Tetrahedron Letters,Vol.25,No.18,pp 1945-1946,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

# PHOTOCHEMICAL NITROOXYLATION OF METHYLBENZENES BY CERIUM(IV) AMMONIUM NITRATE IN ACETONITRILE

E.Baciocchi,* C.Rol, G.V.Sebastiani, and B.Serena
Dipartimento di Chimica, Università di Perugia, 06100 Perugia, (Italy)

Summary: The photochemical reaction of substituted toluenes with CAN in $CH_3CN$ leads to good yields of benzyl nitrates under very mild conditions.

Ceric Ammonium Nitrate (CAN)is a convenient reagent for the side-chain oxidation of alkylaromatics. Benzyl acetates are obtained in acetic acid,[1,2] whereas benzaldehydes are the main reaction products in aqueous acetic acid.[1,3]

Recently, it has been observed that, in refluxing acetonitrile, CAN reacts with methylbenzenes to give benzyl nitrates;[4] conversions, however, are quite low and, moreover, significant aromatic nitration also occurs, the latter reaction being in some case the main process. The mechanism suggested for the side-chain process, reported in the scheme, is that proposed earlier[5] for the reactions of CAN with alkylaromatics in acetic acid.

$$ArCH_3 + Ce^{IV}NO_3 \longrightarrow ArCH_3^{+\cdot} + Ce^{III}NO_3$$
$$ArCH_3^{+\cdot} \longrightarrow ArCH_2^{\cdot} + H^+$$
$$ArCH_2^{\cdot} + Ce^{IV}NO_3 \longrightarrow ArCH_2ONO_2 + Ce^{III}$$

In this note we wish to report that,when CAN and a methylbenzene react in $CH_3CN$ under irradiation by a high pressure lamp, a clean side-chain oxidation takes place under very mild conditions, leading to high yields of benzyl nitrates (along with minor amounts, 5-10%, of benzaldehyde) with complete suppression of the competing aromatic nitration.

In a typical experiment a magnetically stirred solution of methylbenzene 0.07M and CAN 0.14M in 60 ml of $CH_3CN$ (at 40°C), is irradiated for 0.5 - 2.5h with an immersion high pressure mercury lamp (Hanau TQ 150) whose emission was filtered through Pyrex. The reaction mixture is worked up as usual and the crude product is first analyzed by NMR (comparison with authentic samples) and then subject to column chromatography for the isolation of the benzyl nitrate. The results are reported in the Table, where the dramatic effect of light is shown by the comparison of the dark and photochemical reactions of toluene.

The scope of the reaction is quite wide, fair yields of product being obtained even with toluenes ring substituted by electron-withdrawing groups, and the process can therefore have useful application as a direct synthesis of benzyl nitrates from methylbenzenes.

Whereas the detailed mechanism of the reaction is under investigation, preliminary experiments have shown that, in the absence of the substrate, no significant reduction of CAN takes place

TABLE. Yields of $ArCH_2ONO_2$ in the CAN-promoted photochemical oxidation of $ArCH_3$ in acetonitrile, at 40°C.

| Ar | Reaction time, h | $ArCH_2ONO_2$ yield, %[a] |
|---|---|---|
| 2,4-$Cl_2C_6H_3$ | 2.5 | 47 |
| 4-$BrC_6H_4$ | 2 | 70 |
| $C_6H_5$ | 1 | 75 |
| $C_6H_5$[b] | 3 | no reaction |
| 4-$AcOC_6H_5$ | 2.5 | 80 |
| 4-$CH_3C_6H_5$ | 0.5 | 96 |
| 3,5-$(CH_3)_2C_6H_3$ | 1 | 85 |
| 3-$CH_3C_6H_4$ | 1.5 | 67 |

[a] Based on the starting material (quantitative NMR analysis, with an internal standard, of the crude reaction product; the yields of isolated product are about 10% less than those reported).

[b] At 60°C in the dark.

under irradiation. Thus, the photochemical process might involve an electron transfer reaction between the excited state of CAN or, more probably, of some $Ce^{IV}$ species formed by the interaction of CAN with the solvent, and the ground state of aromatic compounds.[6] Since the $Ce^{IV}$ species increases its oxidizing capacity on going to the excited state,[7] an increase in the rate of the side-chain oxidation is possible.[8] This would allow this process to take place under very mild reaction conditions without any competition by the aromatic nitration, certainly a thermal reaction.[4]

Acknowledgement: This work has been supported by the "Progetto Finalizzato CNR per la Chimica Fine e Secondaria". Thanks are also due to ACNA (Cesano Maderno) and Fondazione Donegani for providing a fellowship to B.S.

## References

1. W.S.Trahanovsky and L.B.Young, J.Org.Chem. 31, 2033 (1966).
2. E.Baciocchi, L.Mandolini and C.Rol, J.Org.Chem., 42, 3682 (1977).
3. L.Syper, Tetrahedron Letters, 4493 (1966).
4. S.Dincturk and J.H.Ridd, J.Chem.Soc.Perkin Trans.II, 961, 965 (1982).
5. E.Baciocchi, L.Mandolini and C.Rol, J.Am.Chem.Soc., 102, 7597 (1980). Actually, in acetic acid too nitrates are first formed which then solvolyse to acetates.
6. A solution of CAN in $CH_3CN$ displays a broad maximum at 328nm ($\epsilon$= 7400). No significant absorption is exhibited by the aromatic compound above 280nm (Pyrex filter).
7. V.Balzani, F.Bolletta, M.T.Gandolfi and M.Maestri, Topics in Current Chemistry, 75, 1 (1978)
8. Electron transfer reactions of alkylaromatics with Ce(IV) should occur by an outer sphere mechanism.[9] Therefore the reaction rate might depend on the oxidation potential of the metal complex.
9. L.Eberson, Advances in Physical Organic Chemistry, 18, 79 (1981).

(Received in UK 21 February 1984)