# Simple, Convenient, and Direct Conversion of Anilines and Anilides into Arynes †

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Reaction of aniline with pentyl nitrite and acetic anhydride in benzene, or other solvents, gives benzyne in up to 32% yield as measured by trapping with anthracene, and tetraphenylcyclopentadienone and its 2,5-di-*p*-tolyl analogue. The role of the anhydride is to by-pass the suppressive effect of water on benzyne formation from the diazonium acetate ion pair. Reaction in benzene of aniline–acetic anhydride or (better) acetanilide with *p*-chloro-benzoyl nitrite (PCBN) (from silver *p*-chlorobenzoate and nitrosyl chloride) gives benzyne in up to 71% yield as measured by trapping as before and by 9,10-dimethoxyanthracene, and by the ene reaction with methyl methacrylate to give ethyl 2-methylene-3-phenylpropionate (31%). *meta*-Substituted anilines and acetanilides (*m*-XC$_6$H$_4$·NHAc; X = F, Cl, Br, I, CO$_2$Et, MeO, Bu^t, CF$_3$, or NO$_2$) and 3-aminopyridine behave like aniline and acetanilide, the *para*-isomers give lower yields, and the *ortho*-isomers give little or no arynes, with the exception of ethyl anthranilate and 2,5-dimethoxy- and 2,5-dichloroaniline.

PREVIOUS reports [1] have established that decompositions of certain *N*-nitroso-anilides in solution lead to the production of arynes *via* the corresponding isomeric diazonium acetates (Scheme 1), this reaction being in competition with the long known radical decomposition to give aryl radicals. In accord with this, reaction of benzenediazonium fluoroborate with potassium acetate gives benzyne.[2]

SCHEME 1
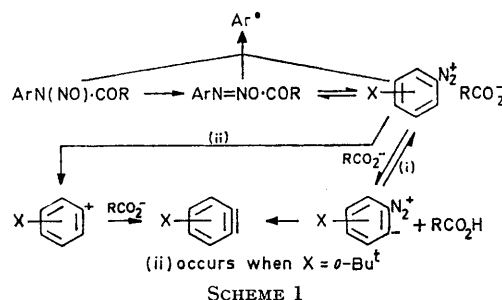
In those cases of nitrosoacylarylamines giving arynes, two classes of behaviour have been identified; a choice between them depends on the timing of the loss of nitrogen from the diazonium cation. One is the special case of a t-butyl group *ortho* to the diazonium function, in which steric acceleration of the loss of nitrogen is predominant with production of an *o*-t-butylphenyl cation and hence *o*-t-butylbenzyne, by subsequent proton loss; [1g,3] the other case involves prior loss of the proton *ortho* to the diazonium function.

The special effect of the *o*-t-butyl group has been confirmed by the observation [4] that *in situ* diazotisation by butyl nitrite [5] of 2,5-di-t-butylaniline leads to the corresponding aryne.

It appeared from these observations that application of the *in situ* diazotisation method [5] to anilines in the presence of acetate ions should lead to the corresponding arynes *via* a 'one-pot' method. The investigation, and subsequent realisation, of this possibility, which would be attractive in view of the mildness of the conditions and the general availability of anilines, is now reported.

We found at the outset [6] that reaction of aniline with pentyl nitrite in the presence of acetate ions in benzene, with tetraphenylcyclopentadienone as a trap, did not give the benzyne adduct in significant yields (<1%). This was anomalous in view of the previously established formation of benzyne in reactions of *N*-nitrosoacetanilide [1] or benzenediazonium fluoroborate–potassium acetate.[2] Other anilines behaved similarly. Thus
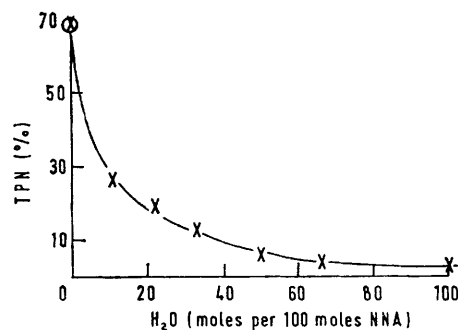
Effect of water on yield of TPN from NNA–tetraphenylcyclopentadienone

the reported case of 2,5-di-t-butylaniline [4] was unique and did not represent a general route to arynes from anilines.

The resolution of this anomaly came from our previous

† Preliminary communication, J. I. G. Cadogan, J. R. Mitchell, and J. T. Sharp, *Chem. Comm.,* 1971, 1.

[1] (*a*) J. I. G. Cadogan and P. G. Hibbert, *Proc. Chem. Soc.,* 1964, 338; (*b*) J. I. G. Cadogan, *J. Pure and Appl. Chem.,* 1967, **15**, 153; (*c*) D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Comm.,* 1967, 727; (*d*) J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *ibid.,* 1970, 299; (*e*) J. I. G. Cadogan in 'Essays in Free Radical Chemistry,' *Chem. Soc. Special Publ.,* No. 24, 1970, p. 71; (*f*) J. I. G. Cadogan, *Accounts Chem. Res.,* 1971, **4**, 186; (*g*) D. L. Brydon, J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *J. Chem. Soc. (B),* 1971, 1996.

[2] C. Rüchardt and C. C. Tan, *Angew. Chem. Internat. Edn.,* 1970, **9**, 522.

[3] J. I. G. Cadogan, J. Cook, M. J. P. Harger, P. G. Hibbert, and J. T. Sharp, *J. Chem. Soc. (B),* 1971, 995.

[4] R. M. Franck and K. Yanagi, *Tetrahedron Letters,* 1966, 2905; *J. Amer. Chem. Soc.,* 1968, **90**, 5814.

[5] J. I. G. Cadogan, *J. Chem. Soc.,* 1962, 4257; J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *J. Chem. Soc. (C),* 1966, 1249.

[6] D. L. Brydon, Ph.D. Thesis, St. Andrews University, 1967.

observation [1e,7,8] now confirmed, that benzyne formation from *N*-nitrosoacetanilide (NNA) is significantly suppressed by small quantities of water (Figure). This also applies to the formation of benzyne from benzenediazonium fluoroborate and potassium acetate. Since water is formed in the *in situ* diazotisation of anilines by pentyl nitrite,[5] the failure of this method, in the presence of acetate ions, as a route to arynes becomes clear. Since the formation of the aryne is

$$ArNH_2 + RONO + PhH \longrightarrow ArPh + ROH + N_2 + H_2O$$
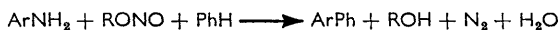
dependent on the existence of the diazonium carboxylate ion pair (Scheme 1), the observed effect of water is explicable: it could interfere with the removal of the aromatic proton by solvation of the constituents of the ion pair, *e.g.* by making the acetate ion less ' basic '. The possibility that it could reverse the equilibrium (i) (Scheme 1) also cannot be discounted. That aryne formation from the 2,5-di-t-butylbenzenediazonium salt is not suppressed by water is also consistent with the foregoing, since Scheme 1 requires the formation of the aryl cation in which the *ortho*-proton would be expected to be more acidic and hence more easily removed by basic species.
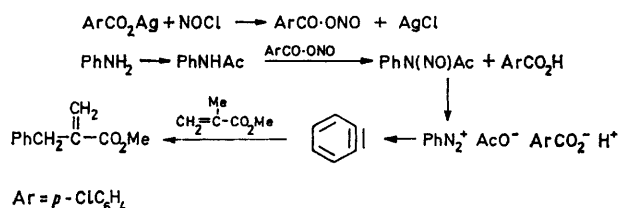
To overcome the suppressive effect of water, the reaction of aniline with pentyl nitrite in the presence of acetic anhydride was used in the expectation that it might fulfil one, or all, of three roles: (*a*) in causing the prior formation of acetanilide; nitrosation by pentyl nitrite would then give *N*-nitrosoacetanilide *in situ*. Since this reaction does not involve the formation of water, the nitrosoacetanilide cycle leading to benzyne might then be unhindered; (*b*) by removing water, formed

$$PhNHAc + RONO \longrightarrow PhN(NO)Ac + ROH$$
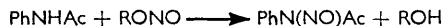
in the *in situ* diazotisation, and thus giving the required acetate ion; and (*c*) by reaction with pentyl nitrite to give acetyl nitrite which is potentially a more powerful nitrosating agent. In accord with this a mixture of aniline (1 mol. equiv.), pentyl nitrite (1·5 mol. equiv.), and acetic anhydride (3 mol. equiv.) in benzene (34 mol. equiv.) at 80° in the presence of tetraphenylcyclopentadienone (1 mol. equiv.), as described in the Experimental section, gave 1,2,3,4-tetraphenylnaphthalene in 32% yield. A similar reaction with anthracene as trap gave triptycene in 10% yield. Reaction of pentyl nitrite and preformed acetanilide gave only 7% of the benzyne adduct, whereas that involving acetanilide, acetic anhydride, and pentyl nitrite gave 21% of the adduct. Relevant to the relative success of the latter reaction, it was found that pentyl alcohol, but not acetic acid, also reduced benzyne formation. The presence of excess of acetic anhydride therefore is beneficial, probably causing conversion of pentyl alcohol into pentyl acetate, which is formed quantitatively in the reaction.

Thus a contribution to the overall process by reaction

(*a*) is indicated, leaving reaction (*b*), which is not fast in benzene, and reaction (*c*), which cannot be discounted. This led to the development of *p*-chlorobenzoyl nitrite (PCBN) as a new reagent for the conversion of aniline into benzyne (Scheme 2). The *p*-chlorobenzoate system was selected because (i) we had previously found [1c,8] that *N*-nitroso-*p*-chlorobenzoylanilines gave high yields of arynes as compared with the corresponding acetyl derivatives and (ii) because we found that PCBN is relatively easily synthesised, from silver *p*-chlorobenzoate and nitrosyl chloride, and stored as a solution in benzene. Reactions of preformed acetanilide in dry benzene with PCBN, as described in the Experimental section, with tetraphenylcyclopentadienone, anthracene, 9,10-dimethoxyanthracene, and methyl methacrylate traps gave the corresponding aryne adducts, 1,2,3,4-tetraphenylnaphthalene (70%), triptycene (16%), 9,10-dimethoxytriptycene (14%), and, by the ene reaction,[9] ethyl 2-methylene-3-phenylpropionate (31%), respectively (Scheme 2). Prior reaction of aniline with

$$ArCO_2Ag + NOCl \longrightarrow ArCO \cdot ONO + AgCl$$

$$PhNH_2 \longrightarrow PhNHAc \xrightarrow{ArCO \cdot ONO} PhN(NO)Ac + ArCO_2H$$

$$PhCH_2 \cdot \overset{\overset{CH_2}{\|}}{C} - CO_2Me \longleftarrow \overset{Me}{\underset{CH_2 = C \cdot CO_2Me}{\longleftarrow}} \text{[benzyne]} \longleftarrow PhN_2^+ \, AcO^- \, ArCO_2^- \, H^+$$

$$Ar = p\text{-}ClC_6H_4$$

SCHEME 2

acetic anhydride to give acetanilide, followed by addition of PCBN and tetraphenylcyclopentadienone, led to a reduced but still acceptable (51%) yield of 1,2,3,4-tetraphenylnaphthalene, which was not improved (45%) by the use of *p*-chlorobenzoic instead of acetic anhydride or by the use of 4-chlorobenzanilide instead of acetanilide (48%). The use of aniline and PCBN in the absence of acetic anhydride led to very low isolated yields of products.

Thus, we can point to two simple procedures for the direct conversion of aniline into benzyne, *viz.* use of aniline plus pentyl nitrite plus acetic anhydride, or use of aniline plus acetic anhydride followed by PCBN, the latter process being made more efficient by using preformed acetanilide. The scope of these reactions in converting substituted anilines into the corresponding arynes as indicated by the trapping reaction with tetraphenylcyclopentadienone is outlined in Table 1, from which the following points emerge. (i) The yield of aryne adduct is higher when the preformed acetanilide–PCBN rather than acetic anhydride–substituted aniline–pentyl nitrite is used. (ii) *meta*-Substituted anilines give far higher yields than the corresponding *para*-isomers, which in turn are often much better than those from the *ortho*-derivatives, many of which give no

[7] J. I. G. Cadogan, M. J. P. Harger, and J. T. Sharp, *Amer. Chem. Soc. Div. Petrol Chem.*, 1969, **14**, p. C19.

[8] J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *J.C.S. Perkin I*, 1972, 1296.

[9] I. Tabushi, K. Okazaki, and R. Oda, *Tetrahedron*, 1969, **25**, 4401.

aryne adduct at all. These substituent effects are under investigation; they will be subject to many so far unassessed complicating factors; including the rate of formation, and hence concentration of the diazonium acetate ion pair, the nature of the subsequent deprotonation–protonation equilibrium, and the related question of interconversion of isomeric benzyne precursors in the *meta*-cases. In this connection it is significant that our preliminary results indicate that *o*-bromo-*N*-nitrosoacetanilide, which gives no aryne, rearranges to *o*-bromobenzenediazonium acetate seven times more slowly than the *meta*-isomer (which gives aryne) and *ca.* 50 times more slowly than *N*-*m*-bromophenyl-*N*-nitroso-*p*-chlorobenzoylamine, which is a particularly good source of the aryne.[1c]

TABLE 1

Formation of arynes, as measured by 1,2,3,4-tetraphenyl-naphthalenes (TPN), from (a) $C_5H_{11}ONO$–$XC_6H_4\cdot NH_2$–Ac_2O; (b) PCBN–X $C_6H_4\cdot NHAc$ *

| | Aryne adduct (%) | | | |
| | 5-X-TPN | | 6-X-TPN | |
X	(a)	(b)	(a)	(b)
H	32	70		
3-F		75		0
3-Cl	17	78	0	0
3-Br	17·5	77	0	0
3-I	16	57	0	6
3-CO$_2$Et	5	21·5	10	43
3-MeO	28	59	7	0
3-Bu^t	4	8	18	32
3-CF$_3$		69·5		11·5
3-NO$_2$	38	52	0	0
4-Br			4	5
4-NO$_2$			0	0
4-MeO			0	24
4-Bu^t			10	35
4-CO$_2$Et			17	46
4-CF$_3$				50
2-NO$_2$	0	0		
2-Me		0		
2-CO$_2$Et	17	23		
2-CF$_3$		0		
2,5-(MeO)$_2$	3	49		
2,5-Cl$_2$	3	4		
3-NH$_2$·C$_5$H$_4$N				18
2-NH$_2$·C$_5$H$_4$N		0		
4-NH$_2$·C$_5$H$_4$N	13			

* The yield of tetraphenylnaphthalene was not improved by the use of (a) cyclohexane, tetrahydrofuran, or 1,2-dimethoxyethane instead of benzene, (b) *p*-chlorobenzoic anhydride or acetyl chloride instead of acetic anhydride, (c) nitrosyl chloride instead of pentyl nitrite, or (d) *p*-chlorobenzanilide instead of acetanilide, although in all cases the reactions were successful.

All the experiments summarised in Table 1 were carried out under standard conditions at the b.p. of benzene. It was later discovered that the reaction of PCBN with acetanilide proceeded equally well at room temperature, so the same may also apply to the cases given in the Table.

EXPERIMENTAL

Alumina for dry column chromatography[10] was of activity III and contained an inorganic fluorescing agent (254 nm). Nylon tubing was supplied by W. Coles and Co. Ltd., London, S.E.1.

p-Chlorobenzoyl Nitrite.—To a solution of sodium hydrogen carbonate (9 g, 0·11 mol) in water (40 ml) was added 4-chlorobenzoic acid until a slight excess of acid remained (17 g, 0·12 mol). The solution was filtered hot and silver nitrate (19 g, 0·11 mol) in water (100 ml) was added to the stirred filtrate. The precipitate of silver *p*-chlorobenzoate was washed with ethanol and dried (P$_2$O$_5$) at 0·01 mmHg.

To a stirred suspension of silver *p*-chlorobenzoate (20 g, 75 mmol) in dry carbon tetrachloride (180 ml) at −10° was added nitrosyl chloride (8 g, 125 mmol) during 30 min. The mixture was stirred for a further 20 min at −10° and for 1 h at room temperature, then rapidly filtered. The residue was washed with dry carbon tetrachloride (20 ml); the filtrates were combined and evaporated under reduced pressure. The residue was distilled to yield *p*-chlorobenzoyl nitrite (10 g, 53 mmol, 71%), b.p. 70° at 1 mmHg. This compound was dissolved in benzene (16% w/v solution) and stored at −30°. The product is extremely easily hydrolysed by moisture.

Benzene (sodium-dried) was freshly distilled from calcium hydride.

Reactions of Substituted Anilines with Pentyl Nitrite in the Presence of Tetraphenylcyclopentadiene.—General method. To a stirred solution of the amine (5 mmol), 2,3,4,5-tetraphenylcyclopentadiene (5 mmol), and acetic anhydride (15 mmol) in benzene (10 ml) at its b.p. was added pentyl nitrite (7·7 mmol) in benzene (5 ml) during 1 h. The solution was boiled under reflux for 12 h, maleic anhydride (10 mmol) was added, and the mixture was boiled to remove the excess of 2,3,4,5-tetraphenylcyclopentadienone. When the violet colour had disappeared (2 h), alumina (3 g) was added and the solvent was evaporated off, leaving the reaction mixture adsorbed on the alumina. The mixture was added to the top of a dry column of alumina (50 × 2 cm) and eluted with cyclohexane. Illumination of the column with u.v. light showed the products as distinct bands which were extracted from the alumina with ether. Evaporation of the extracts yielded the products: (*a*) substituted biphenyls which were characterised by comparison of i.r., n.m.r., and mass spectra with those of authentic samples where possible, (*b*) substituted 1,2,3,4-tetraphenylnaphthalenes, which were recrystallised from benzene–ethanol (1 : 2) and characterised similarly, and by m.p. and mixed m.p. determinations (Table 2).

In the cases of *meta*-substituted anilines, where both the corresponding 5- and 6-substituted 1,2,3,4-tetraphenylnaphthalenes were possible products the ratio of isomers was determined by [1]H n.m.r. spectroscopy. In addition in all cases it was possible to obtain pure specimens of the 5- and 6-isomers by chromatography, the former being eluted more slowly.

Reactions of Pentyl Nitrite–Aniline with Various Benzyne Traps.—(i) *Anthracene.* Pentyl nitrite (1·75 g, 15 mmol) in benzene (5 ml) was added dropwise during 5 h to a mixture of aniline (1 g, 10 mmol), potassium acetate (1 g, 10 mmol), acetic anhydride (3·06 g, 30 mmol), and anthracene (5·4 g, 20 mmol) in boiling benzene. The mixture was boiled under reflux for a further 24 h, then evaporated, and the residue was boiled under reflux with maleic anhydride (2 g) in chlorobenzene (15 ml) for 1 h. Chromatography of a portion of the mixture on alumina gave triptycene, m.p. and mixed m.p. 256° (i.r. spectrum). G.l.c. of

[10] B. Loev and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.

the reaction mixture (2% NPGS, 204°; 1% SE30, 158°) with fluoranthene as internal standard showed the presence of triptycene (10%).

(ii) *3,4-Diphenyl-2,5-di-p-tolylcyclopentadienone.* Pentyl nitrite (0·59 g, 5 mmol), aniline (0·46 g, 5 mmol), 3,4-di-phenyl-2,5-di-*p*-tolylcyclopentadienone (1·03 g, 5 mmol),[19] potassium acetate (0·5 g, 5 mmol), acetic acid (0·05 ml), and acetic anhydride (1·53 g, 15 mmol) were boiled under reflux in benzene (15 ml) for 24 h. Work-up as in (i) gave 2,3-diphenyl-1,4-di-*p*-tolylnaphthalene (0·35 g, 15%), m.p. and mixed m.p. 225·5° (i.r. spectrum).

1 h to a solution of acetanilide (0·675 g, 5 mmol) and 9,10-dimethoxyanthracene in boiling benzene 100 ml. Work-up as before gave 9,10-dimethoxytriptycene, m.p. and mixed m.p. 192° (i.r. spectrum). G.l.c. (2% NPGS, 214°) with triptycene as marker showed the yield of 9,10-dimethoxytriptycene to be 14%.

(iii) *Methyl methacrylate.* To a boiling solution of acetanilide (0·675 g, 5 mmol) in methyl methacrylate (2·28 g, 20 mmol) and benzene (100 ml), a solution of *p*-chloro-benzoyl nitrite (1·6 g, 8·5 mmol) in benzene (50 ml) was added dropwise during 1 h. The mixture was boiled

TABLE 2

Substituted 1,2,3,4-tetraphenylnaphthalenes

| Substituent | M.p. (°C), lit. m.p. (ref.) | Analysis (%) * | | M^+ | N.m.r.† |
		C	H		
5-F	267			450	2·55—2·75 (2H, m), 2·83 (5H, s), 2·92 (5H, s), 3·00—3·13 (1H, m), 3·25br (10H, s)
		90·7	5·1	450	
5-Cl	257, 257 (1*g*)	87·6	4·9	468/466	2·40—2·70 (3H, m), 2·84 (5H, s), 2·95 (5H, s), 3·26br (10H, s)
		87·4	4·9	468/466	
5-Br	232, 235 (8)	79·7	4·3	512/510	2·25—2·37 (2H, m), 2·89 (5H, s), 3·00br (6H, s), 3·30br (10H, s)
		79·8	4·5	512/510	
6-Br	238, 243 (8)			512/510	
				512/510	
5-I	206	73·5	4·4	560	1·8—2·42 (3H, m), 2·70—2·73 (10H, m), 3·1—3·3 (10H, m), (in CDCl₃)
		73·2	4·1	560	
5,8-Cl₂	229	81·2	4·3	504/502/500	2·65 (2H, s), 2·98 (10H, s), 3·1—3·5 (10H, m) (in CDCl₃)
		81·5	4·4	504/502/500	
5,8-(MeO)₂	199—200	87·9	5·5	492	3·05br (10H, s), 3·20—3·50 (12H, m), 6·76 [6H, s, (MeO)₂]
		87·9	5·7	492	
5-NO₂	252, 254 (8)	85·2	5·2	477	
		85·5	4·8	477	
6-But	288—290, 288—290 (1*g*)	93·3	6·5		2·37—2·52 (3H, m), 2·80br (10H, s), 3·20 (10H, s), 8·78 (9H, s, Me₃C) (in CDCl₃)
		93·6	6·4		
5-CO₂Et	210	87·8	5·4	504	2·30—2·40 (1H, dd), 2·48—2·55 (1H, dd), 2·87 (5H, s), 2·99 (5H, s), 3·20—3·44br (10H, s), 6·54—6·67 (2H, q, CH₃·CH₂·O), 8·89—9·01 (3H, t, CH₃·CH₂·O)
		88·1	5·6	504	
6-CO₂Et	220·5	88·4	5·5	504	1·72 (1H, d), 2·06—2·17 (1H, dd), 2·37—2·43 (1H, d), 2·82 (5H, s), 2·85 (5H, s), 3·23 (10H, s), 5·62—5·83 (2H, q, CH₃·CH₂·O), 8·61—8·77 (3H, t, CH₃·CH₂·O)
		88·1	5·6	504	
5-CF₃	187	83·8	4·6	500	2·07—2·26 (2H, m), 2·58—2·64 (1H, d), 2·68 (5H, s), 3·03 (5H, s), 3·10—3·50 (10H, m)
		84·0	4·6	500	
6-CF₃	248	84·0	4·7	500	2·12 (1H, s), 2·22—2·31 (1H, d), 2·47—2·58 (1H, dd), 2·82 (10H, s), 3·23 (10H, s)
		84·0	4·6	500	
5-MeO	217—218	90·7	5·7	462	2·73 (1H, s), 2·88br (7H, s), 3·02 (5H, s), 3·30br (10H, s), 6·68 (3H, s, MeO)
		90·9	5·6	462	
6-MeO	274—275	90·8	5·8	462	2·50—2·58 (1H, d), 2·85 (10H, s), 3·00—3·11 (1H, dd), 3·15—3·30br (11H, s), 6·38 (3H, s, MeO)
		90·9	5·6	462	
4,5,6,7-Ph₄-Isoquinoline	218 220—222 (11)	91·2	5·3	433	1·06 (1H, s), 1·60—1·63 (1H, d), 2·62—2·69 (1H, d), 2·80br (10H, s), 3·20br (10H, s)
		91·4	5·3	433	

* Upper row Found; lower row Calc. † 100 MHz; standard Me₄Si, in CCl₄ unless otherwise stated.

Reactions of p-*Chlorobenzoyl Nitrite–Acetanilide with Various Benzyne Traps.*—(i) *Anthracene.* *p*-Chloroben-zoyl nitrite (1·6 g, 8·5 mmol) in benzene (50 ml) was added during 1 h to a boiling solution of acetanilide (0·675 g, 5 mmol) and anthracene (0·9 g, 5 mmol) in benzene (100 ml). The mixture was boiled under reflux for 12 h and then concentrated. Maleic anhydride (1 g) was added and the solution was boiled for 3 h. Chromatography of a portion of the mixture on alumina (60 g) with benzene as eluant gave triptycene, m.p. and mixed m.p. 256°, indistinguishable [i.r. spectrum (Nujol)] from an authentic sample. G.l.c. (2% NPGS, 214°) analysis with fluor-anthene as internal standard showed the yield of tripty-cene to be 16%.

(ii) *9,10-Dimethoxyanthracene.* *p*-Chlorobenzoyl nitrite (1·6 g, 8·5 mmol) in benzene (50 ml) was added during

under reflux overnight and a portion was chromatographed on alumina to give biphenyl, m.p. and mixed m.p. 70°, and ethyl 2-methylene-3-phenylpropionate (i.r. and n.m.r. spectra)[9] (Found: C, 75·3; H, 7·1. Calc. for C₁₁H₁₂O₂: C, 75·0; H, 6·8%). Quantitative examination of the mixture by g.l.c. (2% CAR, 115°) with naphthalene as internal standard showed the yields of biphenyl and the ester to be 8·5 and 31%, respectively.

Reactions of Substituted Acetanilides with p-*Chlorobenzoyl Nitrite in the Presence of Tetraphenylcyclopentadienone.*—The reaction is exemplified by the case of *m*-chloroacetanilide: to a solution of the anilide (0·789 g, 5 mmol) and tetra-phenylcyclopentadienone (3·84 g, 10 mmol) in dry benzene (freshly distilled from sodium; 100 ml) at the b.p. was

[11] G. W. Fleet and I. Fleming, *J. Chem. Soc. (C)*, 1969, 1758.

added, during 1 h, *p*-chlorobenzoyl nitrite (1·6 g, 8·5 mmol) in benzene (50 ml) under strictly anhydrous conditions. After 10 h at the b.p. excess of benzene was removed and maleic anhydride (1 g, 10 mmol) was added. The mixture was worked up by dry chromatagraphy as already described to give 5-chloro-1,2,3,4-tetraphenylnaphthalene (1·84 g, 78%), m.p. and mixed m.p. 257°.

The results of similar experiments at the b.p. with other anilides are summarised in Table 2. An experiment carried out later with *m*-chloroacetanilide at room temperature overnight gave an almost identical yield (69%).

Decomposition of N-*Nitrosoacetanilide in Benzene in the Presence of Tetraphenylcyclopentadienone and Water, Pentyl alcohol, or Acid.*—*N*-Nitrosoacetanilide (0·82 g, 5 mmol) was allowed to decompose in a solution of tetraphenylcyclopentadienone (1·92 g, 5 mmol) in benzene (10 ml) containing amounts of water ranging from 0·09 g (5 mmol) to zero.

The mixtures were stirred at room temperature for 12 h and then boiled under reflux for 1 h. Maleic anhydride (1 g) was added to each and the mixtures were boiled under reflux until the tetracyclone colour had gone. Chromatography on dry alumina columns (70 g), with cyclohexane as eluant, gave almost constant yields of biphenyl (0·04 mol./mol. equiv.) but yields of tetraphenylnaphthalene varied (Figure). In parallel experiments it was found that pentyl alcohol had a similar repressant effect upon the yield of 1,2,3,4-tetraphenylnaphthalene but that acetic acid had no effect. A similar suppressive effect of water was observed in the generation of benzyne from benzenediazonium fluoroborate and potassium acetate in benzene.