# New Aspects of the Decomposition of *N*-Nitrosoacylarylamines: the Question of Aryne Participation

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The long-standing problem of the mechanism of the decomposition of *N*-nitrosoacetanilide in aromatic solvents has been rationalised[1] as follows (Scheme A):

$$\mathrm{PhN(NO)Ac \rightarrow PhN{:}N{\cdot}OAc \rightleftharpoons PhN_2^+ + AcO^-}$$

$$\mathrm{AcO^- + PhN{:}N{\cdot}OAc \rightarrow PhN_2O^- + Ac_2O} \ldots (\mathrm{i})$$

$$\mathrm{PhN_2^+ + PhN_2O^- \rightarrow (PhN_2)_2O \rightarrow Ph{\cdot} + N_2 + PhN_2O{\cdot}}$$

$$\mathrm{Ph{\cdot} + ArH \rightarrow (PhArH){\cdot} \xrightarrow{PhN_2O\cdot} PhN_2OH + PhAr}$$

$$\mathrm{PhN_2OH + PhN_2^+AcO^- \rightarrow AcOH + PhN_2^+, PhN_2O^-,}\ etc.$$

Scheme A

In view of the apparent intermediacy of an aryne in the decomposition of *o*-t-butyl-*N*-nitrosoacetanilide[2] (*cf.* also ref. 3), the decompositions of various *N*-nitrosoacylarylamines, including *N*-nitrosoacetanilide itself, in various solvents in the presence of arynophiles have been investigated. In this connection, we now report the formation of adducts identical with those formed by reaction of authentic arynes with 2,3,4,5-tetraphenylcyclopentadienone and/or anthracene or 1,3-diphenylisobenzofuran.

Other significant observations are as follows: reactions of *N*-nitroso-*p*-chlorobenzanilides [$\mathrm{ArN(NO){\cdot}CO{\cdot}C_6H_4Cl}$-*p*] in carbon tetrachloride gave *p*-chlorobenzoic acid as a *primary* product, indicating that abstraction of hydrogen as well as loss of nitrogen from the nitrosoamide had occurred. Also formed was *p*-chlorobenzoic anhydride (*ca.* 0·15 moles/mole of nitrosamide) thus providing evidence for the participation of a

TABLE

*Decomposition of* N-*nitrosoacylarylamines in solvents in the presence of arynophiles*

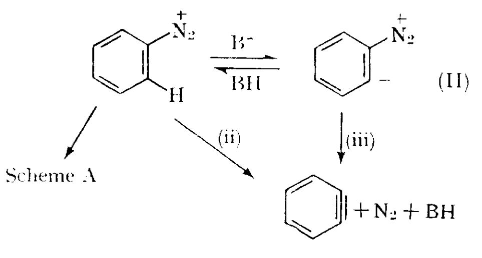
| ArN(NO)COR (I) Ar | R | Solvent | Adducts (% based on I) from t.p.c.p.† | anthracene |
|---|---|---|---|---|
| Ph | Me | PhH,‡ $CCl_4$, $CH_2Br_2$ or $(CH_2)_4O$ | 17—34 | 1—3 |
| Ph | *p*-Me·$C_6H_4$ | $CCl_4$ | 29 | |
| Ph | *p*-$NO_2$·$C_6H_4$ | $CCl_4$ | 13 | |
| Ph | *p*-Cl·$C_6H_4$ | $CCl_4$ or PhH | 37 | 3 |
| *p*-Br·$C_6H_4$ | *p*-Cl·$C_6H_4$ | $CCl_4$ | 4 | |
| *m*-Br·$C_6H_4$ | *p*-Cl·$C_6H_4$ | $CCl_4$ | 70 | |
| *p*-Me·$C_6H_4$ | *p*-Cl·$C_6H_4$ | $CCl_4$ | 1 | |
| *m*-Me·$C_6H_4$ | *p*-Cl·$C_6H_4$ | $CCl_4$ | 33 | |

† 2,3,4,5-Tetraphenylcyclopentadienone.

‡ 9,10-Diphenylanthracene (14%) was obtained after reduction of the products of the reaction carried out with 1,3-diphenylisobenzofuran.

reaction such as (i). Secondly, in the decomposition of *N*-nitrosoacetanilide in benzene, the yield of biphenyl was 50% in the absence, and 0·02% in the presence, of 2,3,4,5-tetraphenylcyclopentadienone (t.p.c.p.). Considering first the case of *N*-nitrosoacetanilide in benzene, which follows Scheme A in the absence of arynophiles, the latter observation indicates the interception of a phenyl radical or its *precursor* by the diene. The "benzyne adduct", 1,2,3,4-tetraphenylnaphthalene, was not formed, however, when phenylazotriphenylmethane, an authentic source of phenyl radicals, was allowed to decompose in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone (t.p.c.p.). Since the products and the course of the reaction in benzene in the absence of tetraphenylcyclopentadienone are adequately explained in terms of Scheme A, this suggests that the intermediate which reacts with t.p.c.p. to give the benzyne-adduct is in equilibrium with a precursor of the phenyl radical.

It is tempting to suggest the participation of benzyne in these cases, *e.g.*, *via* reaction (ii) or, if stepwise, (iii), but, since reactions (ii) or (iii) are unlikely to be reversible, it is difficult to accept that benzyne could be the intermediate in equilibrium with the precursor of the phenyl radical, referred to above. Moreover, decomposition of *N*-nitrosoacetanilide in the presence of furan, which is a well tried aryne trap, did not give the benzyne–furan adduct (< 0·1%).



[$B^-$ = AcO or PhN$_2$O ]

It seems, therefore, that the intermediate in question is not benzyne itself but that it is benzynoid in the sense that it gives "benzyne adducts" with the more reactive dienes, but not with furan. Further unexplained observations involve nitrosoacylarylamines which do not conform to Scheme A at all. Thus 2,5-di-t-butyl-*N*-nitrosoacetanilide in furan gives a good yield of the aryne–*furan* adduct,[4] while *N*-nitrosobenzanilides in carbon tetrachloride behave abnormally by loss of aromatically bound hydrogen in the absence as well as presence of arynophiles (see above).

Current experiments are designed to investigate the part played, if any, by intermediates such as arylcarbonium ions, diazonium cations, or (II), the latter being detectable only when irreversibly removed by an arynophile. In the meantime it is clear, despite the elegant work of Rüchardt and his co-workers, that the full story of the decomposition of *N*-nitrosoacylarylamines has yet to be told.

Some of these results were communicated in August 1966 at the Gomberg Centenary Symposium at Ann Arbor.

*Note added in proof.* G. R. Chalfont and M. J. Perkins (*J. Amer. Chem. Soc.*, 1967, **89**, 3054) have now challenged Rüchordt and Freudenberg's Scheme A and have suggested an alternative. Neither alternative accommodates the experimental observations reported in this Communication.

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[1] C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, 1964, 3623; G. Binsch and C. Rüchardt, *J. Amer. Chem. Soc.*, 1966, **88**, 173; G. Binsch, E. Merz, and C. Rüchardt, *Ber.*, 1967, **100**, 247.

[2] J. I. G. Cadogan and P. G. Hibbert, *Proc. Chem. Soc.*, 1964, 338.

[3] R. W. Franck and K. Yanagi, *Tetrahedron Letters*, 1966, 2905.

[4] J. I. G. Cadogan, M. J. P. Harger, and J. T. Sharp, unpublished observations.