oxide was formed in the amount of ca. 1 mol equivalent to the amine formed in each photolysis.

b) Mostly the oxazepine.

c) A mixture of the oxazepine and the α-oxo compound (e.g., carbostyrils).

d) Irradiation of these N-oxides in the absence of phosphine in an aprotic solvent has already been reported: see refs 1 (for Ia), 3 (for Ib), 4 (for IIa, IIc, and IIIa) and 5 (for IVa).

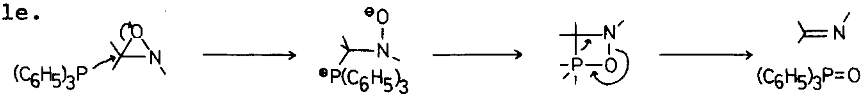


oxaziridine species (e.g., the longer the life time of the oxaziridine, the larger the amount of the deoxygenated product).[9]

Though triphenylphosphine was reported to reduce aromatic amine N-oxides under a forced condition (heating over 230°),[10] it was assured that none of the N-oxides nor their photo-rearrangement products (e.g., the oxazepine) reacted with the phosphine in a dark even in a refluxed dichloromethane.

## References and Notes

1. Studies on the N-Oxides of $\pi$-Deficient N-Heteroaromatics, XXIX. Part XXVIII: C. Kaneko, R. Hayashi, M. Yamamori, K. Tokumura, and M. Itoh, *Chem. Pharm. Bull.(Tokyo)*, **26**, in press.
2. The photochemical deoxygenation of N-oxides in presence of $BF_3$-etherate in benzene[a] or potassium iodide in aqueous media[b] was reported: a) N. Hata, I. Ono, and M. Kawasaki, *Chem. Lett.*, **1975**, 25; b) N. Hata and I. Ono, *Bull. Chem. Soc. Japan*, **49**, 1794 (1976).
3. E.C. Taylor and G.G. Spence, *Chem. Commun.*, **1968**, 1037 and refs cited.
4. C. Kaneko, Sa. Yamada, and M. Ishikawa, *Tet. Lett.*, **1966**, 2145.
5. By irradiation of IVa in $CH_2Cl_2$, 4-cyanonaphth[2,1-d][1,3]-oxazepine (82%; mp 137-138°) and the parent amine (9.5%) were obtained: unpublished work.
6. For recent reviews on this topic, see: a) C. Kaneko, *Yukigosei Kyokaishi*, **26**, 758 (1968); b) M. Ishikawa and C. Kaneko, *Kagaku no Ryoiki*, **Suppl.92**, 149 (1970); c) G.G. Spence, E.C. Taylor, and O. Buchardt, *Chem. Rev.*, **1970**, 231; d) F. Bellamy and J. Streith, *Heterocycles*, **4**, 1391 (1976).
7. J.S. Splitter and M. Calvin, *J. Org. Chem.*, **30**, 3427 (1965).
8. L. Horner and E. Jurgens, *Chem. Ber.*, **90**, 2184 (1957): The mechanism for the reduction of an oxaziridine derived from a nitrone with triphenylphosphine is the following and fits nicely to the observed difference between IIa and IIc (the former was reduced more efficiently). Because the presence of a bulky group such as phenyl may make the four-membered ring intermediate less accessible.



9. A currently accepted mechanism for the formation of oxazepines from oxaziridines involves a 1,5-oxygen shift (thermal by nature). Thus, the formation of the former would become easier in the following order: oxazepines from I < oxazepines from II < oxazepines from IV. For example, in the oxygen walk process, an oxaziridine from I should lose two benzenoid systems simultaneously, while only one benzenoid system is lost in an oxaziridine from II. For the experimental supports and the detailed discussions, see ref. 1.
10. E. Howard, Jr. and W.F. Olszewski, *J. Amer. Chem. Soc.*, **81**, 1483 (1959).