Acylarylnitrosamines. Part II.[1] The Formation of Arynes in the Anomalous Decompositions of *o*-t-Butyl- and 2,5-Di-t-butyl-*N*-nitrosoacetanilide

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Decompostion of *o*-t-butyl-*N*-nitrosoacetanilide in benzene gives *o*- and *m*-t-butylphenylacetates (55%) rather than the expected high yield of 2-t-butylbiphenyl. The isolation of aryne adducts in the presence of furan, anthracene, and 2,3,4,5-tetraphenylcyclopentadienone and the results of aryne-competition experiments involving anthracene and 9,10-dimethoxyanthracene, establish the participation of 3-t-butylbenzyne. 2,5-Di-t-butyl-*N*-nitrosoacetanilide similarly decomposes, in part, *via* 3,6-di-t-butylbenzyne. These abnormal decompositions are considered to arise as a result of preferential steric acceleration of unimolecular decomposition of the *o*-t-butylaryldiazonium cations to the corresponding carbonium ions, which either are converted into the *ortho*-acetates or to the aryne, which reacts with acetic acid to give *m*-acetate. These arynes, in turn, are considered to be less reactive as a result of steric hindrance.

DECOMPOSITION of acylarylnitrosamines in benzene has been a well known route to biaryls[2] for 60 years, and in Part I[1] we presented evidence concerning the mechanism of the reaction. Cadogan, Hey, and Williams,[3] however, noted without explanation that the decomposition of *o*-t-butyl-*N*-nitrosoacetanilide in benzene was anomalous in that a negligible yield of the expected 2-t-butylbiphenyl was formed, the major product being what appeared to be a mixture of isomeric t-butylphenyl acetates, although this was not characterised at the time. Decomposition of the *para*-isomer took the normal course. Later, Rondestvedt and Blanchard[4] confirmed the anomalous lack of 2-t-butylbiphenyl. Cadogan and Hibbert[5] in a preliminary communication reported that the acetates consisted exclusively of the *ortho*- and *meta*-isomers and postulated decomposition *via* an aryne, a postulation supported by the isolation of 1-t-butyltriptycene from an experiment carried out in the presence of anthracene. Following this, Franck and Yanagi[6] showed that diazotisation of 2,5-di-t-butylaniline also appeared to proceed *via* an aryne. The decompositions of *o*-t-butyl-*N*-nitrosoacetanilide and related compounds were therefore clearly anomalous and this paper describes the full investigation of the mechanism of the former reaction and those involving 2,5-di-t-butyl-*N*-nitrosoacetanilide.

EXPERIMENTAL

G.l.c.—Three instruments were used for analytical investigations: a Perkin-Elmer F.11 chromatograph, with a flame-ionisation detector and 2 m × 2·2 mm i.d. packed columns or 50 m × 0·25 mm i.d. capillary columns; a Varian Aerograph 1520B chromatograph, with a flame-ionisation detector and 2 m × 2·2 mm i.d. packed columns; and a Griffin and George D.6 gas-density balance chromatograph, with 2 m × 5·0 mm i.d. packed columns. Quantitative measurements were made by use of the D.6 instrument, the internal-standard technique being that described by Cadogan and Sadler.[7] All standards were purified before use. Preparative g.l.c. usually made use of a Pye Series 105, Model 15, chromatograph, or occasionally, as indicated, an Aerograph A.700. In all cases the carrier gas was nitrogen. The following stationary phases, supported on 100—120 mesh celite or silocel, were employed. Carbowax 20M (CAR), neopentylglycol succinate (NPGS), polyethyleneglycol adipate (PEGA), 1,4-butanediol succinate

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polyester (BDS), fluorosilicone oil (QF-1), silicone oil (SIL) and apiezon L grease (APL).

Reagents.—o-, m-, *and* p-*t-Butylnitrobenzenes.* Nitration of t-butylbenzene [8] followed by fractional distillation with a 30-plate spinning band column gave pure (g.l.c.) samples of *o*- (b.p. 148° at 38 mmHg) and *m*-t-butylnitrobenzene (b.p. 158° at 36 mmHg). The residue gave the *para*-isomer, m.p. 27°.

o-*t-Butyl*-N-*nitrosoacetanilide.* This compound (m.p. 60°) was prepared as described previously.[3] The isomeric t-butylphenyl acetates prepared by standard methods had b.p. 116° at 12 mmHg (*o*-), 130° at 16 mmHg (*p*-), and m.p. 42—43° (*m*-) (lit.,[9] m.p. 42—43°).

o-*t-Butylpropionanilide.* This compound had m.p. 116° (Found: C, 76·1 H, 9·5, N, 6·95. $C_{13}H_{19}NO$ requires C, 76·1; H, 9·3; N, 6·8%) and gave the corresponding nitrosamide m.p. 44° (decomp.) in the usual way.

2-*t-Butylbiphenyl.* A solution of dibenzoyl peroxide (14·5 g, 0·060 mole) in t-butylbenzene (107 g) was heated at 80° for 3 days in an atmosphere of dry nitrogen. The excess of t-butylbenzene was evaporated under reduced pressure, and the residue distilled to give a colourless liquid (4·44 g), b.p. 40—92° at 0·05 mmHg. G.l.c. examination (20% APL, 233°) indicated three components, A (retention time 18·1 min), B (27·0 min), and C (33·7 min), in the approximate ratio 1 : 3 : 2. The retention times of B and C were identical to those of authentic specimens of 3- and 4-t-butylbiphenyl.[3] Preparative g.l.c. (Aerograph A.700, 8 ft × 0·375 in i.d. aluminium column containing 20% APL on celite at 233°) allowed isolation of a sample of component A, which was crystallised from ethanol at −40° to yield 2-t-butylbiphenyl, m.p. 36—37° (lit.,[3] 31—34°). N.m.r. (CCl_4): τ 2·40—3·25 (complex, 9H) and 8·82 (Bu^t). 2,5-*Di-t-butylbiphenyl* was prepared previously.[3]

2,5-*Di-t-butyl*-N-*nitrosoacetanilide.* *p*-Di-t-butylbenzene[8] was nitrated as described by Legge [10] to yield, after crystallisation from isopropyl alcohol, 1,4-di-t-butyl-2-nitrobenzene, m.p. 84—85° (lit.,[10] 86—86·5°). Reduction by iron powder and hydrochloric acid in ethanol gave 2,5-di-t-butylaniline (85%), m.p. 103—104° (lit.,[11] 103—104°). Nitrosation of the acetyl derivative (m.p. 158—159°, lit.,[10] 155·6—156·4°) (Found: C, 77·3; H, 10·05. Calc. for $C_{16}H_{25}NO$: C, 77·7; H, 10·2%) gave the *N*-nitroso-compound (96%), m.p. 66—68° (decomp.).

2,5-*Di-t-butylphenyl acetate.* 2,5-Di-t-butylaniline was diazotised by the method of Carpenter *et al.*[11] It decomposed to yield, after steam distillation and crystallisation from ethanol, 2,5-di-t-butylphenol (42%), m.p. 117—119° (lit.,[11] 118—119°). Recrystallisation from light petroleum (b.p. 60—80°) gave needles, m.p. 121—122°. Acetylation (acetic anhydride) of the phenol (1·00 g) gave 2,5-*di-t-butylphenyl acetate* (25%) as colourless needles from light petroleum (b.p. 60—80°), m.p. 52—53° (Found: C, 77·6; H, 9·4. $C_{16}H_{24}O_2$ requires C, 77·4; H, 9·7%) (correct n.m.r. and i.r. spectra).

o-*Bromo-t-butylbenzene.* This compound, b.p. 130—132° at 40 mmHg, was prepared by Crawford and Stewart's method [12] and purified by fractionation by use of a 30-plate spinning band column.

9,10-*Dimethoxyanthracene.* This compound had m.p. 200—201° (lit.,[13] m.p. 202°), was prepared by Meyer's method.[13]

Competition Reaction of o-*t-Butyl*-N-*nitrosoacetanilide with a Mixture of Anthracene and* 9,10-*Dimethoxyanthracene in Benzene.*—*o*-t-Butyl-*N*-nitrosoacetanilide (0·55 g, 0·0025 mol) was allowed to decompose in benzene (20 g, 0·26 mol) containing anthracene (1·78 g, 0·01 mol) and 9,10-dimethoxyanthracene (2·38 g, 0·01 mol) under dry nitrogen at room temperature for 16 h. The reaction mixture was heated slowly to reflux in order to complete the reaction. The benzene was distilled off and replaced with chlorobenzene; maleic anhydride (4·1 g) was added, and the mixture was heated under reflux for 12 h.

The chlorobenzene was distilled off and the residue chromatographed on alumina (100 g). Elution with much benzene ensured that all the triptycenes were collected. The mixture was examined by g.l.c. (5% SE 30, 200° with additional authentication on 2% NPGS, 225° by use of a Varian Aerograph 1520B) which enabled the molar ratio of the triptycenes to be computed as $K^{\mathrm{H}}_{\mathrm{OMe}} = 13{\cdot}5$. Suitable control experiments established the validity of the method of isolation and analysis.

Competition Reaction of Authentic 3-*t-Butylbenzyne* [14] *with a Mixture of Anthracene and* 9,10-*Dimethoxyanthracene.*—A mixture of potassium t-butoxide (0·28 g, 0·0025 mol), *o*-t-butylbromobenzene (0·56 g, 0·005 mol), anthracene (1·78 g, 0·01 mol), and 9,10-dimethoxyanthracene (2·38 g, 0·01 mol) in t-butylbenzene (50 ml) was heated under reflux under dry nitrogen for 18 h. Maleic anhydride (5·0 g) was added and the mixture was heated under reflux for a further 12 h. The solvent was distilled off and the residue was chromatographed on alumina (100 g). Elution with much benzene ensured that all the triptycenes were collected. Examination of the mixture by g.l.c. (5% SE 30, 200° and additional authentication on 2% NPGS 225° by use of a Varian Aerograph 1520B) enabled the molar ratio of the triptycenes to be computed as $K^{\mathrm{H}}_{\mathrm{OMe}} = 13{\cdot}3$.

Reaction of o-*Bromo-t-butylbenzene with Sodamide in Liquid Ammonia.* Sodamide in liquid ammonia (50 ml) was prepared in the usual way from sodium metal (0·92 g). To this was added rapidly *o*-bromo-t-butylbenzene (2·07 g, 0·0097 mol) and the mixture was stirred vigorously for 1·5 h. Ammonium chloride (2·68 g) was cautiously added in small portions and the system was diluted with ether (50 ml) and stirred until all the ammonia had evaporated. Water (100 ml) was added, the layers were separated, the aqueous portion was extracted with ether (2 × 50 ml), and the combined ethereal extracts were washed, and dried ($MgSO_4$).

A sample of the yellow solution was examined by g.l.c. (10% CAR, 159°) with naphthalene as internal standard, and was found to contain *m*-t-butylaniline (27·3%). *o*-t-Butylaniline (0·38% would have been detected) was absent, and no starting material remained.

Reactions of o-*t-Butyl*-N-*nitrosoacetanilide.*—*General procedure.* All reactions were stirred under anhydrous conditions in an atmosphere of oxygen-free nitrogen for 14—16 h at room temperature, or as stated. To ensure complete decomposition of the nitrosamide, the reaction mixture was

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then heated slowly to the reflux temperature, and boiled for 1 h. Measured fractions of the reaction mixture were withdrawn for examination by g.l.c. or in other ways. In general, any structural assignments based solely on g.l.c. retention times were the result of analysis on at least two different stationary phases. In all cases, the relation of a peak in the chromatogram to a particular compound required that the peak be enhanced, relative to other peaks, when authentic material was added to the reaction mixture.

The yield of acetic acid could be determined by a g.l.c. (CAR) by use of the D.6 instrument, or more accurately, by treating a measured sample of the reaction mixture with an excess of sodium hydroxide solution, and back-titrating the excess of alkali against standard hydrochloric acid.

The percentage yields of decomposition products are quoted in terms of moles per 100 moles of nitrosamide or (dinitrosamide).

(1) *Decomposition in benzene.* After decomposition of the nitrosamide (from 20 g of the anilide) in benzene (350 ml) distillation gave a forerun, b.p. 70° at 18 mmHg (1·36 g) and a yellow oil, b.p. 106—130° at 18 mmHg (7·26 g) which partially solidified. I.r. spectroscopy revealed that the latter was largely a mixture of *o*- and *m*-t-butylphenyl acetates. This and the absence of the *para*-isomer was confirmed by qualitative and quantitative g.l.c. by use of fluorene as an internal standard in another experiment in which the reaction mixture was not disturbed by fractional distillation (Table 1). Acetic acid (38%) was determined by titration. From a third experiment, t-butylbenzene (correct i.r. and n.m.r. spectra) (8·2%) was isolated by preparative g.l.c.

TABLE 1

Reactions of *o*-t-butyl-*N*-nitrosoacetanilide *

	Yield (% by g.l.c.)		
	Reaction		
Product	1(PhH)	2(PhH + T.C.) †	3(PhH + Furan)
t-Bntylbenzene	10	3	3·5
o-t-Butylphenyl acetate	38	50·5	37
m-t-Butylphenyl acetate	17	0	0
Biphenyl	4	Trace	1
2-t-Butylphenyl	2	3	3
o-t-Butylacetanilide	Trace	1	2
5-t-Butyl-1,4-epoxy-1,4-dihydronaphthalene			20·5
5-t-Butyl-1,2,3,4-tetraphenylnaphthalene		34	
Acetic acid	38	52·5	56·5
AcO accountance (%)	93	104	95
Ar accountance (%)	68	91	66

* 3- and 4-t-Butylbiphenyls (0·5% would have been detected), *p*-t-butylphenyl acetate (1·0) and *o*-, *m*-, and *p*-t-butylphenols (0·7) were absent. In experiments 2 and 3, the *m*-acetate would have been detected at the level of 0·8—1·0%. † T.C.: 2,3,4,5-tetraphenylcyclopentadienone.

(2) *Decomposition in benzene in the presence of* 2,3,4,5-*tetraphenylcyclopentadienone.* *o*-t-Butyl-*N*-nitrosoacetanilide (5·47 g, 24·9 mmol) was allowed to decompose in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (12·7 g, 32·9 mmol) in benzene (39·0 g, 0·500 mol). The cooled reaction mixture was filtered, the solid material washed with benzene, and samples of the combined filtrate and washings were examined by g.l.c. (Table 1), with fluorene as internal standard. Acetic acid (52·5%) was determined by titration.

The major part (21·6 mmol of nitrosamide) of the filtrate and all the solid matter collected by filtration were combined and chromatographed on alumina (1000 g). Elution with petroleum–benzene (5 : 1) gave an oily solid (0·168 g) which, from ethanol at −40°, afforded colourless crystals of 2-t-butylbiphenyl (0·080 g, 1·8%; crude yield, 3·7%), m.p. and mixed m.p. 36—37°. The i.r. spectrum was identical to that of the authentic biaryl.

Elution with petroleum–benzene (1 : 1) gave a brown solid (3·61 g) which was crystallised from petroleum and from acetic acid to yield colourless 5-*t-butyl*-1,2,3,4-*tetraphenylnaphthalene* (3·005 g, 18·9%; crude yield, 34·2%), m.p. 162—163° (Found: C, 93·4; H, 6·6. $C_{38}H_{32}$ requires C, 93·4; H, 6·6%). N.m.r. ($CDCl_3$): τ 2·24—2·84 (naphthalene 3H); 2·91, 3·10 (2s, 5H); 3·30 (s, 10H); 9·02 (s, 9H, Bu^t). 2,3,4,5-Tetraphenylcyclopentadienone (7·77 g) was eluted in benzene.

(3) *Decomposition in a mixture of benzene and furan.* The nitrosamide (6·39 g, 29·05 mmol) was allowed to decompose in a solution of furan (3·95 g, 58·0 mmol) in benzene (45·3 g, 0·580 mol), and a sample of the orange reaction mixture was examined by g.l.c. (Table 1), with fluorene as internal standard. Acetic acid (56·5%) was determined by titration.

The bulk (24·15 mmol of nitrosamide) of the reaction mixture was distilled at 0·04 mmHg to give (i) a liquid (1·14 g), b.p. 49—54° and (ii) several fractions (2·26 g), b.p. 54—110°. G.l.c. analysis showed that the latter contained most of the furan adduct. These were combined and crystallised from petroleum at −60° to yield 5-t-butyl-1,4-epoxy-1,4-dihydronaphthalene (0·657 g, 13·7%), m.p. 56—57° (Found: C, 83·8; H, 8·5. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%). N.m.r. (CCl_4): τ 2·88—3·28 (complex, 3H, aromatic); 3·08 (m, fine structure visible on expansion, 2H olefinic); 4·01, 4·51 (2m, fine structure visible on expansion, 2H bridgehead); and 8·66 (s, 9H, Bu^t). I.r. (melt): $\nu_{max.}$ 1395 and 1365 (Bu^t), 1125 (C–O–C), and 715 cm^{-1} (*cis*-CH=CH).

The mother liquors were combined with fraction (i) and redistilled (18 mmHg) to give four colourless liquid fractions: (iii) 0·074 g, b.p. ⩽123°, (iv) 0·626 g, b.p. 123—126°, (v) 0·669 g, b.p. 126°, and (vi) 0·597 g, b.p. 126—138°. Fraction (v) was identified as *o*-t-butylphenyl acetate by comparison of its refractive index and i.r. spectrum with those of the authentic ester. G.l.c. examination (2% NPGS, 140°) indicated that fractions (iv)—(vi) consisted of *ca.* 90% of the acetate (*ca.* 1·70 g, 36·8%).

Decomposition in benzene in the presence of anthracene. *o*-t-Butyl-*N*-nitrosoacetanilide (2·80 g, 0·013 mol) was allowed to decompose in benzene (40 g, 0·52 mol) containing anthracene (4·62 g, 0·026 mol) under dry nitrogen at room temperature for 16 h. The reaction mixture was then heated slowly to reflux to complete the reaction. The benzene was distilled off and replaced with chlorobenzene; maleic anhydride (4·6 g) was added and the mixture heated under reflux for 12 h. The chlorobenzene was distilled off and the residue chromatographed on alumina (100 g). Elution with petroleum–benzene (9 : 1) gave a white fluorescent solid which gave after recrystallisation from petroleum ether (b.p. 60—80°) 1-*t-butyltriptycene* (0·76 g, 19·3%), m.p. 209°, n.m.r. ($CDCl_3$): τ 2·80 (centre of aromatic pattern); 3·80 [bridgehead H(9)]; 4·60 [bridgehead H(10)]; and 8·50 (Bu^t) (Found: C, 92·6; H, 7·1. $C_{24}H_{22}$ requires C, 92·9; H, 7·1%). Elution with petroleum–benzene (4 : 1) gave a dark red solid (0·20 g) and with benzene gave a black tar (0·60 g).

The low-boiling components of the original reaction mixture were examined by g.l.c. The analysis was not quantitative but it showed a considerable reduction in the proportion of *m*-t-butylphenyl acetate present in the reaction mixture (t-butylbenzene 8·4, biphenyl 1·2, 2-t-butylbiphenyl 1·3, *o*-, and *m*-t-butylphenyl acetates 20·3%).

Decomposition in benzene in the presence of 9,10-*dimethoxyanthracene*. *o*-t-Butyl-*N*-nitrosoacetanilide (1·0 g, 0·0045 mol) was allowed to decompose in benzene (20 g, 0·26 mol) containing 9,10-dimethoxyanthracene (2·16 g, 0·009 mol) under dry nitrogen at room temperature for 16 h. The reaction mixture was then heated slowly to reflux to complete the reaction. The benzene was distilled off and replaced with chlorobenzene, maleic anhydride (2·16 g) was added and the mixture heated under reflux for 12 h. The chlorobenzene was distilled off and the residue chromatographed on alumina (100 g). Elution with petroleum–benzene (9 : 1) gave after recrystallisation from light petroleum (b.p. 60—80°) 1-t-butyl-9,10-dimethoxytriptycene (0·069 g, 4·2%), m.p. 235·5—236° (Found: C, 84·6; H, 7·1. $C_{26}H_{26}O_2$ requires C, 84·3; H, 7·0%), n.m.r. ($CDCl_3$): τ 2·55 (centre of aromatic pattern); 5·68 and 5·92 (OMe); and 8·50 (Bu^t). Elution with petroleum–benzene (4 : 1) gave a red oil (1·18 g) and with benzene a black tar (0·50 g).

Decomposition of o-*t-Butyl*-N-*nitrosopropionanilide in Benzene*.—The nitrosamide from the anilide (14·7 g) was allowed to decompose in benzene (260 ml) in the usual way. Distillation gave fractions (7·26 g) boiling in the range 68—150° at 30 mmHg. G.l.c. analysis gave the following results: t-butylbenzene (13), biphenyl (2·5), 2-t-butylbiphenyl (1·7), *o*- and *m*-t-butylphenyl propionates (46%). The *p*-isomer was absent. The *o*- and *m*-isomers could not be completely separated on the columns available at the time of the analysis, but it appeared that the *o*-isomer predominated.

Reactions of 2,5-*Di-t-Butyl*-N-*nitrosoacetanilide*.—(4) *In Benzene*. The nitrosamide (5·00 g, 18·1 mmol) decomposed slowly in benzene (70·2 g, 0·901 mol) to give a dark red solution, a sample of which was examined by g.l.c. (Table 2) with fluorene as internal standard.

The bulk (14·9 mmol of nitrosamide) of the reaction mixture afforded on distillation: (i) a colourless liquid, b.p. 78°, (ii) a white sublimate (0·100 g), bath temp. to 100° at 0·4 mmHg, (iii) a yellow oil which solidified (3·16 g), b.p. 66—70° at 0·05 mmHg, and (iv) a brown residue (0·537 g). Fraction (ii) was *p*-di-t-butylbenzene (crude, 3·5%), m.p. and mixed m.p. 75—76° after crystallisation from methanol.

Fraction (iii), seen by g.l.c. examination (10% SIL, 180°) to contain one major component, was crystallised from petroleum to yield colourless 2,5-di-t-butylphenylacetate (1·05 g, 28·5%; crude, 85%), m.p. 52—53°, mixed m.p. 51—52° (Found: C, 77·4; H, 9·7. Calc. for $C_{16}H_{24}O_2$: C, 77·4; H, 9·7%).

(5) *Reaction with* 2,3,4,5-*tetraphenylcyclopentadienone in benzene*. The nitrosamide (5·62 g, 20·4 mmol) was allowed to decompose in a suspension of 2,3,4,5-tetraphenylcyclopentadienone (23·5 g, 61·2 mmol) in benzene (79·6 g, 1·02 mol). The cooled reaction mixture was filtered, the solid material washed with benzene, and a sample of the combined filtrate and washings was examined by g.l.c. (Table 2) with fluorene as internal standard.

The major part (18·8 mmol of nitrosamide) of the filtrate was distilled to give: (i) a colourless liquid, b.p. 78°, (ii) a white sublimate (0·110 g), bath temp. $\leqslant$80° at 0·05 mmHg, (iii) a yellow oil (3·36 g), b.p. 66—70° at 0·05 mmHg, and (iv) a residue (3·67 g). Fraction (ii) was *p*-di-t-butylbenzene (crude yield, 3·4%), m.p. and mixed m.p. 76—77° after crystallisation from methanol.

Fraction (iii) was 2,5-di-t-butylphenyl acetate (crude yield, 72·3%), m.p. and mixed m.p. 52—53° after crystallisation from light petroleum (b.p. 60—80°).

TABLE 2

Reactions of 2,5-di-t-butyl-*N*-nitrosoacetanilide *

Product	Yield (% by g.l.c.) Reaction 4(PhH)	5(PhH + T.C.)	6(PhH + $C_{14}H_{10}$)	7(Furan)
p-Di-t-butylbenzene	8	8	5	4
Biphenyl	1	0	0	
2,5-Di-t-butylphenyl acetate	79	77	53	63
5,8-Di-t-butyl-1,4-epoxy-1,4-dihydronaphthalene				30
1,4-Di-t-butyltriptycene			16	
Ar (%) accounted for	87	85	74	97

* 2,5-Di-t-butylbiphenyl (0·5% would have been detected) was absent from reactions 4, 5, and 6; 2,5-di-t-butylphenol (1·0) was absent from reactions 4 and 5; 2,5-di-t-butylacetanilide (0·9) was absent from all reactions.

The distillation residue (iv) was combined with all the solid collected by filtration and chromatographed on alumina (500 g). Elution with petroleum containing an increasing proportion of benzene (0—30%) gave 26 × 70 ml fractions before 2,3,4,5-tetraphenylcyclopentadienone was eluted. Fractions 17—21 gave a single diffuse spot on a silica t.l.c. plate developed with petroleum–benzene (1 : 1). They were combined to give an oily red solid (0·241 g) which was repeatedly crystallised from methanol and from isopropanol, but the product obtained was not sharp melting and did not sublime at 170° (block temp.) at 0·05 mmHg. The i.r. spectrum showed an absorption at 3510 cm^{-1} (O–H). This material was not identified.

The remaining chromatography fractions contained only trace amounts of oils.

(6) *Reaction with anthracene in benzene*. The nitrosamide (6·30 g, 22·8 mmol) was allowed to decompose in benzene (60·5 g, 0·775 mol) containing anthracene (10·4 g, 58·4 mmol) in suspension. When the decomposition was complete, unreacted anthracene (8·49 g, 47·6 mmol) was filtered off and washed with benzene. The filtrate and washings were combined, and a sample was examined by g.l.c. (Table 2) with *trans*-stilbene as internal standard.

Volatile matter was distilled out from the bulk (22·3 mmol of nitrosamide) of the filtered reaction mixture, bath temp. $\leqslant$130° at 0·1 mmHg, and *p*-di-t-butylbenzene (crude yield, 0·037 g, 0·9%), m.p. 73—74°, and 2,5-di-t-butylphenyl acetate (crude yield, 2·99 g, 54·0%), m.p. 50—51° were isolated. The brown residue (3·59 g) was dissolved in xylene (22 ml), maleic anhydride (2·05 g) was added, and the mixture was heated under reflux for 25 min. The mixture was set aside at room temperature for 3·5 h, 2N-sodium hydroxide solution (40 ml) was added, and the mixture boiled under reflux for a further 2·25 h. When cool, the organic layer was separated, diluted with ether (100 ml), washed with water (3 × 50 ml), and dried ($MgSO_4$). The residue remaining after evaporation of the solvents under reduced pressure was chromatographed on alumina (300 g). Elution with petroleum–benzene (9 : 1) produced a blue fluorescent solution which was evaporated to a pale orange solid (1·28 g). Crystallisation from light petroleum (b.p. 60—80°) afforded colourless 1,4-*di-t-butyltriptycene* (0·793 g, 9·7%; crude yield, 15·8%), m.p. 233—234° (Found: C, 91·7; H, 8·25. $C_{28}H_{30}$ requires C, 91·75; H, 8·25%). N.m.r. (CCl_4): τ 2·85 (centre of AA'BB', 8H), 3·10 [s, 2H, H(2) and H(3)], 3·80 (s, 2H, bridgehead), and 8·43 (s, 18H, Bu^t). $\lambda_{max.}$ (log ϵ) in methanol: 262·5 (3·17), 271 (3·36), and 279 nm (3·46). I.r. (Nujol) $\nu_{max.}$: 1170, 825, 765, 745, 700, and 645 cm^{-1}.

G.l.c. examination (3% APL, 250°) indicated that the anthracene filtered off from the reaction mixture contained no 1,4-di-t-butyltriptycene, or other contaminant. The quantity of anthracene in the filtrate (3·88 mmol) was determined by g.l.c. (10% SIL, 189°) with *trans*-stilbene as internal standard; this allowed the amount consumed in the reaction (30·3% based on nitrosamide) to be computed.

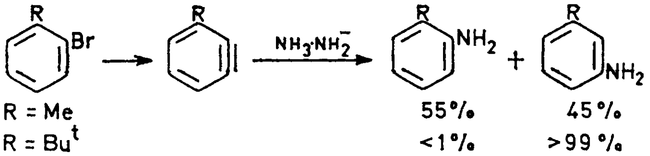
(7) *Decomposition in furan.* The nitrosamide (6·48 g, 23·5 mmol) was allowed to decompose in furan (47·9 g, 0·705 mol), to give a deep orange solution. A sample of the reaction mixture was examined by g.l.c. (Table 2) with phenanthrene as internal standard.

The bulk (22·2 mmol of nitrosamide) of the reaction mixture was distilled to give: (i) a colourless liquid, b.p. 32°, (ii) a white sublimate (0·032 g), bath temp. $\leqslant$70° at 0·04 mmHg, (iii) a yellow sublimate (0·035 g), bath temp. $\leqslant$80° at 0·04 mmHg, (iv) a yellow oil which solidified (3·00 g), b.p. 74—82° at 0·02 mmHg, (v) a yellow oil (1·05 g), b.p. 82° at 0·02 mmHg, (vi) a yellow solid (0·765 g), bath temp. $\leqslant$165° at 0·02 mmHg, and (vii) a black residue (0·609 g). The fractions were examined by g.l.c. (10% SIL, 194°). Fractions (ii) and (iii) were largely *p*-di-t-butylbenzene (crude, 1·6%), which was isolated by crystallisation from methanol, m.p. 75—76°, mixed m.p. 76—77°.

Fractions (iv)—(vi) contained two principal components: 2,5-di-t-butylphenyl acetate, and a compound with a longer g.l.c. retention time. Fraction (vi), crystallised (twice) from petroleum, yielded colourless 5,8-*di-t-butyl*-1,4-*epoxy*-1,4-*dihydro-naphthalene* (0·086 g), m.p. 114—115° (Found: C, 84·3; H, 9·5. $C_{18}H_{24}O$ requires C, 84·3; H, 9·4%). The yield of the epoxide was determined by g.l.c. (Table 2). N.m.r. spectrum ($CDCl_3$): τ 3·06 (s, 2H, aromatic); 2·91 (m, fine structure visible on expansion, 2H olefinic); 3·83 (m, fine structure visible on expansion, 2H bridgehead); 8·62 (s, 18H, Bu^t). I.r. (Nujol): $\nu_{max.}$ 1125 (COC) and 725 cm^{-1} (*cis*-CH=CH).

DISCUSSION

Evidence for the Participation of Arynes.—The normal pattern of products from the decomposition of an acetylarylnitrosamine [ArN(NO)Ac] in benzene includes the biaryl ArPh (35—70%), acetic acid (>90%), and tars.[15] While *m*- and *p*-t-butyl-*N*-nitrosoacetanilide behaved normally in this sense,[3,16] this investigation (Table 1) shows that the *o*-isomer is abnormal in that in benzene only 2% of the expected 2-t-butylbiphenyl was formed; the major product was a mixture of *o*- (38%) and *m*-t-butylphenyl acetate (17%). The *p*-isomer was absent (by g.l.c.). *o*-t-Butyl-*N*-nitrosopropionanilide behaved similarly. Formation of the *m*-acetate points to a dehydro-aromatic intermediate which subsequently reacts by addition of acetic acid, and at first sight it might seem that the *o*-isomer is formed in the same way. On the other hand, it could be argued that the bulky t-butyl group will direct attack on 3-t-butylbenzyne to position one, yielding exclusively *m*-t-butylphenyl acetate. It was not possible to test this hypothesis directly by a study of the addition of acetic acid to 3-t-butylbenzyne, but the reaction of *o*-bromo-t-butylbenzene with sodamide in liquid ammonia was investigated. The result is shown in Scheme 1, together with that from other workers[17] for the corresponding reaction of *o*-bromotoluene:



SCHEME 1

The vast difference between the relative yields of the *ortho*-substituted anilines cannot be attributed to differences in the electronic properties of the two alkyl groups and must therefore be a consequence of steric inhibition of attack at position two in 3-t-butylbenzyne. It thus seems probable that most of the *o*-t-butylphenyl acetate formed by the decomposition of *o*-t-butyl-*N*-nitrosoacetanilide in benzene arises by a non-aryne mechanism, and moreover, since the instability of the acetoxy radical[18] effectively precludes a homolytic pathway, the most plausible mechanism is that in which a carbonium ion is formed, possibly as part of an ion pair (equation 1):

$$\mathrm{ArN(NO)Ar} \longrightarrow \mathrm{Ar{\cdot}N{:}N{\cdot}OAc} \longrightarrow \mathrm{ArN_2{}^{+-}OAc} \longrightarrow \mathrm{Ar^{+-}OAc} \longrightarrow \mathrm{ArOAc} \quad (1)$$

The proposed intermediacy of 3-t-butylbenzyne is supported by the results of trapping experiments with various arynophiles (Table 1), these experiments, incidentally, throwing light on the genesis of *o*-t-butylphenyl acetate. Thus, decomposition (1 mol) in an excess of a mixture of benzene (20 mol) and furan (2 mol), afforded the aryne adduct, 5-t-butyl-1,4-epoxy-1,4-dihydronaphthalene (I) (20·5%), to the exclusion of *m*-t-butylphenyl acetate obtained in 17% yield in benzene alone; the yield of the *o*-isomer remains almost the same as that obtained in benzene alone (Scheme 2). This supports the above contention that addition of acetic acid to 3-t-butylbenzyne gives only the *m*-ester and that the *o*-isomer has a different genesis [*e.g.* equation (1)].

The accountance of the acetate moiety in all these cases is very good (>94%), hence the results suggest that 3-t-butylbenzyne is a very efficient scavanger for acetic acid. This is enigmatic because decomposition of benzenediazonium-2-carboxylate in benzene containing

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[15] G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon Press, London, 1960, p. 27.

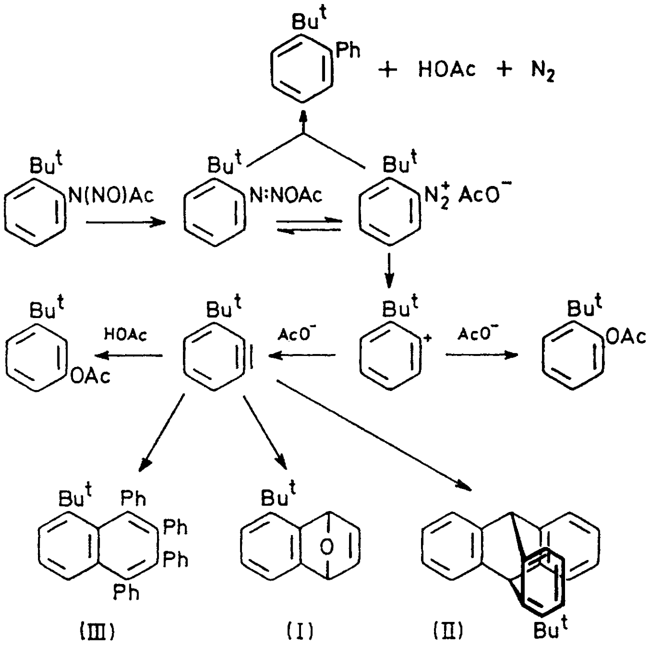
[16] J. I. G. Cadogan, M. J. P. Harger, and J. T. Sharp, to be published.

[17] G. B. R. de Graff, H. J. den Hertog, and W. Ch. Melger, *Tetrahedron Letters*, 1965, 963.

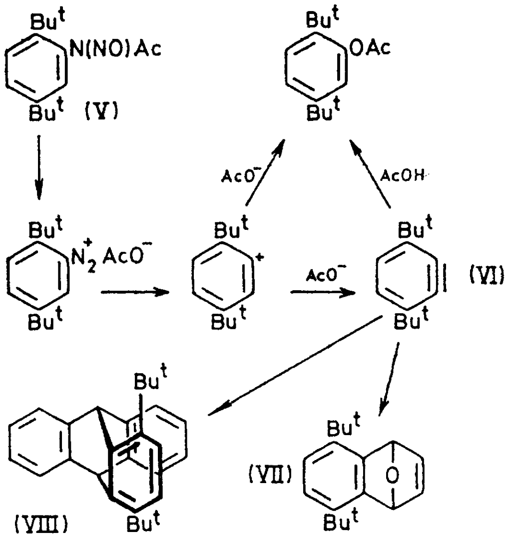
[18] M. S. Kharasch and M. T. Gladstone, *J. Amer. Chem. Soc.*, 943, **65**, 15.

benzoic acid (1·5—2·0 m/m diazonium salt) is reported[19] to give phenyl benzoate in 22—25% yield and we have shown that reaction of pentyl nitrite with anthranilic acid in acetic acid gives only 7% of phenyl acetate. Since the concentration of acid at any instant during the decomposition of *o*-t-butyl-*N*-nitrosoacetanilide is low, it might therefore be concluded that only a small proportion of the aryne generated is accounted for by *m*-t-butylphenyl acetate. The yield of 5-t-butyl-1,4-epoxy-1,4-dihydronaphthalene formed in the presence of furan, an efficient aryne scavenger, is, however, only slightly greater than the yield of *m*-t-butylphenyl acetate produced in its absence. Further, any suggestion that the ester is formed by a cage mechanism, or in a concerted process, must be examined critically in view of the total absence of *m*-t-butylphenyl acetate from the products when the diene is present.

Excluding the unlikely possibility that a cage mechanism operates in pure benzene but not in a mixture of benzene and furan, the rational explanation of these results is that whereas benzyne is rather unreactive towards acetic acid relative to other side reactions which may occur, 3-t-butylbenzyne, being considerably sterically hindered, does not undergo such side reactions and reacts preferentially, by default, with acetic acid, which is the smallest reagent available in this case. In accord with this, the even more sterically hindered 2,3-dehydro-1,4-di-t-butylbenzene (3,6-di-t-butylbenzyne) produced *via* decomposition of *N*-nitroso-2,5-di-t-butylacetanilide, discussed below (Scheme 3), reacts almost exclusively with acetic acid to give 2,5-di-t-butylphenyl acetate. Returning to the *o*-t-butyl case, the above arguments are also supported by the isolation, at the expense of *m*-t-butylphenyl acetate, of 1-t-butyltriptycene (II) (19%) from an experiment involving anthracene as the arynophile, and of 5-t-butyl-1,2,3,4-tetraphenylnaphthalene (III) (34%) from an experiment involving 2,3,4,5-tetraphenylcyclopentadien-1-one. In the latter case it is remarkable, however, that the yield of *o*-t-butylphenyl acetate is increased compared with the reaction carried out in benzene alone. Other than suggesting that this is due to a resultant change in the dielectric constant of the medium favouring decomposition *via* equation (1), we cannot suggest a satisfactory explanation at this time. The yield of the aryne adduct is also higher than with furan and anthracene, which is in accord with the higher efficiency of tetracyclone as an aryne trap and, indeed, 91% of the aryl residue is accounted for in this experiment compared with 66—68% in the case of benzene alone, or benzene with furan.



SCHEME 2



SCHEME 3

The postulated intermediacy of 3-t-butylbenzyne in these reactions receives further support from the results of competition experiments carried out with an excess of an equimolar mixture of two dienes, anthracene and 9,10-dimethoxyanthracene, with (a) authentic 3-t-butylbenzyne produced *via* reaction of potassium t-butoxide with *o*-t-butylbromobenzene[14] and (b) *o*-t-butyl-*N*-nitrosoacetanilide. The resulting mixture of 1-t-butyltriptycene and its dimethoxy-analogue (IV) was quantitatively analysed by g.l.c. and the relative ratio $K^{\mathrm{H}}_{\mathrm{OMe}}$, was almost identical in both cases (13·3 and 13·5 respectively), thus establishing the intermediacy of the aryne in the latter case. It is noteworthy that the rate ratio is inverted and considerably different from that obtained by use of unsubstituted benzyne with anthracene and 9,10-dimethoxyanthracene ($K^{\mathrm{OMe}}_{\mathrm{H}}$ = 3·1).[20] This is attributed to steric hindrance to cycloaddition in the *o*-t-butyl case.

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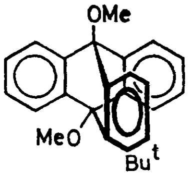
[19] M. Stiles, R. G. Miller, and U. Burckhardt, *J. Amer. Chem. Soc.*, 1963, **85**, 1792.

[20] J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *Chem. Comm.*, 1970, 299; B. H. Klanderman and T. R. Creswell, *J. Org. Chem.*, 1969, **34**, 3426.

The products of decomposition (Table 2) of 2,5-di-t-butyl-*N*-nitrosoacetanilide (V) in benzene in the presence and absence of arynophiles also point to the intermediacy of a hindered aryne, 2,3-dehydro-1,4-di-t-butylbenzene (VI). In benzene alone, as discussed above, a high yield of 2,5-di-t-butylphenyl acetate was obtained, an undeterminable amount of which could be derived from direct ion-pair recombination. In the presence of furan or anthracene (in benzene) the corresponding aryne adducts, 5,8-di-t-butyl-1,4-epoxy-1,4-dihydronaphthalene (VII; 30%) and 1,4-di-t-butyltriptycene (VIII; 16%) respectively were obtained. In the presence of 2,3,4,5-tetraphenylcyclopentadienone no aryne adduct was obtained (Scheme 3). This is attributed to the very high steric hindrance, as shown by models, to the cycloaddition afforded by the presence of two *p*-t-butyl groups.



(IV)

Having established the participation of arynes in the above reactions the question of why such *o*-t-butyl derivatives should so decompose now arises. We attribute this to steric acceleration of the unimolecular loss of nitrogen from the *o*-t-butyl diazonium cation, present in equilibrium with the covalent diazoacetate. The resulting *o*-t-butylphenyl cation can then react to give the *o*-acetate directly or undergo elimination of a proton to give the aryne (Scheme 2). The nitroso-compound is thus preferentially converted into the aryne rather than the aryl radical (*cf*. ref. 6)

The Genesis of Other Products Formed in the Reactions.—*o-t-Butyl-*N*-nitrosoacetanilide.* From the foregoing, the low yield (2%) of 2-t-butylbiphenyl can be attributed to the steric diversion of the decomposition of the precursory diazonium cation (Scheme 2). The alternative suggestion that the bulk of the *o*-t-butyl group in the *o*-t-butylphenyl radical merely reduces the rate of substitution is not supported by experiment. Thus decomposition of di-*m*-t-butylbenzoyl peroxide in benzene, a reaction in which steric effects are not great, affords 3-t-butylbiphenyl (65 mol/100 mol peroxide) in a yield greater, but only a factor of two, than that in which 2-t-butylbiphenyl (34 mol/100 mol peroxide) is formed from the *o*-substituted peroxide.[3] In contrast, *m*-t-butyl-*N*-nitrosoacetanilide yields eight times as much t-butylbiphenyl as does the *o*-nitrosamide.[16] Abstraction of hydrogen from the solvent provides an alternative, and less hindered, reaction for *o*-t-butylphenyl radicals. Although it is not recorded whether t-butylbenzene is formed in the reactions of di-*o*-t-butylbenzoyl peroxide, it is undoubtedly an important product (10%) of the decomposition of *o*-t-butyl-*N*-nitrosoacetanilide in benzene. The phenyl radicals released by abstraction of hydrogen would be expected to appear mainly as biphenyl which is also a decomposition product (4%) of the nitrosamide [equation (2)].

$$\mathrm{Ar}\cdot + \mathrm{PhH} \longrightarrow \mathrm{ArH} + \mathrm{Ph}\cdot \xrightarrow{\mathrm{PhH}} [\mathrm{PhArH}]\cdot \xrightarrow{\mathrm{R}} \mathrm{PhPh} + \mathrm{RH} \quad (2)$$

It is possible but unlikely in view of the low concentrations of radicals involved, that the greater than equivalent amount of t-butylbenzene, compared with biphenyl, may be in part due to reaction as in equation (2) where R = Ar. Consideration of the results obtained from experiments involving furan and 2,3,4,5-tetraphenylcyclopentadien-1-one suggest that part of the t-butylbenzene might arise *via* reduction of 3-t-butylbenzyne. Thus, in both cases, the yield of t-butylbenzene falls considerably to 3—3·5%. Since the yield of 2-t-butylbiphenyl does not fall, the former change cannot be due to scavenging of *o*-t-butylphenyl radicals by the diene. There is therefore good reason to suppose that only part (3—3·5 mol/100 mol) of the t-butylbenzene found in the decomposition in benzene results from radical abstraction. The remainder could arise *via* reduction of 3-t-butylbenzyne by an as yet undetermined route. A similar, but less pronounced, variation of the yield of *p*-di-t-butylbenzene was observed in the corresponding decomposition of 2,5-di-t-butyl-*N*-nitrosoacetanilide (Table 2). In support of this suggestion, it is noteworthy that Franck and Yanagi[6] found a similar reduction in the diazotisation of 2,5-di-t-butylaniline and, on the basis of deuterium incorporation studies, also attributed this to direct reduction of the corresponding aryne.

The award of an S.R.C. Research Grant (to J. I. G. C.) and a Studentship (to J. C.) and of a Carnegie Scholarship (to M. J. P. H.) are gratefully acknowledged.

[0/1774 *Received, May* 11*th*, 1970]