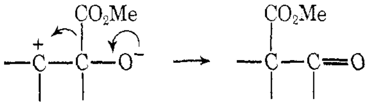
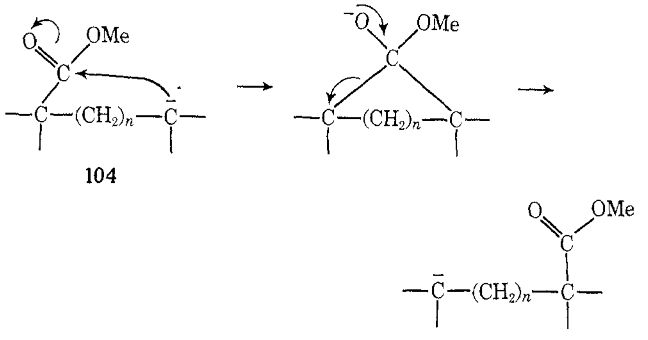
tion. However, the mechanism outlined has been established by following the movement of the ^{14}C-labeled methyl group, indicated by an asterisk, and by the incorporation of ^{14}C-labeled carbon monoxide bubbled through the reaction mixture.[55] Similar apparent migrations of ester groups are clearly possible but do not appear to have been recorded.

Conclusions

The idea that ester groups can migrate has been put forward to account for the formation of particular structures from others under the influence of conditions inducing chemical change. Although detailed mechanistic studies need to be carried out on all the rearrangements described in this Account before one can be certain of exactly what is going on, it is possible, on the basis of commonly accepted theory, to make two generalizations. Ester groups can undergo 1,2 shifts with their bonding electrons to adjacent positive centers (**102** → **103**). Ester groups can also move to nucleophilic centers, through the formation of three- to six-membered rings (**104** → **105**), relinquishing their original bonding electrons in the process.



102 **103**



104 **105**

Photolysis can also induce ester shifts, and ester groups appear to undergo 1,5-sigmatropic shifts and to move through processes involving radicals. One B_{12}-containing enzyme catalyzes a reversible thiol ester shift (**89** → **90**) which must occur in most living systems. Ester groups also can migrate in preference to both alkyl and aryl groups. The migration of ester groups, although rare, is therefore a widespread phenomenon, and it is already clear that great care should be taken in interpreting experimental results which indicate that either an ester group, or another substituent, could migrate.

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(55) J. Meinwald, H. C. Hwang, D. Christman, and A. P. Wolf, *J. Amer. Chem. Soc.*, **82**, 483 (1960).

Decomposition of Acylarylnitrosamines. A Multipathway Reaction

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The behavior of acylarylnitrosamines in solution, exemplified by *N*-nitrosoacetanilide ($C_6H_5N(NO)COCH_3$), has puzzled generations of chemists since its synthesis in 1876[1] and Bamberger's discovery, 20 years later,[2] that it decomposed easily in benzene at room temperature to give biphenyl and acetic acid (eq 1). This apparently simple reaction, quite apart

$$C_6H_5N(NO)COCH_3 + C_6H_6 \longrightarrow C_6H_5C_6H_5 + N_2 + CH_3CO_2H \quad (1)$$

from its synthetical utility, played a major part in the development in the 1930's of the concept of the transient existence of radicals in solution.[3] It thus became the subject of much research into the mechanism of its decomposition into phenyl radicals, *via* the isomeric benzenediazo acetate.[4,5]

In the late sixties the demonstration that the decomposition also involved stable radicals,[6-8] detectable by esr spectroscopy, and unstable species such as the aryl carbonium ion and benzyne,[9] sharpened interest

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(1) O. Fischer, *Chem. Ber.*, **9**, 463 (1876).
(2) E. Bamberger, *ibid.*, **30**, 360 (1897).
(3) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).
(4) R. Huisgen and H. Nakaten, *Justus Liebigs Ann. Chem.*, **573**, 181 (1951).
(5) D. H. Hey, J. Stuart-Webb, and G. H. Williams, *J. Chem. Soc.*, 4657 (1952).
(6) G. Binsch and C. Rüchardt, *J. Amer. Chem. Soc.*, **88**, 173 (1966).
(7) G. R. Chalfont and M. J. Perkins, *ibid.*, **89**, 3054 (1967).
(8) J. I. G. Cadogan, R. M. Paton, and C. Thomson, *Chem. Commun.*, 614 (1969).
(9) (a) J. I. G. Cadogan and P. G. Hibbert, *Proc. Chem. Soc. (London)*, 338 (1964); (b) D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Commun.*, 727 (1967).

in the compound, with the result that the study of *N*-nitrosoacetanilide and its analogs has become a textbook example of the role of reactive intermediates in organic chemistry.

After a brief review of the early literature, in which the nature of the anomalies and confusions surrounding the reaction will be described, this Account will go on to describe recent work which, apart from resolving some of the century-old problems associated with the reaction, has led to what appears to be the simplest route to benzyne yet recorded.

Early Work

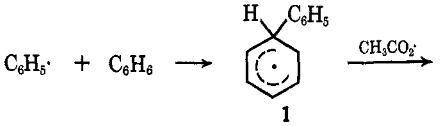
Grieve and Hey[3] were the first to suggest that biphenyl produced in the spontaneous decomposition of *N*-nitrosoacetanilide in benzene arose *via* phenyl radicals, a suggestion which was subsequently supported by the observation that the ratios of isomeric nitrobiphenyls produced in the phenylation of nitrobenzene by *N*-nitrosoacetanilide were close to those produced by authentic sources of phenyl radicals.[10] The phenyl radicals were at first assumed to arise *via* homolysis of the covalent benzenediazo acetate, isomeric with and formed from *N*-nitrosoacetanilide, and subsequently Huisgen and Horeld[11] produced evidence that the rate-determining step in the phenylation reaction was, indeed, isomerization of *N*-nitrosoacetanilide to the diazo acetate (eq 2). Soon after,[4,5] the slow isomerization step was established as an intramolecular reaction proceeding *via* a four-membered transition state (eq 3).

$$C_6H_5N(NO)COCH_3 \xrightarrow{\text{slow}} C_6H_5N{=}NOCOCH_3 \underset{\text{fast}}{\xrightarrow{C_6H_6}} C_6H_5C_6H_5 + N_2 + CH_3CO_2H \quad (2)$$

$$C_6H_5{-}\overset{N=O}{N}{-}COCH_3 \longrightarrow C_6H_5N{=}NOCOCH_3 \quad (3)$$

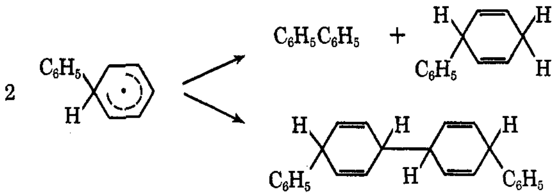
The assumption that biphenyl then arose *via* simple homolysis of the diazo acetate as in eq 4 was not tenable for two major reasons, however. First, eq 4 calls for oxidation of the intermediate phenylcyclohexadienyl radical (**1**) by an acetoxyl radical. In theory this would be expected to give the observed products, acetic acid and biphenyl, were it not for the fact that there is ample independent evidence[12] that under these conditions the acetoxyl radical decomposes to give methyl and carbon dioxide. Second, in other, well-characterized reactions of benzene with phenyl radicals, generated by dibenzoyl peroxide or phenylazotriphenylmethane,[13,14] products of dimerization and disproportionation of the intermediate phenylcyclohexadienyl radical (**1**) are formed (*e.g.*, eq 5). In the case of *N*-nitrosoacetanilide such products are absent, thus suggesting that the required oxidant for the radical **1**, in this case, is very efficient.

$$C_6H_5N{=}NOCOCH_3 \longrightarrow C_6H_5\cdot + N_2 + CH_3CO_2\cdot$$



1

$$C_6H_5C_6H_5 + CH_3CO_2H \quad (4)$$



(5)

Rationalizations of these obstacles to the understanding of the phenylation step, based on cage reactions of the cyclohexadienyl radical **1** and the acetoxyl radical, were put forward but were shown to be untenable.[15] There the matter rested until Rüchardt and Freudenberg[16] published an apparently complete explanation of the reaction in 1964.

Mechanism of Radical Phenylation of Benzene by *N*-Nitrosoacetanilide

Suschitzky and his coworkers[17] had previously made the significant discovery that arenediazonium acetate ion pairs are present in benzene solutions of substituted *N*-nitrosoacetanilides (eq 6). Freudenberg and Rüchardt[16] drew on this in putting forward the mechanism outlined in Scheme I, the key step of which involved the stable (π-type) phenyldiazotate radical, $C_6H_5N{=}NO\cdot$ (**2**), capable of abstracting hydrogen, and thus cleanly oxidizing phenylcyclohexadienyl (**1**) to biphenyl.

$$C_6H_5N(NO)COCH_3 \longrightarrow C_6H_5N{=}NOCOCH_3 \rightleftharpoons C_6H_5N_2{}^+CH_3CO_2{}^- \quad (6)$$

Another satisfactory feature of the mechanism was the postulate of the formation of acetic acid by a chain process from acetate ions and not from the unstable acetoxyl radical. The proposed mechanism involved a chain reaction initiated by acetate ion attack on benzenediazo acetate, thus leading to the requirement that trace amounts, only, of acetic anhydride should be formed. Rüchardt[6,18] supported this mechanism with the observation of a long-lived esr signal which he attributed to the $C_6H_5N{=}NO\cdot$ radical.

Very soon afterwards this apparently satisfactory explanation was brought into question by Hey, Per-

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[10] D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1475 (1956).

[11] R. Huisgen and G. Horeld, *Justus Liebigs Ann. Chem.*, **562**, 181 (1951).

[12] F. G. Edwards and F. R. Mayo, *J. Amer. Chem. Soc.*, **72**, 1265 (1950).

[13] D. F. DeTar and R. A. J. Long, *ibid.*, **80**, 4742 (1958).

[14] E. L. Eliel, M. Eberhardt, and O. Simamura, *Tetrahedron Lett.*, 749 (1962).

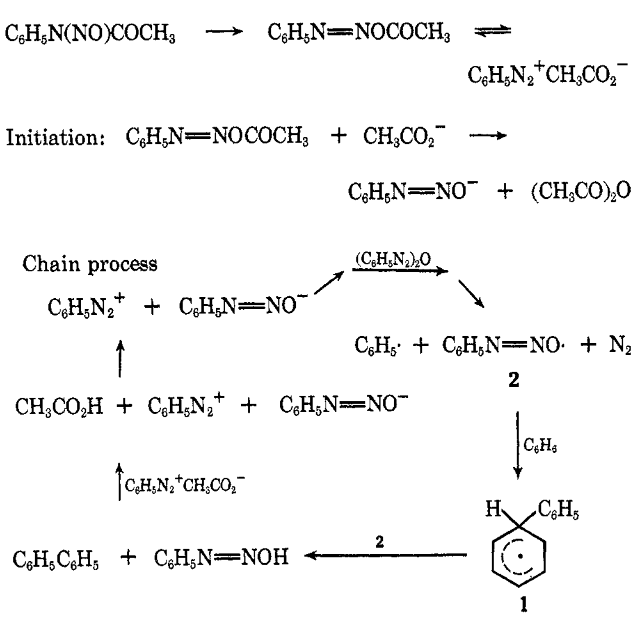
[15] E. L. Eliel and J. G. Saha, *J. Amer. Chem. Soc.*, **86**, 3581 (1964).

[16] C. Rüchardt and B. Freudenberg, *Tetrahedron Lett.*, 3623 (1964).

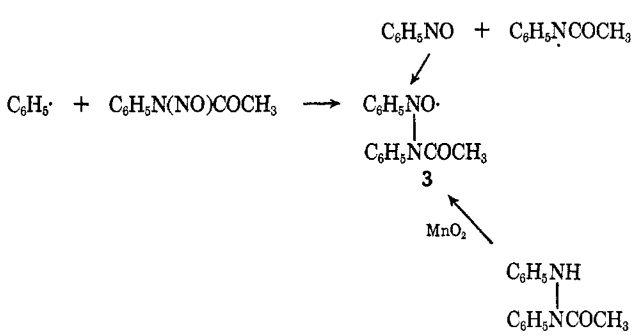
[17] P. Miles and H. Suschitzky, *Tetrahedron*, **18**, 1369 (1962); I. K. Barber and H. Suschitzky, *J. Chem. Soc.*, 2735 (1960); H. Suschitzky, *Angew. Chem., Int. Ed. Engl.*, **6**, 596 (1967).

[18] G. Binsch, E. Merz, and C. Rüchardt, *Ber.*, **100**, 247 (1967).

Scheme I



Scheme II



kins, and colleagues,[19] who suggested that the observed esr signal was that of a nitroxide ((*N*-phenylacetamido)phenyl nitroxide, **3**) produced by scavenging of a phenyl radical by *N*-nitrosoacetanilide itself (Scheme II). This suggestion was quickly given substance when Chalfont and Perkins synthesized (Scheme II) (*N*-phenylacetamido)phenyl nitroxide[7] and showed that its esr signal was identical with that from *N*-nitrosoacetanilide. Two more independent syntheses confirmed this assignment.[20] On the strength of this Chalfont and Perkins[7] went on to propose a new chain mechanism for the decomposition of *N*-nitrosoacetanilide in benzene, based on the very stable nitroxide **3** as the chain-propagating, oxidizing radical (Scheme III).

Examination of both Schemes I and II reveals that they differ only in the identity of the oxidizing radical ($C_6H_5N{=}NO\cdot$ or **3**) and the nature of the initiation step. Both involve a possible redox reaction involving the diazonium cation.

This was still not the end of the story, however, for in 1969 Cadogan, Paton, and Thomson[8] produced new esr evidence which went far in reconciling the apparently conflicting views expressed by Schemes I and III. These workers found that the signal attributable to the radical **3** (a_N = 11.6 G) was *not* present in all solvents used (as it should be if Scheme III is to be the major route to products) and that the intensity of this signal when it appeared was very weak in all solvents having an easily abstractable atom leading to a stabilized radical (*e.g.*, $C_6H_5CH_3 \rightarrow C_6H_5CH_2\cdot$). Further, in all solvents used there was a second, weak, signal consisting of nine lines arranged as a 1:1:1 triplet of 1:1:1 triplets indicating the presence in all cases of a new radical (**4**) containing two nitrogen atoms (a_{N_1} = 30.5 G; a_{N_2} = 2.3 G). Thus, in benzene, the signal of **3** was intense and almost obliterated that from the new radical (**4**). The latter became clear only at lower modulation amplitude and for this reason, presumably, was overlooked by the previous workers. In mesitylene the signal resulting from the new radical (**4**) was dominant. This new radical (**4**) was assigned the structure $C_6H_5N{=}NO\cdot$,[8] *i.e.*, the elusive phenyldiazotate radical essential to Freudenberg and Rüchardt's Scheme I, *with the important difference that it is a* σ[21] *radical* rather than the π radical postulated by Rüchardt. This followed by analogy with the splitting constants previously recorded[22] for the closely related iminoxy radicals (*e.g.*, *syn*-$C_6H_5CH{=}NO\cdot$, a_N = 29.2 G), by the fact that the signal obtained from various $ArN{=}NO\cdot$ was not influenced by the nature of para substituents, in contrast to the corresponding substituted **3**, and by the excellent agreement with theoretical calculations.[25] The constancy of the appearance of the σ $C_6H_5N{=}NO\cdot$ radical, regardless of solvent, led Cadogan, Paton, and Thomson[8,25a] to favor Rüchardt and Freudenberg's Scheme I rather than that of Chalfont and Perkins (Scheme III), on the ground that in those solvents which do not exhibit the nitroxide **3** signal there is no case for invoking a mechanism which incorporates it. On the other hand, in those cases where both signals appear (*e.g.*,

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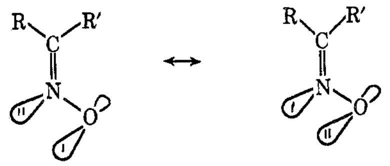
(19) G. Chalfont, M. J. Perkins, D. H. Hey, and K. S. Y. Liang, *Chem. Commun.*, 367 (1967).

(20) A. R. Forrester, *Chem. Ind.* (*London*), 1483 (1968); S. Terabe and R. Konaka, *J. Amer. Chem. Soc.* **91**, 5655 (1969).

(21) For iminoxy radicals produced by oxidation of oximes[22] the orbital containing the unpaired electron is derived from a nitrogen sp^2 orbital and an oxygen p orbital, which lies in the nodal plane of the CN π bond. This orbital is orthogonal to the molecular π system, so that the radicals are described as σ radicals.[23] This orbital type has a larger s:p ratio;[24] hence, since the hyperfine coupling constant depends on the spin density at the nucleus, iminoxy radicals are characterized by large a_N values in the region of 30 G.



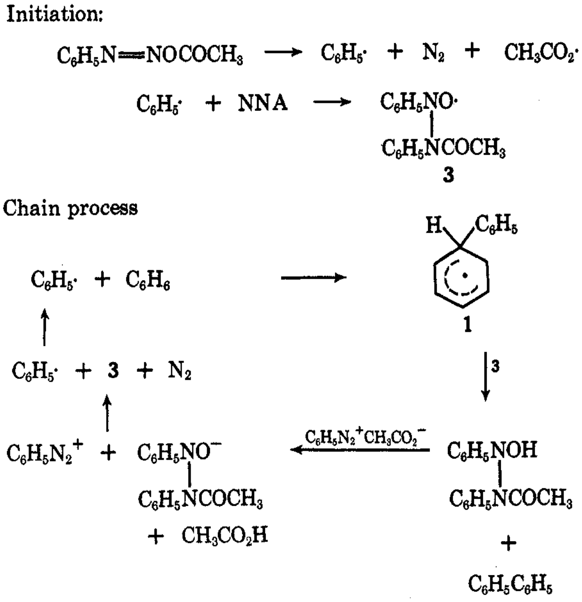
(22) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 68 (1966).

(23) M. C. R. Symons, *ibid.*, 2276 (1965); M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1985 (1964).

(24) M. C. R. Symons, *J. Chem. Soc.*, 1189 (1963); B. C. Gilbert and R. O. C. Norman, *Advan. Phys. Org. Chem.*, 1, 283 (1963).

(25) (a) J. I. G. Cadogan, R. M. Paton, and C. Thomson, *J. Chem. Soc. B*, in press; (b) C. Thomson, *Theor. Chim. Acta*, in press.

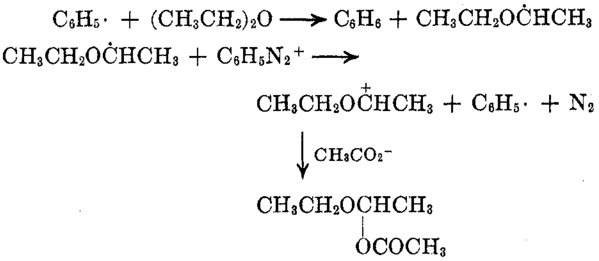
Scheme III



benzene), it is possible that both schemes may be operative.[25a]

It must be emphasized, however, that the conditions under which strong esr signals are obtained (high concentration of N-nitrosoacetanilide) are usually not those used in preparative experiments, and Cadogan, Paton, and Thomson[25a] pointed out that, once the decomposition has been initiated by a reaction depicted by Scheme I (or possibly in certain circumstances Scheme III), it is very likely replaced by an alternative, and simpler, chain process involving a redox reaction of the intermediate cyclohexadienyl radical (**1**) with unchanged diazonium cation (Scheme IV) leading to a phenyl radical, which continues the chain, and a phenylcyclohexadienyl cation, which reacts with acetate ion to give acetic acid and biphenyl.

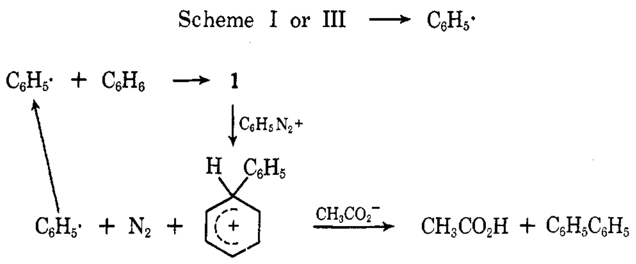
A similar redox reaction of the diazonium cation had previously been postulated, as a key step (eq 7), to explain the products of decomposition of N-nitrosoacetanilide in diethyl ether,[26] and both reactions adumbrate the use of N-nitrosoacetanilide as an indirect means of generating carbonium ions.



$$\begin{gathered}C_6H_5\cdot + (CH_3CH_2)_2O \longrightarrow C_6H_6 + CH_3CH_2O\dot{C}HCH_3\\ CH_3CH_2O\dot{C}HCH_3 + C_6H_5N_2^+ \longrightarrow\\ CH_3CH_2O\overset{+}{C}HCH_3 + C_6H_5\cdot + N_2\\ \big\downarrow CH_3CO_2^-\\ CH_3CH_2O\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCH_3\end{gathered} \tag{7}$$

The Question of Aryne Participation in the Decomposition of N-Nitrosoacetanilide and Its Derivatives

Scheme IV



The mechanism of the long-known decomposition of N-nitrosoacetanilide in benzene to give biphenyl and acetic acid, as thus far presented in this Account, is therefore best represented by Scheme IV. This scheme, however, has to be augmented to account for recent results from our laboratory which clearly point to the participation of arynes and aryne precursors (arynoids) in such decompositions.

The lead into this intriguing aspect of the chemistry of N-nitrosoacetanilide came with the observation that *o-tert*-butyl-N-nitrosoacetanilide (**5**) decomposed abnormally in benzene to give, instead of the expected 2-*tert*-butylbiphenyl, a mixture of what appeared to be the isomeric *tert*-butylphenyl acetates, "the m-isomeride preponderating."[27a] The para isomer behaved normally. Ten years later Cadogan and Hibbert[27b] returned to the reaction, showed that only the *o*- and *m-tert*-butylphenyl acetates were present (38 and 17% respectively), suggested that this indicated the intermediacy of *o-tert*-butylbenzyne, and confirmed it by the isolation of triptycene in a trapping experiment with anthracene. This has been further confirmed by trapping experiments with furan and 2,3,4,5-tetraphenylcyclopentadienone[28] and by competition reactions whereby *o-tert*-butylbenzyne, formed authentically from *o*-bromo-*tert*-butylbenzene and potassium *tert*-butoxide,[29] and *o-tert*-butyl-N-nitrosoacetanilide, respectively, were allowed to react with an excess of a mixture of arynophiles, anthracene, and 9,10-dimethoxyanthracene, the resultant rate ratios being almost identical in each case ($K_{OMe}{}^H = 13.5, 13.3$).[28] Such arynophiles all selectively suppress the formation of the *m*-acetate, leaving the *o*-acetate at the same level, thus suggesting that this special case involves rapid formation of the *o-tert*-butylphenyl carbonium ion through steric acceleration (it is known that *o-tert*-butyldiazonium salts are very unstable) (Scheme V), which can then either combine with acetate ion to give the *o*-acetate or lose a proton to give the aryne.

Control experiments with the authentic aryne having confirmed that addition of nucleophiles occurs at the meta position, it is then reasonable to suppose that addition of acetic acid to give the *m*-acetate follows.[28] The addition of acetic acid to arynes is normally not very efficient, however. That it is so in this case can be attributed to the steric shielding of the aryne by the

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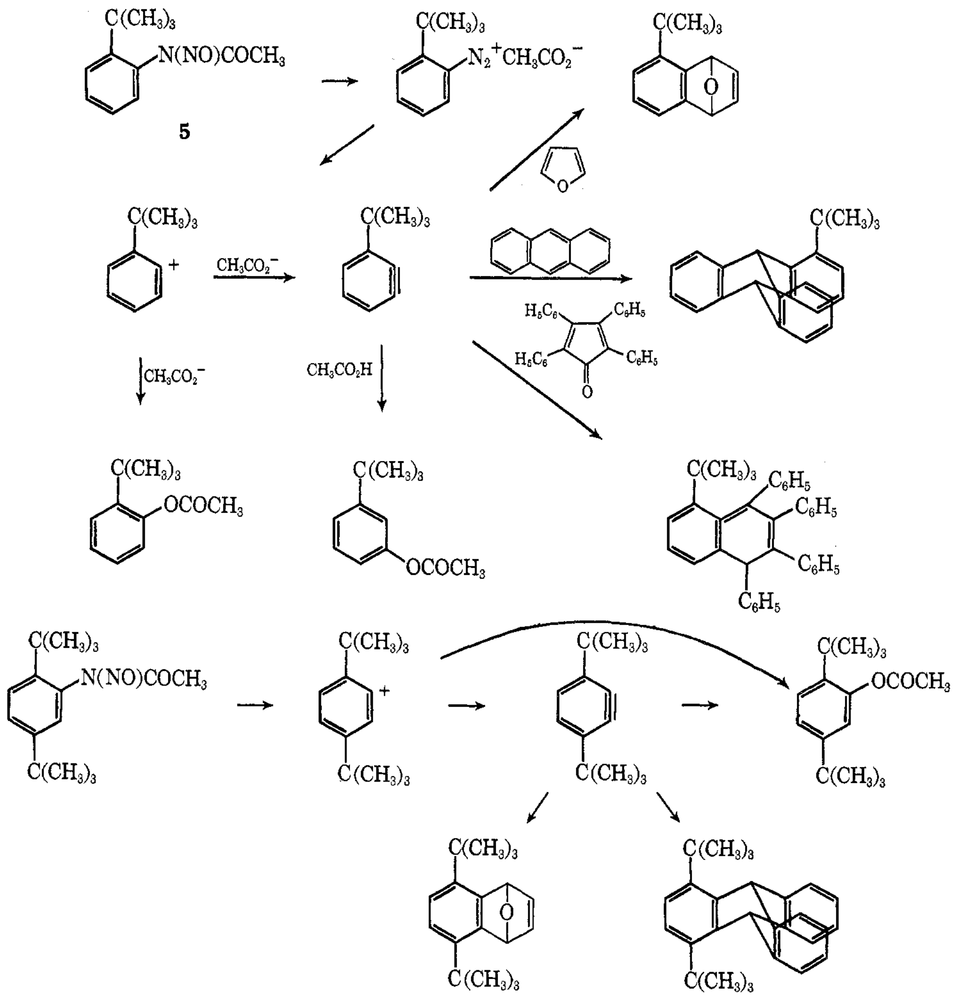
(26) J. I. G. Cadogan, R. M. Paton, and C. Thomson, *Chem. Commun.*, 229 (1970).

(27) (a) J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3352 (1954); (b) J. I. G. Cadogan and P. G. Hibbert, *Proc. Chem. Soc. London*, 338 (1964).

(28) J. I. G. Cadogan, J. Cook, M. J. P. Harger, P. G. Hibbert, and J. T. Sharp, *J. Chem. Soc. B*, in press.

(29) J. I. G. Cadogan, J. K. A. Hall, and J. T. Sharp, *ibid.*, *C*, 1860 (1967).

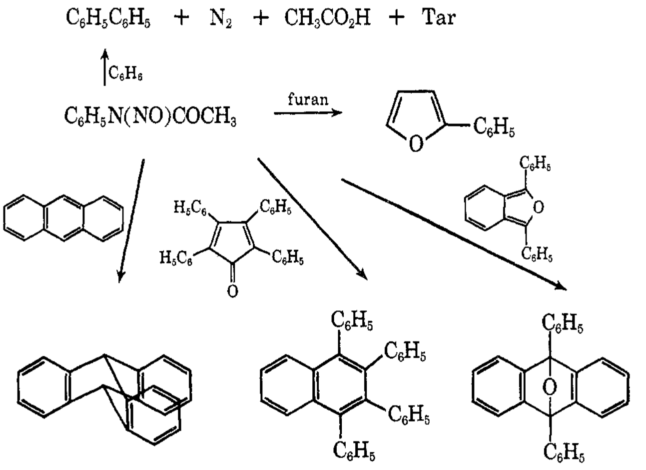
Scheme V



bulky *o-tert*-butyl group leading to a suppression of otherwise more energetically attractive side reactions (*i.e.*, it reacts with acetic acid by default). This is borne out by the decomposition of the highly hindered 2,5-butyl-*N*-nitrosoacetanilide, which gives a 79% yield of the acetate in benzene and fair yields of aryne adducts with various arynophiles (Scheme V). In accord with these observations Franck and Yanagi[30] similarly detected the corresponding aryne on decomposition of 2,5-di-*tert*-butyldiazonium salts.

Thus the anomalous case of *o-tert*-butyl-*N*-nitrosoacetanilide can be accommodated as an extension of the general Scheme IV proposed for the decompositions of *N*-nitrosoacetanilide itself. The position became very much less clear, however, when it was shown that other acylarylnitrosamines, *including N-nitrosoacetanilide itself,*[9b] also gave "aryne adducts" with tetracyclone, anthracene, and 1,3-diphenylisobenzofuran, thus suggesting aryne intermediacy, but against this, not with furan, which gave 2-phenylfuran, the "normal" product of radical phenylation (Scheme VI). The furan–benzene adduct was shown to be stable under these conditions. Further, furan, but not tetrahydrofuran, depressed the formation of aryne adducts with

Scheme VI



the former arynophiles. Substituted acylarylnitrosamines behaved similarly, and in some cases yields of aryne adduct as high as 80% were obtained [*e.g.*, *m*-$BrC_6H_4N(NO)COC_6H_4Cl$-*p* and tetracyclone; *N*-nitrosoacetanilide and 2,5-di-*p*-methoxyphenyl-3,4-diphenylcyclopentadienone, both in benzene],[9b,23,31,32]

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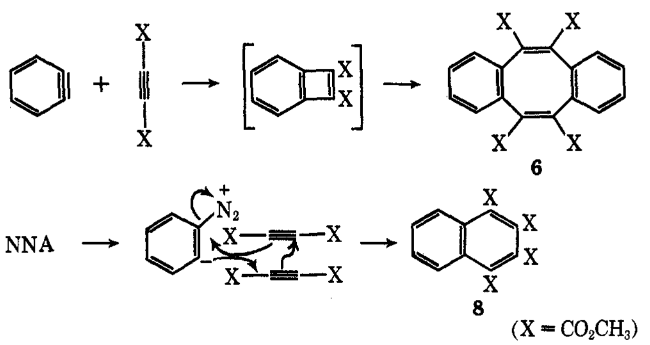
[30] R. W. Franck and K. Yanagi, *Tetrahedron Lett.*, 2905 (1966); *J. Amer. Chem. Soc.*, **90**, 5814 (1968).

[31] J. I. G. Cadogan, M. J. P. Harger, and J. T. Sharp, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**, C 19 (1969).

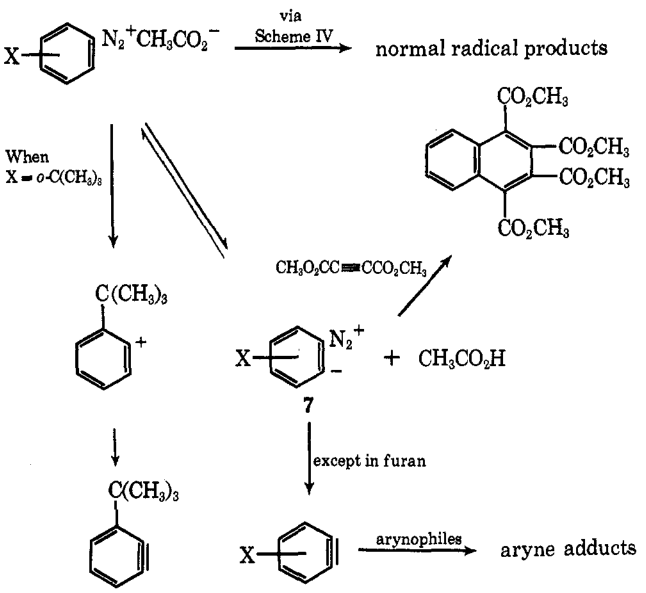
[32] J. I. G. Cadogan, J. Cook, and J. T. Sharp, unpublished observations.

Scheme VII



although in others the yield was zero, this aspect being currently under investigation. Since in former cases, *i.e.*, those giving higher yields, omission of the arynophile led to yields of biaryl as high as 50%, it appears that the arynophile is diverting some of the acylarylamine from a free radical to an aryne or arynoid route. Thus the situation is markedly different from the special case of *o-tert*-butyl-*N*-nitrosoacetanilide. It is also particularly noteworthy that the presence of water causes the reaction between the acylarylamine and the arynophile to proceed as it would in the absence of the arynophile, a point which became of great importance in subsequent adaptations (see below) of the reaction as a source of arynes. It is also of interest that reactions of *N*-nitroso-*p*-chlorobenzanilides [ArN(NO)COC$_6$H$_4$-Cl-*p*] in dry carbon tetrachloride gave *p*-chlorobenzoic acid as a *primary* product, indicating that abstraction of hydrogen as well as loss of nitrogen from the nitrosamide had occurred (this took place in the absence of tetracyclone).[9b] Also formed was *p*-chlorobenzoic anhydride (*ca.* 0.15 ml/mole), thus providing evidence for the participation of a reaction such as the first step of the Rüchardt mechanism (Scheme I).

Scheme VIII



Further experiments bearing on the nature of the intermediate included those which disposed of the possibility of the formation of aryne adducts *via* a monodentate species (*e.g.*, a radical or carbonium ion) and competition experiments wherein authentic sources of benzyne were allowed to react with pairs of arynophiles, excluding furan, the results being identical with those corresponding competition reactions involving *N*-nitrosoacetanilide.[33] These latter results would appear to point clearly to an aryne intermediate were it not for the failure of furan as a trap. To be satisfactory, any postulated mechanism must also account for the observation that, whereas authentic benzyne, from pentyl nitrite and anthranilic acid, reacts with dimethyl acetylenedicarboxylate to give a low yield of the dibenzocyclooctatetraene (**6**; Scheme VII), the intermediate from *N*-nitrosoacetanilide under the same conditions gave, among other products, tetramethyl naphthalene-1,2,3,4-tetracarboxylate (**8**; Scheme VII),[32] suggesting the intermediacy of an arynoid species such as **7**. These results point to the overall reaction sequence illustrated in Scheme VIII, which involves the intermediacy of the arynoid species **7**, in equilibrium with the diazonium cation, which can be trapped by the reactive dimethyl acetylenedicarboxylate. Scheme VIII can accommodate the effect of furan by assuming either that the acidity of the hydrogen atom ortho to the diazo group is reduced by π donation involving furan and the diazonium cation and/or that removal of the diazonium acetate ion pair *via* Scheme IV is fast (which might be considered to be reasonable in view of the low aromatic character and relatively high degree of diene localization of furan). Scheme VIII can accommodate the apparent diversion of diazonium acetate from a radical to an aryne pathway by certain added arynophiles if it is assumed that the arynophile either converts **7** into the aryne or reacts with **7** as well as with the aryne, although the latter possibility is difficult to reconcile with the results of the competitive experiments. Scheme VIII also accounts for the special case of *o-tert*-butyl-*N*-nitrosoacetanilide (and the 2,5-di-*tert*-butylbenzenediazonium cation[30]). The difference between this and other cases is one of the timing of the loss of nitrogen from the diazonium cation. With *o-tert*-butyl, this occurs first to give the aryl cation, whereas in all other cases so far investigated removal of the acidic proton ortho to the diazonium function occurs before loss of nitrogen.

Pyridine also exhibits behavior similar to that of furan in that it depresses the formation of aryne adducts. It is likely in this case, however, that this is due to preferential capture of the diazonium cation by pyridine, as suggested by Abramovitch and Saha[34] (eq 8). Experimental verification of each of these

$$C_6H_5N_2{}^+CH_3CO_2{}^- + C_5H_5N \longrightarrow C_6H_5N_2N^+C_5H_5CH_3CO_2{}^- \quad (8)$$

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(33) J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *Chem. Commun.*, 299 (1970).

(34) R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **12**, 3297 (1965).

suggestions has still to be made. In the meantime, Scheme VIII represents a fairly simple rationalization of the complex behavior although it is confidently expected that further experiments will lead to refinements (or even abandonment!) of the scheme. In particular, Scheme VIII will have to be extended to account for the behavior of *N*-nitrosoacetanilides in polyhalomethanes, which is different yet again. Thus in carbon tetrachloride benzenediazonium chloride is formed,[3] while in bromotrichloromethane at room temperature the major products are bromobenzene and benzenediazonium chloride, with some benzenediazonium acetate.[32] Among the possible intermediates which must be considered in these cases is the trichloromethyl anion and hence dichlorocarbene and the chloride ion.

Regardless of these details, however, the investigation of the mechanism of this reaction has led to new routes to arynes. Thus, Rüchardt and Tan showed[35a] that reaction of benzenediazonium fluoroborate with potassium acetate in the presence of tetracyclone and anthracene gave the benzyne adducts in good yield (40% based on $C_6H_5N_2{}^+BF_4{}^-$; 80% based on tetracyclone taken). They also noted the failure of furan to react.[35b] More recent work in our laboratory, however, has led to what appears to be the simplest route to benzyne yet recorded, in which aniline is converted in a single operation into benzyne,[36] *via* reaction with acetic anhydride and pentyl nitrite, as shown by trapping with tetracyclone (32% based on $C_6H_5NH_2$; Scheme IX).

The rationale of this reaction is based on the previously recorded[37] *in situ* diazotization of aniline using pentyl nitrite and the fact that benzenediazonium acetate gives benzyne, as shown by the above discussion of *N*-nitrosoacetanilide (Scheme VIII). Previously it had been shown that *in situ* diazotization of 2,5-di-*tert*-butylaniline in the presence of carboxylate ion gives the corresponding aryne.[30] The corresponding reaction with other anilines did not occur, however.[36] Our contribution has been to recognize the special nature of the *o*-*tert*-butyl *vs.* other cases and the fact that water inhibits aryne formation from acylarylnitrosamines and hence diazonium acetates (with the exception of the *o*-*tert*-butyl case). Since water is produced in the *in situ* diazotization of arylamines, the reason for the above failure of the *in situ* conversion

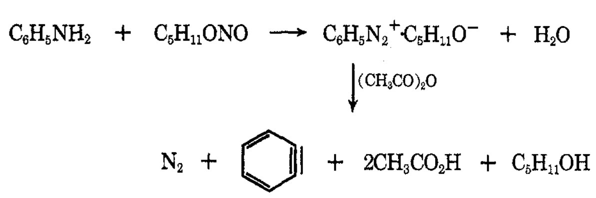
$$ArNH_2 + RONO \longrightarrow ArN_2{}^+OR^- + H_2O$$

of arylamines to arynes is obvious (in confirmation of this we find that Rüchardt and Tan's conversion of benzenediazonium fluoroborates, in the presence of acetate ion, into benzyne fails in the presence of water). This barrier is overcome by the use of acetic anhydride instead of acetic acid. This can act in a dual role as a dehydrating agent, and hence a source of acetate, and/or as an acetylating agent (and source of acetate). In the latter case pentyl nitrite would act, not as a direct diazotizing agent, but as a nitrosating agent for acetanilide[38] to give *in situ* nitrosoacetanilide, a reaction which does not give water.

$$ArNH_2 \longrightarrow ArNHCOCH_3 \xrightarrow{RONO} ArN(NO)COCH_3 + ROH$$

That acetic anhydride may fulfill both functions appears to follow from the fact that acetanilide in the presence of pentyl nitrite gives 9% of the benzyne adduct under similar conditions. Following this, the use of the much more efficient combined nitrosating and acylating agent *p*-chlorobenzoyl nitrite, with preformed acetanilide, gives benzyne in 51% yield.[36]

Scheme IX



In any event, the reaction of aniline with acetic anhydride in the presence of pentyl nitrite appears to have great promise of development as a route to certain arynes under mild conditions. In accord with this the reaction has been shown to be successful for *m*-anisidine, *m*-toluidine, *m*-chloroaniline, and *m*-bromoaniline. It is to be expected, however, that there will be limitations of the type recorded for the corresponding acylarylnitrosamines,[9b] but within these, the reaction will allow synthetic applications of arynes to be exploited much more readily than has been possible hitherto.

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(35) (a) C. Rüchardt and C. C. Tan, *Angew. Chem., Int. Ed. Engl.*, 522 (1970); (b) personal communication.

(36) J. I. G. Cadogan, J. R. Mitchell, and J. T. Sharp, *Chem. Commun.*, 1 (1971).

(37) J. I. G. Cadogan, *J. Chem. Soc.*, 4257 (1962).

(38) E. B. McCall and E. J. Blackmann, British Patent 929,093; *Chem. Abstr.*, **59**, 12,704 (1963).