Acylarylnitrosamines. Part IX.[1] Use of Benzyne Promoters in the Conversion of *N*-Nitrosoacetanilide into Benzyne

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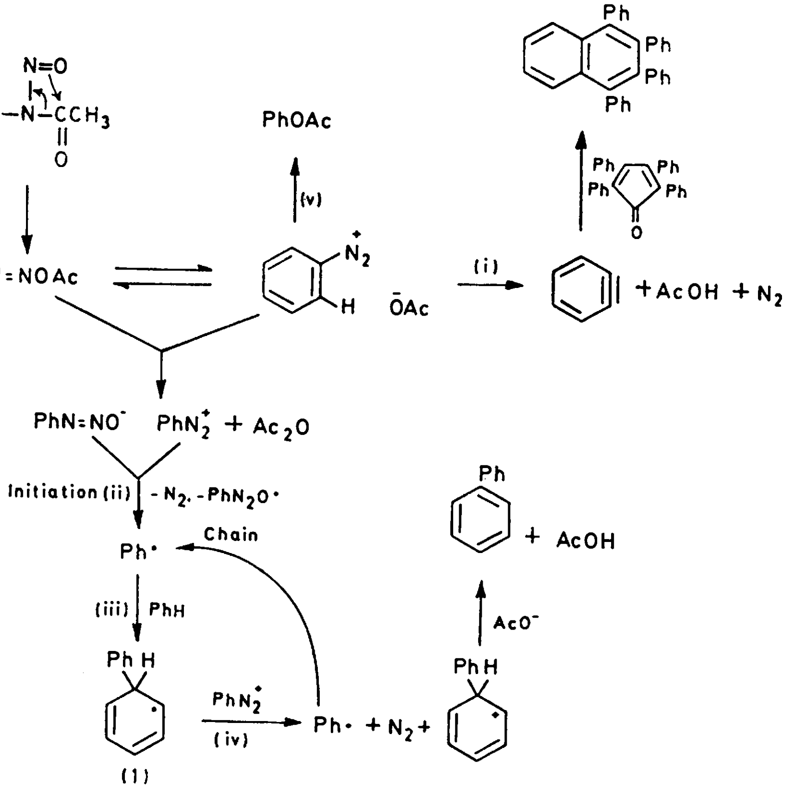
N-Nitrosoacetanilide (NNA), and hence benzenediazonium acetate, decomposes in solution to give benzyne and/or phenyl radicals. Tetraphenylcyclopentadienone diverts the decomposition to give benzyne mainly, while furan, despite being an arynophile, diverts the reaction towards phenyl radicals. The addition of 1,1-diphenylethylene, styrene, 2,3-diphenylindenone, *trans*-stilbene, triphenylethylene, 1,3,4-triphenylbut-2-ene-1,4-dione, or 3,4-diphenylbut-3-en-2-one to the latter reaction promotes the formation of benzyne relative to phenyl radicals, even in the presence of furan. The relevance of these results to the tetracyclone effect is discussed in terms of removal of chain-initiating phenyl radicals by reaction with the unsaturated compounds thus allowing the competing eliminative formation of benzyne from benzenediazonium acetate to become dominant.

N-NITROSOACETANILIDE (NNA), and hence benzenediazonium acetate decomposes in benzene by two competing routes[1,2] to give benzyne *via* acetate-induced elimination[3] [Scheme 1, step (i)] and/or phenyl radicals. There is good evidence that the radical route involves a chain process initiated as in step (ii) of Scheme 1[4] and sustained by redox reaction of the intermediate phenylcyclohexadienyl radical (1) with unreacted diazonium cation[2a,5] [Scheme 1, steps (iii) and (iv)]. Recently Nonhebel produced further good evidence for the reality of this redox reaction.[6]



SCHEME 1

An unexplained feature of the reaction lies in the observations that while yields of up to 80% of biphenyl have been recorded on decomposition of NNA alone in benzene, decomposition in the presence of added tetraphenylcyclopentadienone (tetracyclone), as a benzyne trap, led to equally high yields of the benzyne adduct 1,2,3,4-tetraphenylnaphthalene. We have discounted[1] an explanation based on the reversibility of step (i), as a result of isotopic labelling experiments, and in this and the succeeding paper we describe an investigation of the more likely possibility that the tetracyclone effect is due

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[1] Part VIII, J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Perkin II*, 1975, 546.

[2] (*a*) J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, **4**, 186; (*b*) B. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J.C.S. Perkin I*, 1972, 2563.

[3] J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Perkin II*, 1974, 1321.

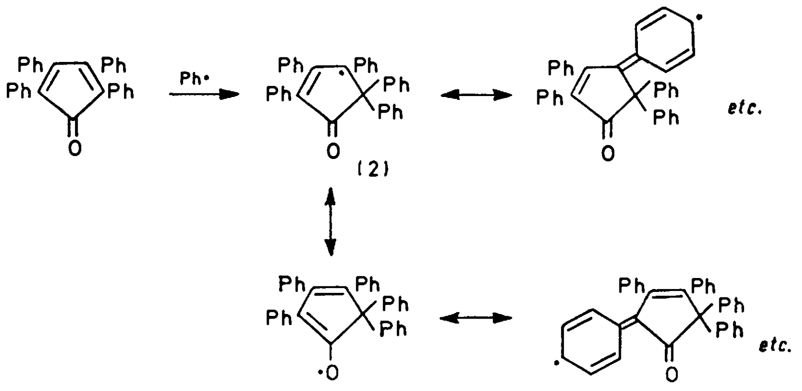
[4] C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, 1964, 3623.

[5] J. I. G. Cadogan, R. M. Paton, and C. Thomson, *J. Chem. Soc.* (*B*), 1971, 583.

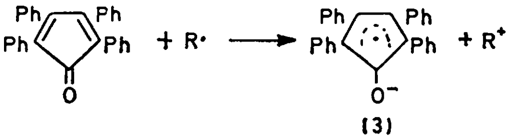
[6] R. Henriquez, A. R. Morgan, P. Mulholland, D. C. Nonhebel, and G. G. Smith, *J.C.S. Chem. Comm.*, 1974, 987.

to inhibition of the competing radical chain phenylation [steps (iii) and (iv)]. This would allow the benzyne-forming step (i) to become dominant, with ultimate trapping of the intermediate by tetracyclone, which would thus have a dual role.

In theory, such inhibition could occur in two ways: either by removal of the chain-initiating phenyl radicals by addition to the dienone system (Scheme 2), to give radicals such as (2) which would be expected to be long lived as a result of spin delocalisation and by resistance to oxidation by the diazonium cation, there being no available hydrogen atoms. Alternatively, direct oxidation by tetracyclone of any radicals present to give the long lived, and hence chain-inhibiting, tetracyclone radical-ion (3) would have the same effect (Scheme 3).



SCHEME 2



SCHEME 3

Regardless of the nature of the inhibiting radical, which we will return to later, it might be expected that unsaturated compounds, such as those given in Table 1, which are structurally related to tetracyclone, but which are not arynophiles, would exhibit the tetracyclone effect by promoting the formation of benzyne from NNA at the expense of phenyl radicals.

Accordingly we allowed NNA to decompose in the presence of an equimolar amount of the benzyne promoters given in Table 1, in a mixture of furan (12 mol) and benzene (28 mol). The basis of our experiments was the known high reactivities of furan and the resulting radical (4) in the radical chain phenylation *via* NNA (Scheme 4),[7,8] which lead to high yields of 2-phenylfuran but to no more than 7% of the furan-benzyne adduct. If the above argument concerning the function of tetracyclone as a benzyne promoter is correct we would then expect inhibition of the chain reaction with concomitant formation of benzyne which would then be trapped by furan. Table 1 records the experimental realisation of these expectations. In each case we measured the yields of the radical-derived products, biphenyl and 2-phenylfuran, the benzyne adduct, 1,4-dihydro-1,4-epoxynaphthalene (5), and phenyl acetate. Each of the olefinic benzyne promoters markedly increased the yield of benzyne adduct relative to phenylated products. 2,3-Diphenylindenone, which is closely related to tetracyclone, but is not an arynophile, increased the yield of the benzyne-furan adduct from 7 (in the absence of a promoter) to 37%, while the ratio of benzyne to phenyl radicals

TABLE 1

Reactions of addenda with NNA in benzene–furan at 60° *

	Product (%)			
(A) Addendum	Phenyl acetate	2-Phenyl-furan	1,4-Dihydro-1,4-epoxy-naphthalene	Bi-phenyl
None	4	50	7	10
2,3-Diphenyl-	21	8	37	2
indenone	9 †	40	19	
BzCH=CPhBz	18	13	43	4
AcPhC=CHPh	11	30	23	6
$Bz_2C=CH_2$ §	5	45	5	4
$Ph_2C=CH_2$	25	6	46	2
PhCOCOPh	7	42	11	10
$Ph_2C=CHPh$	15	25	27	6
trans-PhCH=CHPh	17	18	32	5
$PhCH=CH_2$	22	9	42	2
(B) Dependence on concentration of $Ph_2C=CH_2$				
NNA : $Ph_2C=CH_2$ molar ratio				
1.0	23	5	44	1
0.5	23	5	43	1
0.1	17	15	29	4
(C) Dependence on concentration of furan ‡				
Furan : NNA molar ratio				
0.9	20	1	29	9
2.6	22	2	39	6
9.0	22	6	43	5
26	18	16	40	2

* Except in series (C), the molar ratio of benzene to furan was 2.4 : 1 and that of furan to NNA was 12 : 1. † In neat furan. ‡ With $Ph_2C=CH_2$ as promoter, $Ph_2C=CHPh$ (6—8%) was also formed in these reactions. § This experiment was kindly carried out by Mr. J. Brennan.

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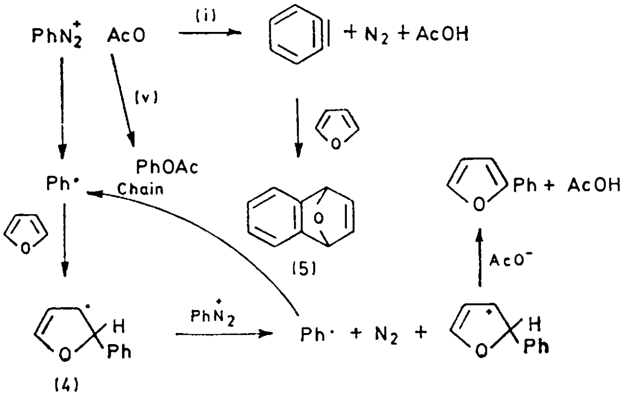
[7] D. L. Brydon, J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *J. Chem. Soc.* (*B*), 1971, 1996.

[8] V. Hassmann, C. Rüchardt, and C. C. Tan, *Tetrahedron Letters*, 1971, 3883.

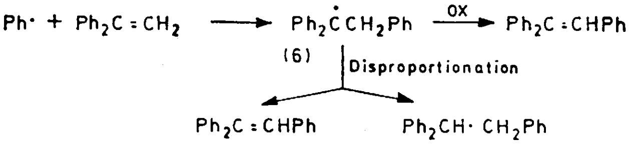
detected increased from 0.1 to 3.7. Even the presence of a large excess of furan undiluted with benzene, when it might be expected that the chain inhibition effect of the promoter would be least and the chain enhancing effect of furan would be greatest, led to a significant increase in the production of benzyne.



SCHEME 4

1,1-Diphenylethylene was found to be the best promoter, followed by 1,3,4-triphenylbut-2-ene-1,4-dione, styrene, 2,3-diphenylindenone, *trans*-stilbene, and triphenylethylene.

Table 1 further illustrates the efficiency of 1,1-diphenylethylene as a benzyne promoter, an appreciable yield (29%) of benzyne–furan adduct being obtained when only 0.1 mol. equiv. of the promoter, based on NNA, was present. Similarly, even in the presence of a large excess of furan, 1,1-diphenylethylene still functions well (Table 1). It is also significant that triphenylethylene (6—8%) and smaller quantities of 1,1,2-triphenylethane were isolated from reactions involving 1,1-diphenylethylene. These are in accord with the intermediacy of the benzyldiphenylmethyl radical in the reaction (Scheme 5) which can be oxidised to the alkene and/or undergo disproportionation to give both alkene and alkane, and there is a precedent for the latter reaction.[9] The isolation of phenylated derivatives of 1,1-diphenylethylene suggests that inhibition *via* radicals such as (2) or (6) are responsible for benzyne promotion rather than radical-anions such as (3), and in the succeeding paper we present e.s.r. spectroscopic evidence which supports this.[10]



SCHEME 5

The relative efficiencies of these promoters also support this concept, the most efficient being those which give ample opportunity for the creation of radical centres conjugated with phenyl groups. Tetracyclone clearly offers the best delocalisation followed by diphenylindenone and the di- and mono-substituted phenylethylenes. Steric crowding, as in triphenylethylene, reduces the ease with which the phenylated product is formed and hence the efficiency of the promoter. The need for conjugated phenyl groups is further demonstrated by the low efficiency of 1,1-dibenzoylethylene.

A feature of the promoted decompositions of NNA is the increase in yields of phenyl acetate, compared with the unpromoted reaction (Table 1). This we attribute mainly to direct nucleophilic displacement on the diazonium cation [Schemes 1 and 4, step (v)] which is more readily available as a result of inhibition of the competing radical chain by the benzyne promoters. Reaction by addition of acetic acid to benzyne cannot be completely discounted but this is known to be an unfavoured reaction except in the special case of the decomposition of *o*-t-butyl-*N*-nitrosoacetanilide.[11]

These results emphasise the major differences in behaviour in the presence of NNA of the two arynophiles, tetracyclone and furan, the former almost completely inhibiting the radical chain phenylation and thus promoting benzyne formation, while the latter does the reverse. It was of interest therefore, to examine the effects of other arynophiles.

Thus NNA, prepared *in situ* by reaction of 4-chlorobenzoyl nitrite and acetanilide,[2b] was allowed to decompose in the presence of an equimolar amount of a series of benzyne traps in a large excess of benzene, and the resulting yields of biphenyl and/or benzyne adducts were determined by isolation and g.l.c. The results in Table 2 show that only those arynophiles closely related to tetracyclone exhibited a marked ' tetracyclone effect ' with good yields (59—64%) of benzyne adducts and low yields of phenylated products (5—9%). Anthracene, pyran-2-one, and methyl 6-oxopyran-3-carboxylate, on the other hand, were intermediate in behaviour between furan and tetracyclone with respect to their effect on benzyne-formation from NNA. The results of experiments designed to examine the effects

TABLE 2

Products from the reaction of 4-chlorobenzoyl nitrite with acetanilide in the presence of benzyne traps

Arynophile	Biphenyl (mol per 100 mol)	Adduct (mol per 100 mol)
Tetraphenylcyclopentadienone	12	71
2,5-Diethyl-3,4-diphenylcyclopentadienone	5	60
2-Methyl-3,4,5-triphenylcyclopentadienone	7	64
Acecyclone	9	59
Pyran-2-one	28	23
Methyl-6-oxopyran-3-carboxylate	26	18
Anthracene	24	16

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[9] D. B. Denney and N. F. Newman, *J. Amer. Chem. Soc.*, 1967, **89**, 4692.

[10] E. A. Bell, J. I. G. Cadogan, P. W. Milburn, C. D. Murray, R. M. Paton, and J. T. Sharp, following paper.

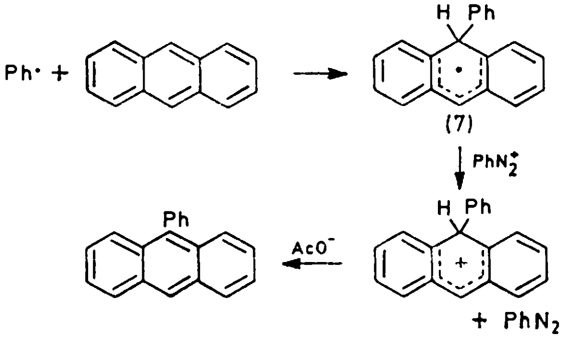
[11] J. I. G. Cadogan, J. Cook, M. J. P. Harger, P. G. Hibbert, and J. T. Sharp, *J. Chem. Soc.* (*B*), 1971, 595.

of benzyne promoters on the decomposition of NNA in benzene in the presence of anthracene (Table 3) were, therefore, at first sight, surprising, in that no benzyne promotion was observed, in contrast to the case of furan (Table 1). The results can be explained, however, if we take into account the known[12] high reactivity of anthracene towards radicals leading, even in the presence of benzyne promoters, to a rapid build up of 9-phenylanthracenyl radicals (7), which are readily oxidised to 9-phenylanthracene thereby regenerating a phenyl radical (Scheme 6). The corollary is that radicals derived from addition of phenyl radicals to promoters *e.g.* (2) are not easily oxidised. These and other aspects of the phenomenon of benzyne promotion are currently being investigated.

TABLE 3

Triptycene yields in the decomposition reactions of *in situ* NNA in the presence of anthracene and various addenda

Addendum	Triptycene (mol per 100 mol)
cis-$EtO_2CCH{=}CHCO_2Et$	18
$CH_2{=}CHCO_2Me$	17
trans-$EtO_2CCH{=}CHCO_2Et$	18
Tetrachlorobenzoquinone	10
$Ph_2C{=}CH_2$	5
PhCH=CPhAc	17
BzPhC=CHPh	18
2,3-Diphenylindenone	15
2,3,4,5-Tetraphenylcyclopent-2-enone	14
None	17



SCHEME 6

EXPERIMENTAL

Chromatography.—For analytical and quantitative g.l.c. investigations, a Pye 104 chromatograph, with flame ionisation detector was used together with 2 m × 2.2 mm i.d. packed columns. Quantitative measurements were made after calibration of the instrument with known mixtures of purified authentic samples and internal standards. For preparative g.l.c. a Pye 105 model 15 was used.

Dry column chromatography was carried out after the method of Loev and Goodman[13] using chromatographic alumina, treated with Woelm fluorescent indicator for shortwave irradiation (254 nm), and deactivated to Brockman activity 3—4. The columns were made up in *C* gauge, 2 in nylon tubing supplied by Walter Coles and Co. Ltd., London. After development, the columns were sliced and the products washed off with ether or chloroform.

Solvents.—Rigorously dried solvents were essential.[2b] Benzene, cyclohexane, and cyclohexene, after standing over sodium, were distilled from calcium hydride under nitrogen. Furan was passed through a short alumina column, distilled from lithium aluminium hydride, and stored over molecular sieve.

Reagents.—The mode of decomposition of *N*-nitrosoacetanilide is markedly influenced even by traces of water.[2b] The best route to the anhydrous product was as follows: acetanilide (10 g, 7.4 mmol), fused potassium acetate (10 g), and phosphorus pentaoxide (1 g) were stirred in a mixture of acetic acid (70 ml) and acetic anhydride (30 ml) at 0° for 10 min. Nitrosyl chloride (6.0 g, 92 mmol), in a 30% w/v solution in acetic anhydride, was added over 30 min. After 30 min at 0° the mixture was poured onto ice–water (500 ml). The yellow *N*-nitrosoacetanilide was collected, washed with cold water, dried between filter papers, then over P_2O_5 (0.05 mm for 3 h), and stored at −15°. The product (9.6 g, 79%) had m.p. 50° (decomp.) [lit.,[14] 50° (decomp.)]. The sample had no NH absorption in the i.r. 4-Chlorobenzoyl nitrite was prepared as described previously.[2b]

Preparation of Arynophiles and Related Compounds.—Tetraphenylcyclopentadienone had m.p. 218—220° (lit.,[15] 218—220°). The following substituted cyclopentadienones were prepared by Allen and Van Allan's method:[16] 2,5-diethyl-3,4-diphenylcyclopentadienone, m.p. 102—103° (lit.,[16] 103°), 2,5-dimethyl-3,4-diphenylcyclopentadienone, m.p. 183—184° (lit.,[16] 181—182°), 2-methyl-3,4,5-triphenylcyclopentadienone, m.p. 197—198° (lit.,[16] 196°). 2,5-Diphenyl-3,4-(α,α-naphthylene)cyclopentadienone (acecyclone), m.p. 287—289° (lit.,[17] 289°) was prepared by a modification of the above method.[17] Methyl 6-oxopyran-3-carboxylate had m.p. 69—72° (lit.,[18] 69—70°), and pyran-2-one had b.p. 102° at 23 mmHg (lit.,[19] 110° at 26 mmHg). 1,4-Diphenylbut-2-ene-1,4-dione had m.p. 126—128° (lit.,[20] 129°), 1,1-diphenylethylene had b.p. 122—124° at 5 mmHg (lit.,[21] 113° at 2 mmHg), 2,3-diphenylindenone had m.p. 149—150° (lit.,[22] 149—151°), and 1,2,3,4-tetraphenylcyclopent-2-enone had m.p. 161° (lit.,[23] 161°). 1,3,4-Triphenylbut-2-ene-1,4-dione had m.p. 126—128° (lit.,[20] 129°).

Reactions of 4-Chlorobenzoyl Nitrite with Acetanilide in the Presence of Arynophiles.—(i) *With tetraphenylcyclopentadienone*. This gave 1,2,3,4-tetraphenylnaphthalene (71%) and biphenyl (12%) as described previously.[2b]

(ii) *With anthracene*. 4-Chlorobenzoyl nitrite (1.6 g, 8.6

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[17] C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, 1952, **17**, 845.

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[22] C. F. H. Allen, J. W. Gates, and J. A. Van Allan, *Org. Synth.*, 1947, **27**, 30.

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mmol) in benzene (50 ml) was added over 30 min to a mixture of acetanilide (0.675 g, 5 mmol) and anthracene (0.9 g, 5 mmol) in boiling benzene (100 ml). The mixture was boiled under reflux for 12 h, concentrated by evaporation, and maleic anhydride (1 g) and chlorobenzene (20 ml) added. After 2 h at the b.p., chromatography on alumina gave biphenyl (0.18 g, 24 mol per 100 mol) and triptycene (0.20 g, 16 mol per 100 mol), m.p. and mixed m.p. 256° after recrystallisation. The i.r. (Nujol) spectrum was indistinguishable from that of an authentic sample. In a replicate experiment the yield of 9-phenylanthracene (5 mol per 100 mol) was established by g.l.c. (1% SE30; 230°) analysis, using triptycene as the internal standard.

(iii) *With acecyclone*. 4-Chlorobenzoyl nitrite (0.95 g, 5.1 mmol) in benzene (25 ml) was added over 30 min to a mixture of acetanilide (0.41 g, 3 mmol) and acecyclone (1.07 g, 3 mmol) in boiling benzene (75 ml). The mixture was boiled under reflux for 5 h, concentrated and applied to an alumina column. Elution with petrol gave biphenyl (0.040 g, 9 mol per 100 mol) and 7,12-diphenylbenzo[*k*]fluoranthene (0.72 g, 59 mol per 100 mol). Recrystallisation of the benzyne adduct from acetic acid gave colourless crystals, m.p. 273—274° (lit.,[17] 273—274°).

(iv) *With pyran*-2-*one*. 4-Chlorobenzoyl nitrite (0.95 g, 5.1 mmol) in benzene (25 ml) was added over 30 min to a solution of acetanilide (0.41 g, 3 mmol) and pyran-2-one (0.29 g, 3 mmol) in boiling benzene (75 ml). After 5 h at the b.p. quantitative examination by g.l.c. (5% NPGS; 130°) using bibenzyl as internal standard gave biphenyl (28 mol per 100 mol) and naphthalene (23 mol per 100 mol). Mass spectral–g.l.c. analysis of the biphenyl and naphthalene peaks gave spectra identical to those of authentic samples.

(v) *With methyl* 6-*oxopyran*-3-*carboxylate*. Similarly were obtained biphenyl (26 mol per 100 mol) and 2-methoxycarbonylnaphthalene (18 mol per 100 mol).[18] Mass spectral–g.l.c. analysis of the product peaks gave spectra identical to those of authentic samples.

(vi) *With furan*. Similarly was obtained biphenyl (54 mol per 100 mol). No peak corresponding to 1,4-dihydro-1,4-epoxynaphthalene [24] was found (0.1 mol per 100 mol would have been detected).

(vii) *With* 2,5-*diethyl*-3,4-*diphenylcyclopentadienone*. 4-Chlorobenzoyl nitrite (0.8 g, 4.25 mmol) in benzene (20 ml) was added over 30 min to a solution of acetanilide (0.34 g, 2.5 mmol) and 2,5-diethyl-3,4-diphenylcyclopentadienone (0.68 g, 2.5 mmol) in boiling benzene (60 ml). The mixture was boiled under reflux for 12 h and maleic anhydride (1 g) added to remove unchanged trap. Dry column chromatography of the mixture on alumina, eluting with cyclohexane, afforded biphenyl (0.019 g, 5 mol per 100 mol) and 1,4-*diethyl*-2,3-*diphenylnaphthalene* (0.50 g, 60 mol per 100 mol), colourless crystals from acetic acid, m.p. 141—142° (Found: C, 92.5; H, 7.1. $C_{26}H_{24}$ requires C, 92.85; H, 7.15%), *m/e* 336 (*M*), τ ($CDCl_3$) 1.8—3.0 (14 H, m, aromatic), 7.16 (4 H, q, CH_2), and 8.84 (6 H, t, CH_3).

(viii) *With* 2-*methyl*-3,4,5-*triphenylcyclopentadienone*. Reaction as in (vii) gave biphenyl (0.031 g, 7 mol per 100 mol) and 1-*methyl*-2,3,4-*triphenylnaphthalene* (0.71 g, 64 mol per 100 mol), as colourless needles from light petroleum (b.p. 60—80°), m.p. 165—166° (Found: C, 93.9; H, 5.9. $C_{29}H_{22}$ requires C, 94.05; H, 5.9%), *m/e* 370 (*M*), τ ($CDCl_3$) 1.8—3.2 (19 H, m, aromatic) and 7.48 (3 H, s, CH_3).

(ix) *In the absence of an arynophile*. To a solution of acetanilide (0.41 g, 3.0 mmol) in boiling benzene (75 ml), 4-chlorobenzoyl nitrite (0.93 g, 5.0 mmol) in benzene (25 ml) was added over 30 min. After 5 h at the b.p. quantitative analysis of the mixture by g.l.c. (5% NPGS; 130°) using bibenzyl as internal standard gave the yield of biphenyl as 63 mol per 100 mol.

Decomposition of N-*Nitrosoacetanilide, prepared* in situ *from* 4-*Chlorobenzoyl Nitrite and Acetanilide, in the Presence of Anthracene and Various Addenda*.—*General method*. 4-Chlorobenzoyl nitrite (1.6 g, 8.6 mmol) in benzene (40 ml) was added over 30 min to a boiling solution of acetanilide (0.675 g, 5 mmol), anthracene (0.9 g, 5 mmol), and the addendum (5 mmol) in benzene (100 ml). The mixture was then boiled under reflux for 12 h and concentrated. Maleic anhydride (1 g) and chlorobenzene (25 ml) were added and the solution was boiled for 3 h. G.l.c. analysis (5% SE30; 220°) of the reaction mixture using fluoranthene as internal standard gave the yield of triptycene. The results obtained are summarised in Table 3.

Reactions of N-*Nitrosoacetanilide in Benzene–Furan Mixtures in the Presence of Various Addenda* (*Table* 1).—(i) *General method*. *N*-Nitrosoacetanilide (0.6 g, 3.6 mmol) was added to a solution of the addendum (3.6 mmol) in furan (3 ml, 0.042 mol) and benzene (9 ml, 0.101 mol) with vigorous stirring at 60°. The reaction mixture was then stirred at this temperature for a further 2 h. Quantitative g.l.c. (2% CAR; 135°) analysis of the mixture, using naphthalene as internal standard, gave the yields of phenyl acetate, phenylfuran, 1,4-dihydro-1,4-epoxynaphthalene, and biphenyl. In all cases g.l.c. peak assignments were verified by g.l.c.–m.s. The results obtained are summarised in Table 1.

(ii) *Dependence on* 1,1-*diphenylethylene concentration*. In parallel reactions, *N*-nitrosoacetanilide (0.4 g, 2.4 mmol) was added to separate mixtures of 1,1-diphenylethylene in furan (3 ml) and benzene (9 ml) at 60° with stirring. The molar ratios of diphenylethylene to NNA in the three solutions were 1.0, 0.5, and 0.1. Product yields were calculated by internal standard calibration as described in the previous experiment. The results are shown in Table 1.

(iii) *Dependence on furan concentration*. In four parallel reactions, *N*-nitrosoacetanilide (0.3 g, 1.83 mmol) was added to well stirred mixtures of 1,1-diphenylethylene (0.16 g, 0.9 mmol) in furan and benzene. The molar ratios of furan to NNA were 0.9, 2.6, 9, and 26. In each reaction, benzene was added in such quantity as to raise the total solvent volume to 7 ml. Product yields were obtained as described in the previous reactions except for triphenylethylene yields which were calculated using fluoranthene as standard (2% CAR; 220°). In all of these reactions, trace amounts (*ca.* 1%) of triphenylethane were also produced. The identities of the triphenylethylene and triphenylethane products were established by g.l.c.–m.s.

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