Acylarylnitrosamines. Part IV.[1] Aryne Participation in Decompositions of *N*-Nitrosoacetanilide and its *m*- and *p*-t-Butyl-, *o*-, *m*-, and *p*-Chloro-Derivatives in Benzene †

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Decompositions of *N*-nitrosoacetanilide, *m*- and *p*-t-butyl-, *m*-, *p*-, and *o*-chloro-*N*-nitrosoacetanilides in benzene, and other solvents, in the presence of arynophiles such as anthracene and its derivatives, 2,3,4,5-tetra-arylcyclopentadienones, and 1,3-diphenylisobenzofuran gave, with the exception of the last named nitrosamide, aryne adducts corresponding to the anilide used, in yields varying from 4 to 82%. None of these nitrosamides gave the corresponding aryne adduct with furan at 15°. *p*-t-Butyl-*N*-nitrosoacetanilide in the presence of tetraphenylcyclopentadienone gave 6-t-butyl-1,2,3,4-tetraphenylnaphthalene, rather than the isomeric 1-(*p*-t-butylphenyl)-2,3,4-triphenylnaphthalene, thus indicating the intermediary of a bidentate rather than a monodentate species. Competition experiments in which pairs of arynophiles were allowed to compete (*a*) for authentic benzyne (*b*) for the intermediate produced by *N*-nitrosoacetanilide gave almost identical results in both cases, indicating that benzyne is involved in case (*b*) also. A mechanism involving removal of a proton *ortho*- to the diazonium function in the intermediate benzenediazonium acetate is proposed and an explanation for the anomalous behaviour of furan is advanced in terms of a fast competing radical chain reation of the latter.

In Part I [2] we described experiments relating to the mechanism of decomposition of acylarylnitrosamines, *via* aryl radicals, exemplified by *N*-nitrosoacetanilide, in various solvents, *e.g.* equation (i). In Parts II [3] and III [1] we drew attention to anomalous reactions involving

$$ArN(NO)COCH_3 + PhH \longrightarrow ArPh + N_2 + CH_3CO_2H \quad (i)$$

o-t-butyl-substituted *N*-nitrosoacetanilides and established, in particular,[3] that the presence of the bulky *o*-t-butyl led to preferential decomposition to the *o*-t-butylphenyl carbonium ion and hence, in the presence of the acetate counter-ion, to *o*-t-butylbenzyne. It was, therefore, of considerable interest to determine whether decomposition of other acylarylnitrosamines, possibly all, also proceeded in part *via* the hitherto unsuspected aryne route. To this end we now report reactions of *N*-nitrosoacetanilide, *m*- and *p*-t-butyl-, *o*-, *m*-, and *p*-chloro-*N*-nitrosoacetanilides in benzene and other solvents in the presence and absence of arynophiles, such as furan and derivatives, anthracene and derivatives, and tetra-arylcyclopentadienones.

EXPERIMENTAL

Gas-liquid chromatography was carried out as described earlier.[3] Acetylarylnitrosamines were freshly prepared before use by standard methods from the corresponding acetanilides and nitrosyl chloride.[2]

Preparation of Aryne Precursors.—*4-t-Butylanthranilic acid.* *p*-t-Butylbenzyl chloride (b.p. 124—128°/14 mm.) (128 g., 0·70 mole) was nitrated by the method of Nelson and Brown [4] for the nitration of t-butylbenzene. The crude product was fractionally distilled through a Vigreux column under nitrogen to give a viscous orange oil (137·4 g.), b.p. 107—118°/0·1 mm. Examination by g.l.c. (2% NPGS, 180°) revealed two partially resolved components, A (70—80%) and B (20—30%); τ (CCl_4) 1·96, 2·36, 2·50 and 2·69 (all multiplets, H_3); 5·10 and 5·48 (singlets, H_2, ratio 3·5 : 1); 8·62 (s, CMe_3). The product appeared to be a mixture of 4-t-butyl-2-nitrobenzyl chloride (A) and 4-t-butyl-3-nitrobenzyl chloride (B) (total, 86%).

The isomeric mixture (125 g., 0·55 mole) was oxidised with alkaline potassium permanganate as described by Skinner and Zell [5] to yield, after repeated crystallisation from benzene–petroleum and from carbon tetrachloride, pale pink 2-nitro-4-t-butylbenzoic acid (23·1 g., 0·01 mole, 19%), m.p. 152—154° (lit.,[5] 138—143°). N.m.r. (CCl_4–$CDCl_3$, 4 : 1), τ 2·64 (sharp s, H_1), 1·95—2·45 (complex, H_3) and 8·60 (CMe_3).

The nitro-acid (10·05 g.) in super-dry ethanol (185 ml.) was shaken at room temperature with platinum dioxide (Adams catalyst, 0·49 g.) in an atmosphere of hydrogen. After 2·5 hr., 3 l. of hydrogen had been consumed, and no further uptake occurred. After filtration, work-up of the filtrate gave pale yellow crystals of 4-t-butylanthranilic acid (6·02 g., 0·031 mole, 69%), m.p. 166—168° (from aqueous ethanol) (lit.[5] 167—168°); $\nu_{max.}$ (Nujol) 3510 and 3390 (NH_2), 3500—2000br (O–H), and 1670 $cm.^{-1}$ (C=O).

3-Chloroanthranilic acid. 2-Chloroisonitrosoacetanilide (m.p. 148—152°; lit.,[6] m.p. 152°); was converted into 7-chloroisatin (m.p. 181—182°; lit.,[6] m.p. 175°) and hence into 3-chloroanthranilic acid (m.p. 190—192°; lit.,[6] m.p. 192°).

2-Bromo-4-t-butylfluorobenzene. 2-Bromo-4-t-butyl-acetanilide (m.p. 160—161°; lit.,[7] m.p. 158°) prepared by Klouwen and Boelens' method [8] was converted by standard

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routes into 2-bromo-4-t-butylbenzenediazonium fluoroborate [m.p. 148—149° (decomp.)] and hence 2-*bromo*-4-*t*-*butylfluorobenzene* (75%; b.p. 67—69°/2 mm.) (Found: C, 51·6; H, 5·55. $C_{10}H_{12}BrF$ requires C, 52·0; H, 5·2%) (Correct n.m.r.).

Preparation of Arynophiles.—2,3,4-*Triphenyl*-5-(p-*t*-*butylphenyl*)*cyclopentadienone*. This was prepared by condensation of 1-phenyl-3-*p*-t-butylphenylpropan-2-one with benzil.

To the Grignard reagent from benzyl chloride (48·1 g., 0·38 mole) in ether (600 ml.) stirred under nitrogen was added cadmium chloride (55·8 g.) in ten portions at 1 min. intervals. Stirring was continued at 0° for a further 2 hr., and then a solution of *p*-t-butylphenylacetyl chloride (31·4 g., 0·149 mole), [prepared from *p*-t-butylphenylacetic acid, m.p. 79—80° (lit.,[9] m.p. 78—79°)] in ether (120 ml.) was added during 10 min. The mixture was stirred at 0° for 8 hr., and was then poured into an agitated mixture of 20% sulphuric acid (120 ml.) and crushed ice (300 g.). The aqueous layer was extracted with ether (2 × 100 ml.), and work up of the combined ether extracts gave a colourless liquid (36·8 g.), b.p. 141—143°/0·18 mm. Crystallisation from petroleum at −40° afforded 1-*phenyl*-3-(p-*t*-*butylphenyl*)*propan*-2-*one* (32·6 g., 0·123 mole, 82%), m.p. 32—33° (Found: C, 85·8; H, 8·2. $C_{19}H_{22}O$ requires C, 85·7; H, 8·3%); τ (CCl_4) 2·51—3·05 (complex, H_9), 6·42 (CH_2), 6·47 (CH_2) and 8·69 (CMe_3); $\nu_{max.}$ (melt) 1710 (C=O) and 1395 and 1365 cm.$^{-1}$ (CMe_3). The ketone (15·96 g., 0·060 mole) and benzil (12·60 g., 0·060 mole) in ethanol (125 ml.) were heated under reflux to a temperature slightly below the b.p. while potassium hydroxide (1·25 g.) in ethanol (12·5 ml.) was cautiously added during 10 min. After 20 min. at the b.p. the purple mixture was allowed to cool, and the solid material was filtered off and washed with ethanol. Crystallisation from benzene–ethanol (1 : 1) yielded dark indigo 2,3,4-*triphenyl*-5-(p-*t*-*butylphenyl*)*cyclopentadienone* (22·8 g., 0·052 mole, 86%). A sample gave fine needles, m.p. 225—227° (from acetone) (Found: C, 89·7; H, 6·7. $C_{33}H_{28}O$ requires C, 90·0; H, 6·4%); τ ($CDCl_3$) 2·55—3·20 (complex, H_{19}) and 8·73 (CMe_3); $\nu_{max.}$ (Nujol) 1705 cm.$^{-1}$ (C=O).

2,5-*Di*-p-*methylsulphonylphenyl*-3,4-*diphenylcyclopentadienone*.—*p*-Methylthioacetophenone [b.p. 90—111°/0·1 mm. (lit.,[10] b.p. 134—140°/0·35 mm.)] was converted into *p*-methylthiophenylacetate [m.p. 92—94° (lit.,[11] m.p. 92—94°)] and hence to the ethyl ester [m.p. 55—56° (lit.,[12] m.p. 55—56°)]. This (50 g.) was self condensed using isopropylmagnesium bromide as described by Coan *et al.*[13] to give the corresponding acetoacetic ester (crude 55 g.). This was hydrolysed and decarboxylated by heating under reflux with acetic acid (500 ml.) and hydrochloric acid (*d*, 1·18; 70 ml.), for 5 hr. The mixture was evaporated to low volume and extracted with ether, washed with sodium hydroxide (10%) and water and then dried. Evaporation of the ether left a solid which was recrystallised from hexane to give 1,3-*di*-p-*methylthiophenylpropan*-2-*one* (25 g., 64%), m.p. 79—80° (Found: C, 67·3; H, 6·0. $C_{17}H_{18}OS_2$ requires C, 67·55; H, 5·95%); τ ($CDCl_3$) 2·72—3·80 (A_2B_2, H_8) 6·37 (CH_2, H_4), and 7·77 (CH_3, H_6).

To a solution of the ketone (10 g.) in acetic acid was added dropwise hydrogen peroxide solution (23·2 g., 100 vol.). The solution was heated under reflux for 20 hr. and, after cooling, addition of water (5 ml.) induced crystallisation of 1,3-*di*-p-*methylsulphonylphenylpropan*-2-*one* (8·5 g., 71%), m.p. 187—188° (Found: C, 55·6; H, 4·9. $C_{17}H_{18}O_5S_2$ requires C, 55·7; H, 4·9%); $\nu_{max.}$ (Nujol) 1680 (C=O) and 1080 cm.$^{-1}$ (S=O).

To a solution of the latter (7·32 g., 0·02 mole) and benzil (4·2 g., 0·02 moles) in ethanol (50 ml.), heated under reflux at a temperature slightly lower than the boiling point, was added benzyltrimethylammonium hydroxide (3·0 g., 40% in water); the solution was boiled under reflux for 10 min. The cooled solution was filtered and the precipitate was recrystallised from acetic acid to give 2,5-*di*-p-*methylsulphonylphenyl*-3,4-*diphenylcyclopentadienone* (1·5 g., 14%), m.p. 299—300° (Found: C, 68·7; H, 4·4. $C_{31}H_{24}O_5S_2$ requires C, 68·9; H, 4·4%); τ ($CDCl_3$) 2·05—3·16 (complex, H_{14}) and 6·97 (s, CH_3, H_6); $\nu_{max.}$ (Nujol) 1710 (C=O) and 1080 cm.$^{-1}$ (S=O).

Other arynophiles. 2,5-Di-*p*-methoxyphenyl-3,4-diphenylcyclopentadienone [m.p. 195—196° (lit.,[13] m.p. 195—196°)] and 3,4-diphenyl-2,5-di-*p*-tolylcyclopentadienone [m.p. 179—180° (lit.,[13] m.p. 179—180°)] were prepared as described by Coan *et al.*[13] 1,4-Dimethoxyanthracene had m.p. 136—137° (lit.,[14] m.p. 137°), 9,10-dimethoxyanthracene had m.p. 200—201° (lit.,[15] m.p. 202°), 9,10-dimethylanthracene had m.p. 179—180° (lit.,[16] m.p. 179—180°), 9-nitroanthracene had m.p. 146° (lit.,[17] m.p. 145—146°), and 9-bromoanthracene had m.p. 98° (lit.,[18] m.p. 98—99°).

Preparation of Aryne Adducts

1,2,3,4-*Tetraphenyl*-6-*t*-*Butylnaphthalene*.—A mixture of pentyl nitrite (0·70 g.), tetraphenylcyclopentadienone (2·30 g.) and dichloromethane (20 ml.) was stirred and boiled under reflux under nitrogen. A solution of 4-t-butylanthranilic acid (0·97 g.) in acetone (6 ml.) was added during 4 hr. and the mixture was boiled for a further 2 hr. Volatile material was removed by evaporation under reduced pressure, and the residue was chromatographed on alumina (350 g.). Elution with petroleum–benzene (4 : 1) gave a white solid (1·40 g.) which was crystallised from benzene–methanol to yield colourless 1,2,3,4-tetraphenyl-6-t-butylnaphthalene (1·16 g., 48%), m.p. 286—287°. This material was identical (m.p., mixed m.p., and i.r. and n.m.r. spectra) to the adduct isolated from the reaction of *p*-t-butyl-*N*-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone (see below); n.m.r. spectrum see Table 1.

1,2,3-*Triphenyl*-4-(p-*t*-*butylphenyl*)*naphthalene*.—Anthranilic acid (1·37 g., 10·0 mmoles) was diazotised with pentyl nitrite in the presence of 2,3,4-triphenyl-5-(*p*-t-butylphenyl)cyclopentadienone (4·41 g.) as described above. Chromatography of the reaction product on alumina (500 g.) afforded, by elution with petroleum–benzene (6 : 1), a colourless solid (3·98 g.) which was crystallised from acetic acid and from benzene–methanol (1 : 1) to yield 1,2,3-*triphenyl*-4-(p-*t*-*butylphenyl*)*naphthalene* (3·41 g., 70%), m.p.

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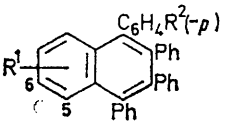
200—201° (Found: C, 93·0; H, 6·7. $C_{38}H_{32}$ requires C, 93·4; H, 6·6%), $\nu_{max.}$ (Nujol) 1070, 1025, 845, 770, 755, 700, 685, and 655 cm.$^{-1}$; for n.m.r. spectrum see Table 1.

TABLE 1

1-Aryl-2,3,4-triphenylnaphthalenes (τ values) [a]



	R^1	R^2	Naphthalene H [b]	Other aromatic		Bu^t [c]
1	H	H	2·20—2·85	2·83 [c]	3·22 [d]	
2	6-Bu_t	H	2·21—2·50	2·77	3·15	8·74
3	6-Cl	H	2·28—2·72	2·82	3·19	
4	5-Bu^t	H	2·24—2·84	2·91, 3·10	3·30	9·02
5	5-Cl	H	2·29—2·72	2·82, 2·90	3·20	
6	H	*p*-Bu^t	2·10—2·85	2·78	3·15	8·72

[a] Solvent: $CDCl_3$ (spectra 2, 3, 5, 6); CCl_4 (spectra 1, 4). [b] Complex. [c] One H_{10} singlet (1, 2, 3); two H_5 singlets (4, 5); one H_9 singlet (6). [d] One H_{10} singlet (1—4, 6); two absorptions (total H_{10}) separated by 1 Hz (5). [e] H_9 singlet.

1,4-*Di*-p-*methoxyphenyl*-2,3-*diphenylnaphthalene*, m.p. 222—223° (lit.,[19] m.p. 221—222°) (Found: C, 88·1; H, 6·0. Calc. for $C_{36}H_{28}O_2$: C, 87·8; H, 5·7%), 1,4-*di*-p-*methylphenyl*-2,3-*diphenylnaphthalene*, m.p. 226—226·5° (Found: C, 94·2; H, 6·4. $C_{36}H_{28}$ requires C, 93·9; H, 6·1%), and 1,4-*di*-p-*methylsulphonylphenyl*-2,3-*diphenylnaphthalene*, m.p. 339—340° (Found: C, 73·3; H, 4·8; $C_{36}H_{28}O_4S_2$ requires C, 73·35; H, 4·8%) were similarly prepared from the corresponding 2,5-diaryl-3,4-diphenylcyclopentadienones. 1-*Chloro*-5,6,7,8-*tetraphenylnaphthalene*, similarly prepared (7·5%) from 3-chloroanthranilic acid, had m.p. 256·5—257·5° (Found: C, 87·2; H, 5·2; Cl, 7·3. $C_{34}H_{23}Cl$ requires C, 87·4; H, 5·0; Cl, 7·6%). The above products had the expected n.m.r. spectra (Table 1).

The following substituted triptycenes were prepared from pentyl nitrite, anthranilic acid, and the corresponding anthracene in acetone by standard routes, excess of the anthracene being removed by maleic anhydride: 9,10-dimethoxy-, m.p. 191—192°; (lit.,[20] m.p. 192—194°) (Found: C, 84·4; H, 5·5%; M^+, 314. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%; M^+, 314), 9-nitro-, m.p. 248—250° (lit.,[21] m.p. 241—243°), 9-bromo-, m.p. 254·5—255·5° (lit.,[21] m.p. 246—248°).

6-*t-Butyl*-1,4-*dihydro*-1,4-*epoxynaphthalene*.—A mixture of pentyl nitrite (2·93 g.), furan (6·80 g.) and dichloromethane (70 ml.) was stirred and boiled under reflux while a solution of 4-t-butylanthranilic acid (3·86 g.) in acetone (20 ml.) was dripped in during 4 hr. After being boiled for a further 2 hr. the mixture was fractionally distilled to yield pale yellow 6-*t-butyl*-1,4-*dihydro*-1,4-*epoxynaphthalene* (1·01 g., 25%), b.p. 83—84°/0·04 mm. (Found: C, 83·9; H, 7·9. $C_{14}H_{16}O$ requires C, 84·0; H, 8·05%); τ ($CDCl_3$) 2·65—3·22 (3H complex), 3·05 (2H multiplet on expansion), 4·46 (2H, multiplet on expansion), 8·71 (9H, s); $\nu_{max.}$ (liquid) 1390, 1360 (Bu^t), 1155 (C–O–C), and 700 cm.$^{-1}$ (*cis* CH=CH); mass spectrum, parent ion *m/e* 200 ($C_{14}H_{10}O$ requires M = 200).

Attempts to prepare the adduct from 2-bromo-4-t-butylfluorobenzene *via* lithium amalgam or the Grignard reagent failed.

The Adduct of 3-*Chlorobenzyne and Phenyl Azide*.—This adduct was prepared from 3-chloroanthranilic acid, pentyl nitrite, and phenyl azide by the standard method described above, to give 4- and/or 7-chloro-1-phenylbenzotriazole (5·5%), m.p. 115—116° (Found: C, 62·8; H, 3·4. $C_{12}H_8ClN_3$ requires C, 62·75; H, 3·5%).

1,4-*Dimethyl*-1,4-*dihydro*-1,4-*epoxynaphthalene*.—This was prepared from 2,5-dimethylfuran, *o*-dibromobenzene, and butyl-lithium, and had m.p. 32—33° (lit.,[22] m.p. 35°).

Reactions of Acetylarylnitrosamines.—*General technique*. This was as described in Part II [3] for *o*-t-butyl-*N*-nitrosoacetanilide. Unless otherwise stated decompositions were carried out at room temperature until evolution of nitrogen had ceased and then at the b.p. for 1 hr.

Reaction of o-*Chloro*-N-*nitrosoacetanilide with* 1,6,7,8-*Tetraphenylcyclopentadienone in Benzene*. The nitrosamide (7·01 g., 35·3 mmoles) was allowed to decompose in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (13·5 g., 35·1 mmoles) in benzene (81·9 g., 1·05 moles) at 38° for 15 hr. and at b.p. for 1 hr. The cooled reaction mixture was filtered, the solid was washed with benzene, and a portion of the combined filtrate and washings were examined by g.l.c. (10% CAR, 198°; 2% NPGS, 130°; 10% SIL, 70° and 200°) with biphenyl as internal standard. The following products were detected: acetic acid (35%), chlorobenzene (0·5), *o*-chlorophenyl acetate (0·4), 2-chlorobiphenyl (28·4), 2-acetoxybiphenyl (3·9), and *o*-chloroacetanilide (6·0). *m*- and *p*-Chlorophenyl acetates (0·02% would have been detected) were absent.

The major part (33·3 mmoles nitrosamide) of the filtrate and all the solid material were chromatographed on alumina (1250 g.). Elution with petroleum containing benzene (1—5%) yielded colourless 2-chlorobiphenyl (crude, 1·55 g., 8·19 mmoles, 24·6%); m.p. 31—31·5°, mixed m.p. 30—31·5°, after crystallisation from petroleum at −40°. The i.r. spectrum was identical to that of the authentic material. Further fractions, eluted with solvents of steadily increasing polarity, were examined by t.l.c., and i.r., and u.v. spectroscopy. No 1-chloro-5,6,7,8-tetraphenylnaphthalene was detected. 2,3,4,5-Tetraphenylcyclopentadienone (8·90 g., 23·2 mmoles) was eluted in benzene.

In a corresponding reaction using phenyl azide instead of the dienone no adduct of 3-chlorobenzyne and the azide was detected.

Reaction of p-*Chloro*-N-*nitrosoacetanilide with Tetraphenylcyclopentadienone in Benzene*.—*p*-Chloro-*N*-nitrosoacetanilide (7·98 g., 40·2 mmoles) was allowed to decompose in a suspension of tetraphenylcyclopentadienone (15·3 g., 39·8 mmoles) in benzene (93·6 g., 1·20 moles). Work-up as described above gave 4-chlorobiphenyl (5%) m.p. and mixed m.p. 75—76°, 2-*chloro*-5,6,7,8-*tetraphenylnaphthalene* (2·7%), m.p. 229—229·5° (Found: C, 87·25; H, 5·05. $C_{34}H_{23}Cl$ requires C, 87·4; H, 5·0%) (n.m.r., Table 1), 2,3,4,5-tetraphenylcyclopentadienone (8·64 g., 22·5 mmoles) was recovered. Quantitative g.l.c. analysis gave the following yields: *p*-chlorophenylacetate (1%), 4-acetoxybiphenyl (0·6%), *p*-chloroacetanilide (1%). *o*- or *m*-Chlorophenyl acetates were absent (0·05% would have been detected).

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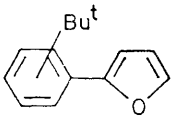
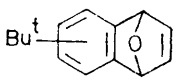
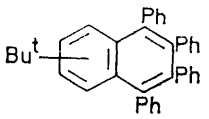
Reaction of m-*Chloro*-N-*nitrosoacetanilide with Tetraphenylcyclopentadienone in Benzene.*—*m*-Chloro-*N*-nitrosoacetanilide, prepared as an oil (caution: violent decomposition sometimes occurs) from the anilide (6·78 g., 40·0 mmoles) was allowed to decompose in benzene (140 ml.) in the presence of tetraphenylcyclopentadienone (15·3 g., 39·9 mmoles) in the usual way. Work-up gave 3-chlorobiphenyl (3%) by comparison (i.r.) with an authentic specimen, and 1-*chloro*-5,6,7,8-*tetraphenylnaphthalene* (19%) m.p. and mixed m.p. 256·5—257·5°, correct n.m.r. spectrum. It was distinguished from the 2-chloro-isomer, obtained in the n.m.r. and i.r. spectra). Control experiments having established where the isomeric 1,2,3-triphenyl-4-(*p*-t-butylphenyl)naphthalene, if present, was likely to appear in the above chromatographic separation, all relevant fractions were examined by i.r. spectroscopy using solutions in carbon tetrachloride in silver chloride cells (3 mm). The resulting spectra were compared with those of known mixtures of the two isomers in the region 640—670 cm.$^{-1}$. 1,2,3-Triphenyl-4-(*p*-t-butylphenyl)naphthalene has a band at 655 cm.$^{-1}$ whereas the isomeric 1,2,3,4-tetraphenyl-6-t-butylnaphthalene does not. In this way it was shown that only the latter

TABLE 2

Decompositions of *o*-, *m*-, and *p*-t-butyl-*N*-nitrosoacetanilides in (a) benzene, (b) benzene and furan, (c) benzene and 2,3,4,5-tetraphenylcyclopentadienone at room temperature [a]

	Yields from $Bu^t \cdot C_6H_4 \cdot N(NO)Ac$								
	o-			*m*-			*p*-		
Products	a	b	c	a	b	c	a	b	c
$PhBu^t$	10·2	3·5	3·2	4·2	8·7	0·5	5·9	5·8	0·3
Ph_2	3·9	0·9	0·2	0·3	0·3	0·1	0·4	0·1	0
o-$Bu^t \cdot C_6H_4 \cdot OAc$	37·8	36·9	50·5	0	0	0	0	0	0
m-$Bu^t \cdot C_6H_4 \cdot OAc$	17·4	0	0	7·9	9·0	17·2	0	0	0
p-$Bu^t \cdot C_6H_4 \cdot OAc$	0	0	0	0	0	0	0·5	0·3	8·7
o-$Bu^t \cdot C_6H_4 \cdot Ph$	2·3	3·0	2·6	0	0	0	0	0	0
m-$Bu^t \cdot C_6H_4 \cdot Ph$	0	0	0	19·4	11·2	4·6	0	0	0
p-$Bu^t \cdot C_6H_4 \cdot Ph$	0	0	0	0	0	0	36·4	18·6	4·8
 *m*-					7·0			0	
p-					0			16·6	
 5-		20·5							
6-									
 5-			34·2			3·9 [b]			0
6-						6·3 [b]			12·1
$Bu^t \cdot C_6H_4NHAc$	0·3	1·9	0·7	14·2	13·1	17·1	5·8	8·7	5·7
% Ar accounted for	68·0	65·8	91·2	45·7	49·0	34·4	48·6	50·0	31·6

[a] (a) Nitrosamide (1 mole), benzene (20 moles). (b) Nitrosamide (1 mole), furan (2 moles), benzene (20 moles for *o*- and *p*-isomers, 26 moles for *m*-). (c) Nitrosamide (1 mole), tetraphenylcyclopentadienone (1·3 moles), benzene (20 moles). [b] Total crude yield 12%.

preceding experiment by the absence of absorptions at 894, 877, and 742 cm.$^{-1}$. All relevant fractions were examined by t.l.c. for possible traces of the tetraphenylnaphthalenes. From examination of i.r. spectra of made up mixtures it was estimated that the yield of the 2-chloro-isomer, if present at all, was less than 1%. G.l.c. analysis gave *m*-chlorophenyl acetate (0·5%), 3-acetoxybiphenyl (0·1%), and *m*-chloroacetanilide (8%). *o*- And *p*-chlorophenyl acetates were absent (<0·05%).

Reaction of p-*t-Butyl*-N-*nitrosoacetanilide with Tetraphenylcyclopentadienone in Benzene.*—Several experiments using the nitrosamide (5·79 g., 26·3 mmoles) and the dienone (12·7 g., 33·0 mmoles) in benzene (39·0 g., 0·50 moles) were carried out. The products were examined, in standard fashion, by g.l.c., distilled, and/or worked up by chromatography to give the following products: acetic acid (75%), *p*-t-butylphenyl acetate (10%) (correct i.r. *cf.* authentic specimen), 4-t-butylbiphenyl (5%), m.p. and mixed m.p. 50—51°, 2-*t-butyl*-5,6,7,8-*tetraphenylnaphthalene* (12%), m.p. and mixed m.p. 285·5—286·5° (Found: C, 93·35; H, 6·7. $C_{38}H_{32}$ requires C, 93·4; H, 6·6%) (correct isomer was present (4·3% of the admixed isomer would have been detected, *i.e.* 0·5% based on *N*-nitrosoacetanilide).

Reaction of p-*t-Butyl*-N-*nitrosoacetanilide with Furan in Benzene.*—In the standard fashion, the nitrosamide (6·16 g., 28·0 mmoles) in furan (3·81 g., 56·0 mmoles) in benzene (43·6 g., 0·560 moles) gave 4-t-butylbiphenyl (m.p. and mixed m.p. 50—51°), 2-(p-*t-butylphenyl*)*furan*, b.p. 56°/0·04 mm. (Found: C, 83·5; H, 8·4. $C_{14}H_{16}O$ requires C, 84·0; H, 8·05%) (by prep. g.l.c.); τ (CCl_4) 2·54 (centre of AA'BB'H_4), 2·58 (dd, 5-H), 3·45, (dd, 3H), 3·61 (dd, 4-H), 8·69 (s, C_4H_9); $J_{3,4}$ 3·5 Hz, $J_{3,5}$ 0·8 Hz, $J_{4,5}$ 1·6 Hz. 6-t-Butyl-1,4-dihydro-1,4-epoxynaphthalene was absent (by g.l.c. comparison with an authentic sample).

Results of the above experiments and those carried out in the absence of arynophiles are given in Table 2.

Reaction of m-*t-Butyl*-N-*nitrosoacetanilide with Tetraphenylcyclopentadienone in Benzene.*—The standard procedure using the nitrosamide (30·0 mmole) and the dienone (40·0 mmole) in benzene (0·60 mole) gave 3-t-butylbiphenyl (3%) (correct i.r. spectrum), 1,2,3,4-tetraphenyl-6-t-butylnaphthalene, m.p. and mixed m.p. 286—287°,

correct i.r. spectrum (6%) and 1,2,3,4-tetraphenyl-5-t-butylnaphthalene, m.p. and mixed m.p. 164·5—165·5°,[3] correct i.r. spectrum (separated from the former by fractional crystallisation). Other details of the experiment are summarised in Table 2.

Reaction of m-*t-Butyl*-N-*nitrosoacetanilide with Furan in Benzene*.—From a standard reaction using furan (60·0 mmole) and the nitrosamide (30·0 mmole) in benzene (0·79 mole) was isolated 3-t-butylbiphenyl (correct i.r. spectrum), *m*-t-butylphenyl acetate, m.p. and mixed m.p. 42—43° and 2-*m*-t-butylphenylfuran (b.p. 90°/0·8 mm.) (Found: C, 83·3; H, 8·03. $C_{14}H_{16}O$ requires C, 84·0; H, 8·05%); τ (CCl_4) 2·27—2·85 (complex, H_4), 2·59 (dd, 5-H), 3·43 (dd, 3-H), 3·61 (dd, 4-H) and 8·64 (s, CMe_3); $J_{3,4}$ 3·3, $J_{3,5}$ 0·9, and $J_{4,5}$ 1·8 Hz; mass spectrum: parent ion *m/e* 200. $C_{14}H_{16}O$ requires *M*, 200. $M + 1/M = 16·18\%$. $C_{14}H_{16}O$ requires $M + 1/M$, 15·42%. Results of g.l.c. determinations in this experiment and those of experiments carried out in the absence of arynophiles are given in Table 2.

Reactions of N-*Nitrosoacetanilide with Tetra-arylcyclopentadienones in Various Solvents*.—The general procedure, described above, was followed, the aryne adduct being isolated by chromatography in each case. The results of the experiments are summarised in Table 3. In the absence of arynophiles the major product, in benzene, was biphenyl (57%). The presence of benzobicyclo-[2,2,2]octatriene [23] in the crude product was excluded by the absence of n.m.r. absorptions (τ 5·2) attributable to the bridgehead protons of the latter (0·2% would have been detected).

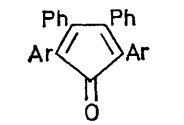
Reactions of N-*Nitrosoacetanilide with Anthracene and Derivatives in Benzene*.—A typical experiment is as follows: the nitrosamide (1·64 g., 10·0 mmoles) was allowed to decompose in benzene (15·60 g., 0·2 moles) containing anthracene (1·78 g., 10·0 mmoles) at 50° for 12 hr.; the mixture was then boiled under reflux. After removal of the solvent, excess of anthracene was removed by boiling under reflux in chlorobenzene (25 ml.) containing maleic anhydride (1·78 g.) for 10 hr. Chromatography on alumina gave the following fractions on elution with benzene–petroleum (1 : 9): (*a*) 0·12 g., yellow solid, (*b*) 0·54 g., yellow solid. Fraction (*a*) was recrystallised from methanol to give biphenyl (0·13 g., 10 m/100 m). Fraction (*b*) was shown by g.l.c. (10% PEGA/200°) to contain one major component. Preparative g.l.c. (2% NPGS/200°) using the D.6 instrument afforded a sample of this compound, which was identified as triptycene, (yield by g.l.c. using the isolated yield of biphenyl as internal standard, 5·0 m/100 m), m.p. 251—252°; $M^+ = 254$. The i.r. and n.m.r. spectra were indistinguishable from those of authentic material.

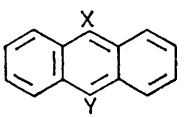
By comparison of the g.l.c. chromatograms before and after work-up, it was observed that the major product of the reaction was absent, after reaction with maleic anhydride. From a parallel reaction, preparative g.l.c. (2% NPGS/200°) afforded a sample of this compound, which was identified as 9-phenylanthracene (yield by g.l.c. 54·0%), m.p. and mixed m.p. 153—154°. The i.r. spectrum was indistinguishable from that of an authentic sample kindly provided by Professor R. O. C. Norman.

Reactions with other anthracenes were carried out similarly. The results are summarised in Table 3.

TABLE 3

Aryne-adducts from *N*-nitrosoacetanilide and arynophiles [a]





Arynophile	Solvent	Aryne Adduct (%)	Ph_2 (%)
None	PhH	0	57 [e]
Ar = Ph	PhH	25	16
Ar = Ph	Furan	1·4 [b]	
Ar = Ph	Tetrahydrofuran	24	
Ar = Ph	C_5H_5N	0	
Ar = Ph	AcOH	4	
Ar = Ph	Durene	34	
Ar = Ph	C_6Me_6	33	
Ar = *p*-MeO·C_6H_4	PhH	82	3
Ar = *p*-MeC_6H_4	PhH	82	0
Ar = *p*-$MeSO_2$·C_6H_4	CCl_4	19	
Ar = Ph	PhH [f]	68	
X = Y = H	PhH	5	10 [c]
X = Y = Me	PhH	30	7·5
X = Y = MeO	PhH	15	7·5 [d]
X = H, Y = Br	PhH	4	0
X = H, Y = NO_2	PhH	7	2·0

[a] All yields based on *N*-nitrosoacetanilide. All aryne adducts were isolated, and characterised by mixed m.p., n.m.r., and analysis. [b] 1,2,3,4-Tetraphenylnaphthalene was isolated. 2-Phenylfuran (22%) was also formed. The furan-benzyne adduct was absent (by g.l.c.). [c] 9-Phenylanthracene (54%) was also formed (m.p. and mixed m.p. 153—154°). [d] Anthraquinone m.p. and mixed m.p. 258° was also formed. [e] Benzobicyclo[2,2,2]octatriene was absent (<0·2% by n.m.r.). [f] Dried over $LiAlH_4$.

Reaction of N-*Nitrosoacetanilide with Furan in Benzene*.—*N*-Nitrosoacetanilide (8·01 g., 48·9 mmoles) was allowed to decompose in a solution of furan (6·8 g., 0·10 mole) in benzene (46·8 g., 0·60 mole). A sample of the reaction mixture was examined by g.l.c. (10% CAR, 180°; 10% SIL, 170°; 3% APL, 130°) with bibenzyl as internal standard, and was found to contain phenyl acetate (1·0%), 2-phenylfuran (22·6), and biphenyl (16·9). 1,4-Dihydro-1,4-epoxynaphthalene (0·15% would have been detected) was absent.

The yield of acetic acid (79·6%) was determined by titration. Control experiments established that 1,4-dihydro-1,4-epoxynaphthalene was stable in boiling benzene in the presence of acetic acid (4 hr.) and in a mixture of boiling benzene, furan and *N*-nitrosoacetanilide under the conditions of the standard experiments.

Competition Reactions of N-*Nitrosoacetanilide with Furan and Tetraphenylcyclopentadienone in Benzene*.—Figure 1 summarises the results of these experiments. In the

[23] R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, 1963, **85**, 1798.

experiment involving no dilution with benzene, *i.e.* using furan only as solvent, biphenyl and 1,4-dihydro-1,4-epoxynaphthalene were absent by g.l.c. (2% NPGS at 130°) and 1,2,3,4-tetraphenylnaphthalene could not be detected by t.l.c. 2-Phenylfuran (b.p. 85—90°/7 mm.) was isolated by preparative g.l.c. (Found: C, 83·5; H, 5·8%. Calc. for $C_{10}H_8O$, C, 83·3; H, 5·55%); τ (CCl_4) 3·62 (4-H), 3·45 (3-H), 2·62 (5-H) ($J_{3,4}$ 3·4 Hz, $J_{4,5}$ 1·8 Hz, $J_{5,5}$ 0·8 Hz) and a complex multiplet 2·28—2·90 (5H). Chemical shifts for furan are at 2·7 (αH) and 3·75 (βH).[24] In 2-phenylfuran 3-H should be deshielded by the phenyl ring causing the chemical shift to be *ca.* 0·2 lower than that for 4H. Average values for $J_{3,4}$, $J_{4,5}$, $J_{3,5}$ are 3·2—3·8 Hz, 1·8—2·0 Hz, and 0·7 Hz respectively.[25] The product is then 2- rather than 3-phenylfuran. Quantitative g.l.c. gave the yield as 28%.

A competition experiment using furan (0·03 mole), tetraphenylcyclopentadienone (0·029 mole), benzene (0·29 mole) and authentic benzyne from anthranilic acid (0·015 mole) and pentyl nitrite gave 1,2,3,4-tetraphenylnaphthalene (82%), m.p. and mixed m.p. 198—200°. 1,4-Dihydro-1,4-epoxynaphthalene was absent (by g.l.c.).

Reaction of N-*Nitrosoacetanilide with* 1,3-*Diphenylisobenzofuran in Benzene.*—The nitrosamide (0·5 g., 0·003 mole) and 1,3-diphenylisobenzofuran (1·65 g., 0·006 mole) in benzene (9·5 g., 0·125 mole), under nitrogen, were left at room temperature for 10 hr. and then boiled under reflux for 6 hr. When cool, powdered zinc (8 g., 0·12 mole) and acetic acid (20 ml., 0·35 mole) were added and the solution was stirred for 8 hr. at 85°, filtered; the volatile components of the filtrate were distilled off and benzene (10 ml.) was added to the residue. Chromatography on alumina and subsequent recrystallisation from acetic acid gave 9,10-diphenylanthracene (0·1371 g., 14%; m.p. and mixed m.p. 246—248°, lit.,[26] 246—247°, and identical i.r. spectrum with an authentic specimen).

Reaction of N-*Nitrosoacetanilide with* 2,5-*Dimethylfuran in Benzene.*—The nitrosamide (4·97 g., 30·3 mmoles) was allowed to decompose in a solution of 2,5-dimethylfuran (5·76 g., 60·0 mmoles) in benzene (28·1 g., 0·36 mole). A sample of the brown solution was examined by g.l.c. (2% NPGS, 103°; 8% BDS, 160°) with bibenzyl as internal standard and was found to contain biphenyl (7·4%) and an unidentified component (*ca.* 4·5 × weight of biphenyl) with a retention time on NPGS of 0·71 relative to biphenyl. Phenyl acetate (0·2% would have been detected) and 1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (0·1) were absent.

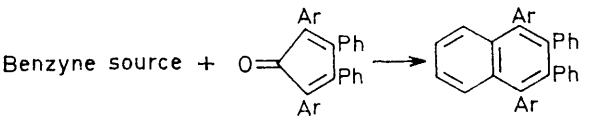
Distillation of the bulk (25·8 mmoles nitrosamide) of the reaction mixture afforded a yellow oil (1·50 g.), b.p. 82—84°/2·2 mm. Preparative g.l.c. (15 ft. × 0·375 in o.d. glass column containing 20% APL on Celite at 215°) afforded samples of biphenyl, m.p. and mixed m.p. 68—69°; and 2-*benzyl*-5-*methylfuran*, a pale yellow liquid, b.p. 130° (block temp.)/12 mm. (Found: C, 83·4; H, 7·0. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%); τ (CCl_4) 2·87 (s, H_5, Ph), 4·29 (s, H_2, 3-H and 4-H), 6·18 (s, CH_2) and 7·79 (s, CH_3); $\nu_{max.}$ (liquid) 1570, 1495, 1455, 1220, 1020, 780, and 715 $cm.^{-1}$. The yield of 2-benzyl-5-methylfuran (29·4 m/100 m) was computed from the quantitative g.l.c. measurements.

In a control experiment acetic acid (2·5 mmoles) was added to a solution of 1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (0·5 mmole) and biphenyl (0·5 mmole) in benzene (30 mmoles). G.l.c. examination (2% NPGS, 103°) showed that the ratio of epoxide to biphenyl was unchanged by the addition of acetic acid. The mixture was then boiled under reflux for 2·5 hr. after which time only a small reduction (2—5%) in the amount of epoxide was detected.

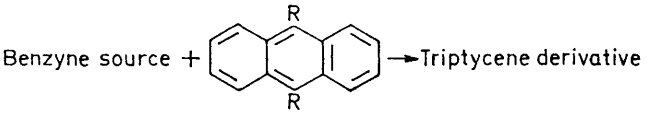
Competition Reactions.—General procedure. Competition reactions involved reaction of the aryne source with an excess (10·2 : 1) of an equimolar mixture of two arynophiles which was either (*a*) a mixture of 2,3,4,5-tetra-arylcyclopentadienones or (*b*) a mixture of anthracenes in benzene (500 mole excess) or CCl_4. After reaction, the mixture was treated with maleic anhydride in chlorobenzene, and after removal of the solvent, the residue was chromatographed on alumina, and the molar ratio, K^1_2 where K^1_2 = moles of adduct 1/moles of adduct 2, computed in case (*a*) by measurement of the individual areas of the two methyl absorptions in the n.m.r. spectrum of the mixture (CH_3 = τ 7·72, OCH_3 = τ 6·26, and SO_2CH_3 = τ 7·00). A Varian HA-100 n.m.r. spectrometer was used, and the integral values taken as the mean of at least three readings. The quantitative response of the instrument was confirmed with known

TABLE 4

Competition reactions using pairs of arynophiles and various benzyne sources



Ar in arynophile pair	Solvent		Competition constant K for various sources NNA	AA	AB *
p-Me·C_6H_4 *p*-MeO·C_6H_4	PhH	K^{OMe}_{Me}	1·0	1·0	1·0
p-Me·C_6H_4 *p*-MeO·C_6H_4	CCl_4	K^{OMe}_{Me}	1·0	1·0	1·0
p-$MeSO_2$·C_6H_4 *p*-MeO·C_6H_4	CCl_4	$K^{OMe}_{SO_2Me}$	2·2	2·1	



R in arynophile pair	Solvent		Competition constant for various sources NNA	AA *
MeO H	PhH	K^{OMe}_{H}	3·2	3·1
Me H	PhH	K^{Me}_{H}	19·7	19·5

* NNA: *N*-nitrosoacetanilide. AA: Anthranilic acid/pentyl nitrite. AB: 1-Aminobenzotriazole/$Pb(OAc)_4$.

mixtures of adducts. The error involved in the measurement of the n.m.r. integral was ±2 mm. on each reading, thus giving a total error in the quotient of ±8 mm. This amounted at maximum to an error of ±10%.

To check for random error, control experiments were performed which showed that mixtures of adducts, when subjected to the complete work-up procedure, were recovered quantitatively, and the difference involved in the n.m.r.

[24] G. S. Reddy and J. H. Goldstein, *J. Phys. Chem.*, 1961, **65**, 1539.

[25] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1966, p. 789.

[26] G. Wittig, E. Knauss, and K. Niethammer, *Annalen*, 1960, **630**, 10.

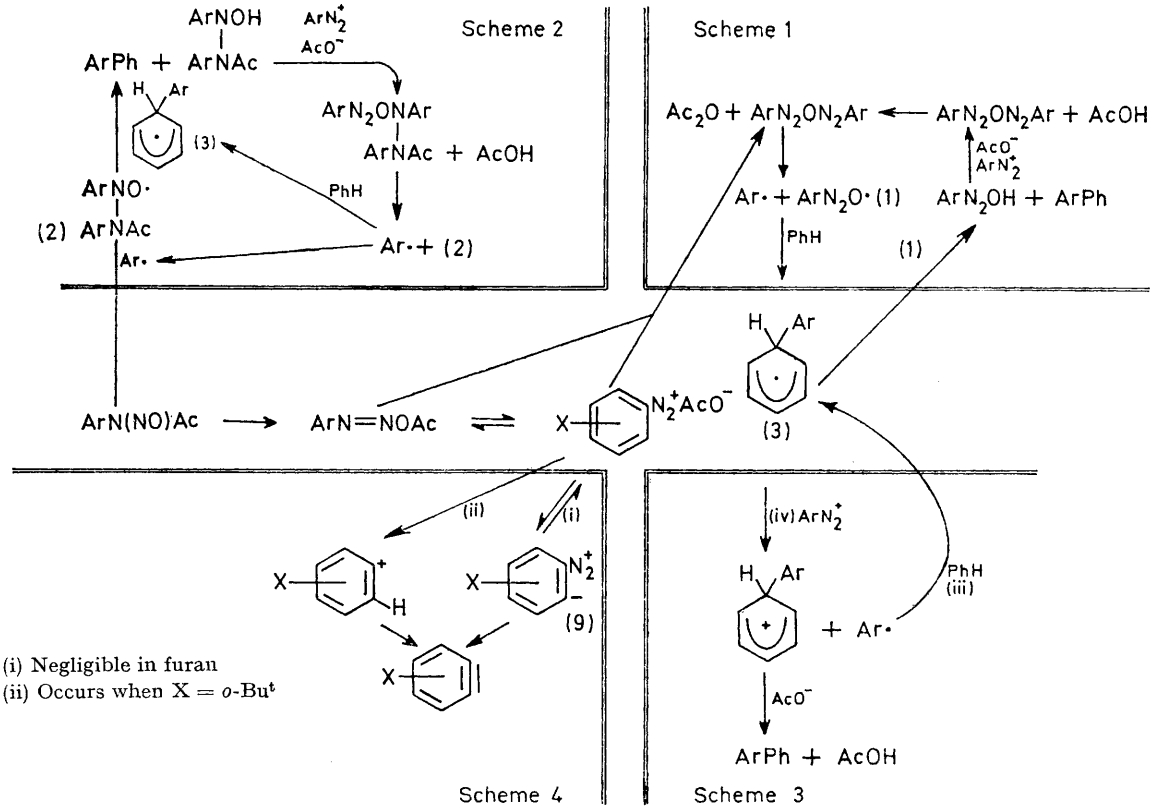
measurement of K^1_2 before and after work-up was always within the ±10% calculated error.

In case (*b*), the ratio K^1_2 was measured by g.l.c. (Pye 104 and Varian Aerograph 1520B), the instrument being calibrated with known mixtures of adducts. Area measurements of g.l.c. peaks showed, at maximum, a variance of ±5%, the total error in the quotient is thus ±10%. Again random error was checked for by control experiments which showed that the difference in K^1_2 before and after work-up was always within the 10% calculated error.

The sources of authentic benzyne used were anthranilic acid and pentyl nitrite,[27] or 1-aminobenzotriazole and lead tetra-acetate.[28] The results are given in Table 4.

DISCUSSION

The Formation of Benzyne Adducts.—It is well known [29] that acylarylnitrosamines such as *N*-nitrosoacetanilide (NNA) readily decompose in benzene to give the biaryl (*ca.* 50%) and acetic acid (>90%) *via* aryl radicals. The other product is a large amount of unidentified tar. Evidence has been presented [2,29] that this reaction proceeds, at least in part, *via* Scheme 1, involving the oxidation of the intermediate arylcyclohexadienyl radical by the σ-aryldiazotate radical (1). In some cases such oxidation by the *N*-arylacetamido aryl nitroxide (2) cannot be excluded (Scheme 2). Once an aryl radical has



Reaction of N-Nitrosoacetanilide with 1,4-Dimethoxyanthracene in Benzene.—*N*-Nitrosoacetanilide (0·82 g., 5·0 mmoles) was allowed to decompose in benzene (7·8 g., 0·1 mole) containing 1,4-dimethoxyanthracene (2·38 g., 10·0 mmoles) at 50° for 12 hr. Analysis of the reaction mixture by g.l.c. (5% SE-30/180°; 2% APL/200°) using the authentic samples of A-ring and B-ring adducts provided by Dr. B. H. Klanderman for peak enhancement, identified 1,4-dimethoxytriptycene and 5,12-dimethoxy-5,12-dihydro-5,12-ethenonaphthacene. Quantitative measurements gave the value of the competition constant as $K_A{}^B = 2·6$.

The corresponding reaction using anthranilic acid and pentyl nitrite gave $K_A{}^B = 2·6$.

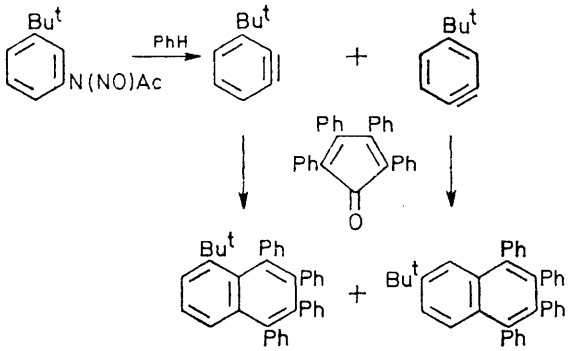
been produced *via* Scheme 1 (and possibly Scheme 2) it is likely that a redox reaction involving unchanged diazonium cation and the intermediate radical (3) occurs (Scheme 3).[2,29,30] The combined Schemes 1—3 satisfactorily account for the genesis of the known products (but not the tars). The anomalous case of *o*-t-butyl-N-nitrosoacetanilide which proceeds almost entirely via *o*-t-butylbenzyne [3,29,30] is accommodated by an extension of Schemes 1—3 (Scheme 4) whereby the bulky *o*-t-butyl group induces loss of nitrogen to give the intermediate *o*-t-butyl phenyl cation which combines with acetate ion to give *o*-t-butylphenyl acetate or loses a proton to give *o*-t-butylbenzyne, which in turn adds acetic acid to give *m*-t-butylphenylacetate. Thus in the latter, special

[27] L. Freidman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.
[28] C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 1964, 296.
[29] J. I. G. Cadogan, *Chem. Soc. Special Publ.*, 1970, **24**, 71.
[30] J. I. G. Cadogan and P. G. Hibbert, *Proc. Chem. Soc.*, 1964, 338.

case, the presence of the aryne manifests itself in the appearance of a high yield of *cine*-acetates (*ca.* 50%) and a negligible yield of the expected biaryl, 2-t-butylbiphenyl (Table 2). In all other cases of acylarylnitrosamine decompositions previously investigated over 70 years, no reports of *cine*-acetate formation had been made, and the possibility of aryne participation had been unsuspected.

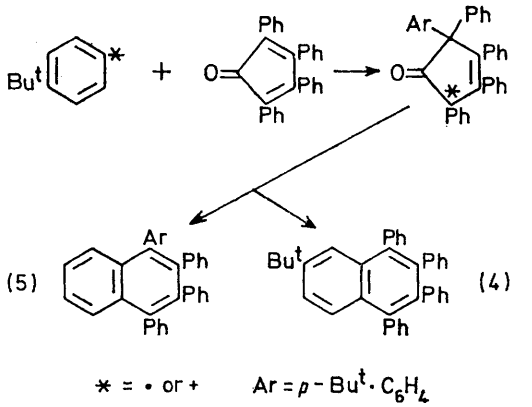
We have now shown (Table 3) that decompositions of NNA in a variety of solvents in the presence of tetraphenylcyclopentadienone, its 2,5-di-(*p*-methoxyphenyl)-, 2,5-di-(*p*-methylphenyl)-, and 2,5-di-(*p*-methylsulphonylphenyl)-derivatives, anthracene, and its 9,10-dimethyl-, 9,10-dimethoxy-, 9-bromo- and 9-nitro-derivatives, and 1,3-diphenylisobenzofuran, all, with the exception of pyridine lead to the isolation of the corresponding benzyne-adducts, *e.g.* 1,2,3,4-tetra-arylnaphthalenes or triptycenes, in yields varying from 4 to 82%, as shown by comparison with authentic samples. The yield of biphenyl resulting from the decomposition of NNA in benzene, alone, under comparable conditions is 57%, thus indicating that in the presence of certain arynophiles, notably 2,5-di-*p*-methylphenyl- and 2,5-di-*p*-methoxyphenyl-3,4-diphenylcyclopentadienone, decomposition of NNA is diverted from the route leading to phenyl radicals into one leading to the ' benzyne adduct.' It is noteworthy in this respect that Stiles and Miller have shown that the reaction of benzyne, from benzene-diazonium carboxylate, with benzene gives benzobicyclo[2,2,2]octatriene, albeit in only 2% yield,[31] and that this product is not formed in our reaction of NNA with benzene.

A similar pattern emerges from decomposition of *m*- and *p*-t-butyl-*N*-nitrosoacetanilides (Bu^t-NNA) (Table 2) and the corresponding *m*- and *p*-chloro-analogues (Cl-NNA). In the absence of arynophiles the decompositions follow the radical route leading to the corresponding biaryls, albeit with low accountance of the starting



SCHEME 5

nitrosamide. In the presence of tetraphenylcyclopentadienone, substituted 1,2,3,4-tetraphenylnaphthalenes were formed. Thus *m*-Cl-NNA gave 1- but not 2-chloro-5,6,7,8-tetraphenylnaphthalene and *p*-Cl-NNA gave the said 2-chloro-isomer; *m*-Bu^t-NNA gave 1- and 2-t-butyl-5,6,7,8-tetraphenylnaphthalenes (Scheme 5) while *p*-Bu^t-NNA gave the 2-t-butyl derivative (4), all at the expense of radical or carbonium ion derived products (*e.g.* 4-t-butylbiphenyl and *p*-t-butylphenylacetate). In the last named case, a careful search for the isomeric 1-(*p*-t-butylphenyl)-2,3,4-triphenylnaphthalene (5) was made without success (0·5% yield would have been detected). Its absence, therefore, excludes Scheme 6 involving the formation of the ' aryne adduct ' *via* an unidentate species such as a radical or carbonium ion (* = · or +). The ' aryne adduct ' therefore, arises *via* cycloaddition involving a bidentate species.



SCHEME 6 [Discounted because (5) is not formed]

These results, taken alone, therefore, can be rationalised on the basis of deprotonation of the aryldiazonium ion by the acetate counter ion followed by loss of nitrogen to give the corresponding aryne (Scheme 4). The process being in competition with the ' normal ' route (Schemes 1—3) giving radicals and being detected only in the presence of the arynophile. The formation of two isomeric adducts from *m*-Bu^t-NNA is in accord with this (Scheme 5), and with the fact that *m*-chlorotoluene gives 3- and 4-methylbenzyne as evidenced by the formation of *o*-, *m*-, and *p*-chloroanilines on treatment with sodamide in liquid ammonia.[32] The formation of 1-chloro-5,6,7,8-tetraphenylnaphthalene but not its 2-chloro-isomer from *m*-Cl-NNA is also in accord with the exclusive formation of 3-chlorobenzyne from *m*-dichlorobenzene on treatment of the latter with sodamide in liquid ammonia.[33] The detection of *m*- but not *o*-t-butylphenyl acetate from decomposition of *m*-Bu^t-NNA (Table 2) is also in accord with the previous supposition that acetic acid adds to *o*-t-butylbenzyne to give exclusively the *meta*-isomer,[3] while the absence of *p*-t-butylphenyl acetate is in accord with the low efficiency of addition of acetic acid to non-hindered arynes.

Further information on the nature of the intermediate was provided by results of competition experiments involving reactions of various reactive arynophiles (Table

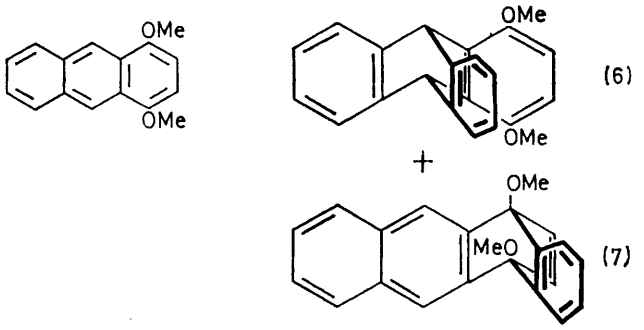
[31] M. Stiles and R. G. Miller, *J. Amer. Chem. Soc.*, 1960, **83**, 3802; 1963, **85**, 1798.

[32] J. D. Roberts, C. W. Vaughan, L. A. Carlsmith, and D. A. Semenov, *J. Amer. Chem. Soc.*, 1956, **78**, 611.

[33] J. H. Wotiz and F. Huber, *J. Org. Chem.*, 1959, **24**, 595.

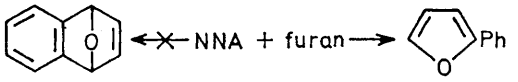
4) with (*a*) authentic benzyne, produced from anthranilic acid/pentyl nitrite and/or 1-aminobenzotriazole/lead tetra-acetate, and (*b*) the species present in the decomposition of NNA in benzene. The results show that the two species, authentic benzyne and that present in the decomposition of NNA, react at identical or near-identical rates.

Klanderman and Criswell [34] have shown that in the reaction of benzyne with 1,4-dimethoxyanthracene the ratio of B-ring adduct (6) to A-ring adduct (7) is independent of the benzyne precursor. They obtained values of $K_A^B = 2{\cdot}1$—$2{\cdot}6$ for such a series. We confirm



the value of 2·6 obtained for pentyl nitrite/anthranilic acid and report an identical figure for the reaction involving NNA in benzene. These results clearly point to the participation of arynes in these reactions.

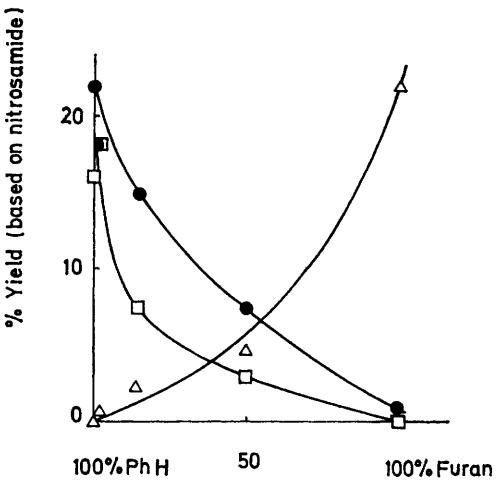
The Non-Formation of Furan–Aryne Adducts on Decomposition of NNA in Furan and the Suppression of the Formation of Tetra-arylcyclopentadienone–Aryne Adducts by Added Furan.—Although the foregoing results clearly point to the participation of benzyne it is necessary to account for the apparently anomalous fact that decomposition of NNA in furan gave little or no benzyne–furan adduct [1,4-dihydro-1,4-epoxynaphthalene (8)], control experiments having established that it is stable under the conditions of the decomposition. The main isolated product was 2-phenylfuran. From a mixture of benzene and furan (6 : 1 molar respectively) was isolated



(8)

biphenyl (17%) in lower yield than 2-phenylfuran (23%), and again the epoxide (8) was absent (0·15% would have been detected). This confirms the great ease of homolytic substitution at position 2 in furan. Further, experiments involving decomposition of NNA in various benzene–furan mixtures in the presence of tetraphenylcyclopentadienone (Figure) show that furan progressively suppresses the yield of 1,2,3,4-tetraphenylnaphthalene from 20% in neat benzene to *ca.* 1% in neat furan (the corresponding reaction of authentic benzyne from pentyl nitrite/anthranilic acid with a mixture of furan and tetraphenylcyclopentadienone gave an 82% yield of 1,2,3,4-tetraphenylnaphthalene). This fall in yield was paralleled by the fall in yield of biphenyl and almost exactly balanced by the formation of 2-phenylfuran. Similar behaviour towards furan is exhibited by *m*- and *p*-Bu^t-NNA in the presence of benzene, when the major products are biphenyl and the corresponding 2-(*m*- or *p*-t-butylphenyl)furans (Table 2). Bearing in mind that these nitrosamides give aryne adducts with tetraphenylcyclopentadienones, their behaviour is in marked contrast to that of the special case of *o*-Bu^t-NNA which gives aryne adducts with anthracenes, tetraphenylcyclopentadienone, *and* furan (Table 2).

Several possible explanations for the anomalous behaviour of furan must be considered: (*a*) that the species responsible for the formation of aryne-type adducts with anthracenes and tetra-arylcyclopentadienones is not a true aryne but is its arynoid precursor (9; Scheme 4) which could conceivably react *via* cycloaddition with



△ = 2-Phenylfuran; ● = tetraphenylnaphthalene, □ = biphenyl

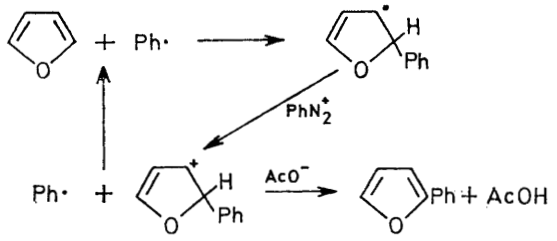
concerted or subsequent loss of nitrogen. This previously considered possibility [29,35] must be discounted in view of the foregoing results of the competition experiments, since this possibility would require benzyne and its precursor (9) to have the same reactivity towards all the arynophiles studied, which is extremely unlikely.* (*b*) That suppression of the formation of the aryne takes place in furan by π-stabilisation of the precursory diazonium cation, thus leading to a less acidic *o*-proton and hence to a smaller probability of occurrence of reaction (i) in Scheme 4. This stabilisation would not be expected to be strong and we have no evidence for or against this possibility. The possibility of σ-donation by furan oxygen can be discounted by the observation that tetrahydrofuran does not suppress the formation of the benzyne-adduct in reaction of NNA with tetraphenylcyclopentadienone. (*c*) That the sequence of

* This is not to say that this precursor is not present.

[34] B. H. Klanderman and J. R. Criswell, *J. Amer. Chem. Soc.*, 1969, **91**, 510.

[35] D. L. Brydon, J. I. G. Cadogan, J. B. Thomson, and D. M. Smith, *Chem. Comm.*, 1967, 727; J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *ibid.*, 1970, 299.

radical and ionic reactions represented by Schemes 1—3 leading to phenylated products is dominant in the case of furan; *e.g.* the chain sequence outlined in Scheme 7 [which corresponds to reactions (iii) and (iv) in Scheme 3] if fast would consume the precursory benzenediazonium cation in successful competition with its conversion to



SCHEME 7

benzyne. In accord with this it is known that furan, as befitting a less aromatic compound than benzene, reacts very readily with phenyl radicals.[36] We favour the last explanation although contributions from explanation (*b*) cannot be discounted. It should be noted in this respect that removal of anthracene by this route to give 9-phenylanthracene (57%) is also competitive, but not overwhelmingly dominant, with cycloaddition to give triptycene. It is also likely that tetraphenylcyclopentadienone is removed in part by this radical route.

Summary of the Mechanism of the Decomposition of NNA in Aromatic Solvents.—The decomposition clearly involves a remarkably complex series of competing reactions and equilibria. Bearing in mind that complete accountance of starting material has never been achieved, the following general framework accounts for the known facts. The formation of radicals and radical derived products is accounted for by Schemes 1—3, which all depend on the key intermediate, the arenediazonium acetate ion pair. In the presence of furan, reaction occurs *via* this route preferentially. In the case of *o*-Bu^t-NNA, sterically assisted unimolecular loss of nitrogen from the *o*-t-butylbenzenediazonium cation occurs in successful competition with Schemes 1—3 and all other reactions to give the t-butylphenylcarbonium ion and hence *o*-t-butylbenzyne, which reacts normally with all arynophiles studied, including furan. In the cases of NNA itself and other substituted NNA derivatives, not subject to such steric acceleration of the loss of nitrogen, further reaction *via* the arynoid precursor, and hence to the aryne, is possible as a result of abstraction by acetate ion of the acidic proton *ortho-* to the diazonium function. The important difference between these cases and that of the *o*-t-butyl case lies in the sequence the loss of nitrogen and of the proton (Scheme 4). Thus in the latter, rapid loss of nitrogen, as the first step, leads to *o*-t-butylbenzyne at the expense of radical-derived products, whereas in *m*-Bu^t-NNA, for example, where this does not occur, competition takes place between reaction of the diazonium cation to give radicals on the one hand and loss of a *proton* followed by nitrogen to give the aryne on the other. Such competition would be expected to depend on many competing factors including the electronic nature and position of the substituent (and hence the acidity of the *ortho*-proton). the equilibrium concentration of the diazonium ion pair and the covalent diazoacetate, in turn dependent on the rate of rearrangement of the initial *N*-nitrosocompound into the diazoacetate, and the rates of the various steps in the competing pathways leading to radical-derived products. The net effect of these factors is not predictable at this time, and the results of experiments relevant to this will be reported in later papers; it would be expected, however, that a widespread variation is likely, *o*-Cl-NNA, for example, gives no aryne adduct under the standard conditions, while *m*-Cl-NNA does not give an adduct with phenyl azide, presumably due to unfavourable competition with other reactions. It would also be expected that temperature would have a marked effect on the course of the reaction.

It is predictable from the postulated reaction scheme that benzyne should be obtainable from benzenediazonium acetate and, following our preliminary communications,[35] this has been achieved by Rüchardt and Tan [37] who obtained benzyne adducts from benzenediazonium fluoroborate in the presence of potassium acetate and anthracene or tetraphenylcyclopentadienone. Further, following the results reported in this paper we have devised a one-step synthesis of benzene from aniline [38] *via* an *in situ* diazotisation,[39] the full scope and mechanism of which will be discussed in a later paper.

Despite the foregoing it should be noted, however, that modification of the general reaction scheme to accommodate the effect of different solvents will be necessary, including, for example, the interpolation of additional steps to account for the reactions of NNA with polyhalogenomethanes, to be reported in a later paper. The case of pyridine is also anomalous in that decomposition of NNA in the presence of tetraphenylcyclopentadienone in pyridine gave no 1,2,3,4-tetraphenylnaphthalene or phenylpyridines. Reaction with 2,5-dimethylfuran also proceeds *via* a different mechanism because reaction of NNA (1 mole) with 2,5-dimethylfuran (2 moles) in benzene (36 moles) gave 2-methyl-5-benzylfuran (29%) in addition to the expected biphenyl (7%). The benzyne adduct, 1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene was not detected. Experiments related to the mechanism of this unusual reaction will also be reported in a later paper.

Added in proof: Recent experiments carried out first by Professor C. Rüchardt and later by us have now removed the anomaly surrounding the case of furan–NNA. Whereas

[36] L. Benati, N. La Barba, M. Tiecco, and A. Tundo, *J. Chem. Soc.* (*B*), 1969, 1253.
[37] C. Rüchardt and C. C. Tan, *Angew. Chem. Internat. Edn.*, 1970, **9**, 522.
[38] J. I. G. Cadogan, J. R. Mitchell, and J. T. Sharp, *Chem. Comm.*, 1971, 1.
[39] J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257; J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *ibid.*, 1966, 1249.

at 15° <0·15% of the furan–benzyne adduct is formed, it is isolated in 5% yield at the b.p. These results are in accord with the mechanism and discussion put forward above. Dr. J. Kampmeier has also informed us that he has isolated 0·3% of the adduct at 60°.

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