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REACTIONS OF ACYLARYLNITROSAMINES—II*

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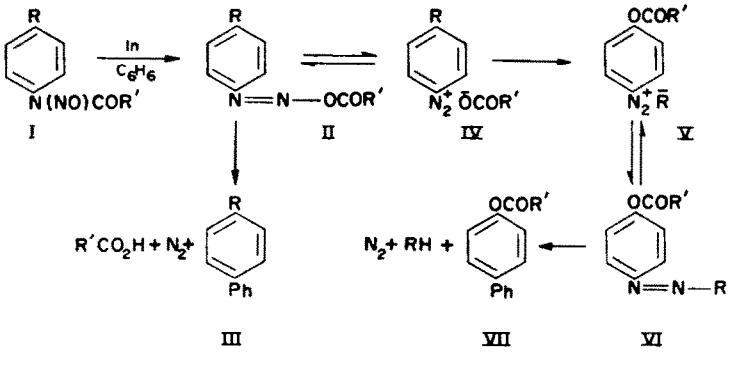
Abstract—Decomposition of acylarylnitrosamines in benzene produces not only free radicals as is well recognized, but also intermediate ion pairs. The generality of this dual mechanism is experimentally demonstrated by use of nucleophilically activated fluorine as a 'label'. The appearance of acylfluoride in the reaction products from fluorine substituted acylarylnitrosamines is interpreted.

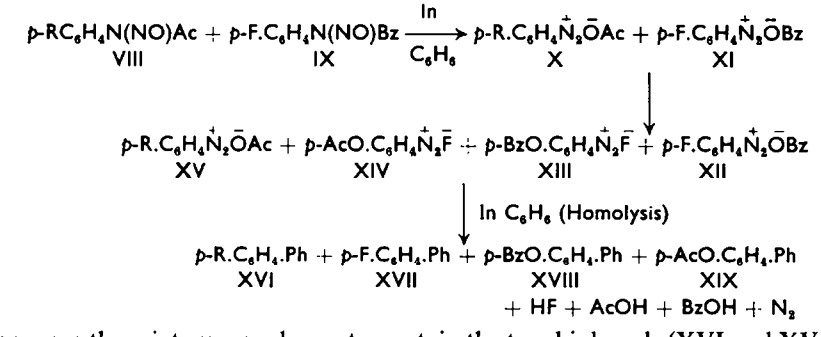
AS A RESULT of earlier work we concluded that acylarylnitrosamines containing fluorine *ortho* or *para* to the nitrosamine group (e.g. I; R = F) undergo a reversible heterolysis (II → IV; R = F) after the rate determining rearrangement into an isomeric diazoester (II) when made to decompose in benzene. It was obviously of interest to establish whether acylarylnitrosamines regardless of the nature and position of their substituents give rise to ionic intermediates on disintegration. With *ortho*- or *para*-substituted fluorine in the ring, occurrence of heterolysis is readily and unambiguously diagnosed from the presence of an acyloxybiphenyl (VII) and hydrofluoric acid (VII; R = F) among the reaction products in addition to the expected fluorobiphenyl (III; R = F). Only a concomitant heterolytic stage (IV) in the sequence of events during the decomposition can rationally account for the ease with which fluorine is replaced by an acyloxy-group (cf. Pt. I).* Substituents other than fluorine are presumably not rendered sufficiently labile by the agency of an intermediate diazonium cation (IV) to suffer nucleophilic displacement by the accompanying acyloxyanion. Thus formation of a "diagnostic" biaryl cannot occur. This supposition is borne out by a literature search which reveals no cases of anionic displacement among the many reported examples of acylarylnitrosamine decompositions.[1,2] Moreover, when we analysed the reaction products from N-nitroso-*p*-chloro-phenylacetamide (I; R = Cl, R′ = Me) by gas-liquid chromatography we found only the expected biphenyl (III; R = Cl) and tests for ionic chlorine were negative.



* Part I was published in *J. Chem. Soc.* 2735, (1960).

[1] H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.* 369 (1940).
[2] D. H. Hey, J. Stuart-Webb and G. H. Williams, *J. Chem. Soc.* 4657 (1952).

In our first experiments designed to demonstrate the participation of ionic intermediates in other than fluorine substituted compounds, we caused a number of acetylarylnitrosamines with substituents of different electronic properties (I; R = Cl, Me, NO_2, H; R′ = Me, and also R = Me in the *meta* position) each separately, to decompose in dry benzene to which some 1-fluoro-2-nitro- or 1-fluoro-2, 4-dinitrobenzene or picryl chloride had been added. It was expected that any acetoxy-anions (IV; R′ = Me) produced by ionic dissociation of the diazoester (II; R′ = Me) would reveal their presence by replacing the labile halogen of the 'foreign' molecule. However, neither ionized halogen nor the diagnostic acetoxynitrophenol could be detected in the reaction mixture. Blank experiments indicated that the halogen in the 'foreign' molecules was not sufficiently labile to suffer replacement by acetate ions under the conditions of the reaction. In order to increase the sensitivity of the halogen we used N-nitroso-*p*-fluorophenyl-benzamide (IX) as the 'foreign' molecule in a second series of experiments involving the above nitrosocompounds. We have previously* shown that fluorine acts as a delicate indicator of anions in this nitrosocompound (IX) by virtue of its rearrangement into a diazonium cation (XI). Provided that decomposition of the N-nitrosoacetylcompound (VIII) under test involved a heterolytic stage and occurred at a rate comparable with that of the added fluorine compound, two species of anions (namely benzoate and acetate) derived from the acyl part of the two nitrosocompounds (VIII and IX) should be competing for displacement of fluorine. Thus each of these mixed decompositions should give four different biphenyls, namely two (XVI and XVII) derived directly from the respective parent nitroso-compounds (VIII and IX) in addition to 4-benzoyloxy-(XVIII) and the diagnostic 4-acetoxybiphenyl (XIX). The sequence of these competition reactions can be set out as annexed:



In every case the mixture was shown to contain the two biphenyls (XVI and XVII) and the diagnostic 4-acetoxycompound (XIX) in quantities ranging from 2–17%. Considering that the decisive stages of the two concurrent nitrosamine reactions are presumably not synchronous and that the competing ionic fragments will not be able to diffuse out freely into the solution, since they are undoubtedly present as closely held ion-pairs surrounded by solvent molecules, the appearance of a 'crossed' product (XIX) albeit in small quantity is significant. The possibility that 4-acetoxybiphenyl formation is not conclusive since it may simply be due to fluorine replacement by acetic acid which derives from the homolytic breakdown of the acetyl nitrosamine (VIII) was ruled out by the following observation: the fluorine compound (IX) when made to decompose in benzene containing acetic acid (0·5 or 1%) yielded only the biphenyls (XVII and XVIII).

* Part I.

These results first demonstrate that exchange of fluorine for the acyloxygroup can be intermolecular, and secondly they provide evidence of ionic intermediates in all acylarylnitrosamines even when undergoing decomposition in a non-polar solvent like benzene. The conventional reaction scheme comprising homolytic steps only should consequently be modified by the addition of a heterolytic stage (XV) in order to express the dual character of the decomposition.

In the biphenyl series nitrosation in the usual way with nitrosyl chloride in a mixture of acetic acid and acetic anhydride caused nitration in the 3-position. For instance, N-4′-fluoro-3-nitro-4-biphenylyl benzamide (XX; R = F; R′ = NO_2; R″ = C_6H_5) was formed in 75% yield instead of the nitrosocompound (XXI; R = C_6H_5). The nitrocompound was orientated by hydrolysis and reduction to a diamine, which could be made to condense with diacetyl to form a dimethylquinoxaline. The occurrence of nitration and even chlorination instead of nitrosation has been reported previously with biphenylyl acetamide (XX; R = H; R′ = H; R″ = Me) and was overcome by redistilling the reagent.[3] This method proved successful to avoid nitration of the fluoroacetamide (XX; R = F, R′ = H, R″ = Me), but failed with the corresponding benzamide. However, addition of a small amount of pyridine to the nitrosating mixture gave the required N-nitrosocompound (XXI; R = C_6H_5) in good yield. Pyridine moreover, proved to be a good solvent for difficultly soluble arylbenzamides and rendered addition of fused sodium acetate as buffer unnecessary. Nitrosation in pyridine as the sole solvent failed owing to decomposition of the nitrosocompound as soon as it was formed. The beneficial effect of pyridine in nitrosations of secondary amines was recently also noticed by Chen *et al.*[4]

Decomposition of the nitrosocompound (XXI; R = Me) gave 4-fluoroterphenyl (XXII) and was not accompanied by fluorine replacement. Failure of the polar effect of the diazonium cation to be transmitted through two benzene rings undoubtedly accounts for this result. In agreement with this observation is also the absence of fluorine mobility when 4-fluoro-4′-nitrobiphenyl was heated under reflux with piperidine.

In view of the pseudohalogen character of the CF_3 group and of recent work on its behaviour as an anion,[5] it was of interest to study its behaviour towards nucleophilic attack by allowing the nitrosamine (XXIII) to decompose. The CF_3 group was, however, unaffected.

We next turned our attention to the naphthalene series. The decomposition of N-(naphthyl)-N-nitrosamides in solvents is known to be more complex than that of the benzene analogues yielding invariably a considerable amount of tar.[6] We found that the fluoronitrosamides (XXIV; R = F; R′ = H Me or C_6H_5—) disintegrated within a few seconds in cold benzene with brisk evolution of nitrogen. Steam distillation of the tarry residue gave a small quantity of 1-fluoronaphthalene whose presence can be ascribed to hydrogen abstraction of the fluoronaphthyl radical. Ionic fluorine could easily be detected in all cases bringing the reaction in line with the benzene series. Fractional distillation of the reaction mixture revealed the presence of yet another product indicative of fluorine replacement in high yield (up to 20%), namely, the acid

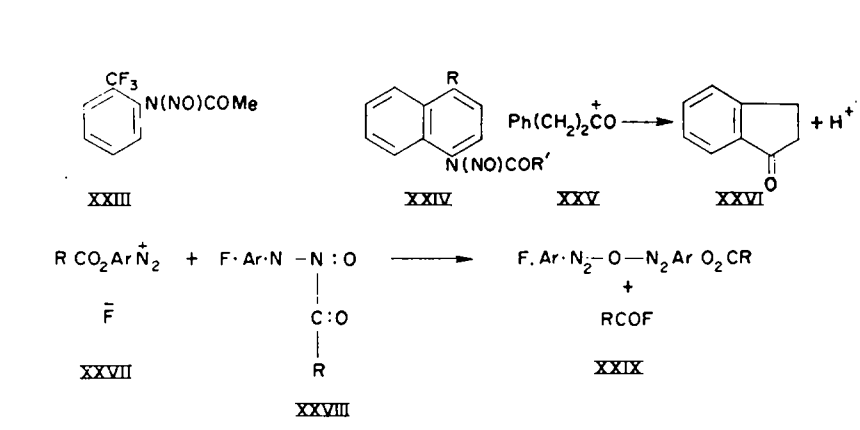
[3] D. I. Davies, D. H. Hey, C. W. Rees and F. C. Saunders, *J. Chem. Soc.* 2317 (1959).
[4] M. M. Chen, A. F. D. Adams and R. I. Walter, *J. Org. Chem.* **26**, 2722 (1961).
[5] I. L. Knunyants and Yu. A. Cheburkhov, *Dokl. Akad. Nauk S.S.S.R.* **137**, 1121 (1961).
[6] D. H. Hey and S. E. Lawton, *J. Chem. Soc.* 374 (1940).

fluoride R'COF corresponding to the acyl part of the starting material (XXIV: R' = H, Me, C_6H_5). The benzene series too yielded acyl fluorides when the method of working up was changed to dry distillation.

In view of the higher reactivity of nucleophilically activated halogen in naphthalene[7] than in benzene, it was thought feasible to study decomposition of the chloro- and bromo-naphthalene compounds (XXIV; R = Cl or Br; R' = Me or C_6H_5). Halogen replacement occurred readily in cold benzene and a quantitative estimation for halogen showed bromine to be more labile than chlorine, which is in agreement with the order of mobility found for these halogens in other nucleophilic substitution reactions.[8]

There are several ways by which acyl fluoride formation in the above reaction can be accounted for. The possibility that it is produced by interaction of hydrogen fluoride on the organic acid in a medium of anhydrous benzene, a situation which is known to develop in the course of the reaction, was eliminated by test experiments. Since fluorine ions are known to be present during the decomposition it is plausible to assume that acyl fluoride formation is the result of an acylium cation ($\overset{+}{R}CO$) combining with a fluorine anion (F^-). Chemical evidence in support of this mechanism was sought by synthesizing an acylarylnitrosamine with an acyl group so constituted that it would cyclize on becoming liberated as a cation and thereby reveal its presence. For this purpose N-(phenyl)-N-nitroso-β-phenyl propionamide (I; R = H; R' = $C_6H_5.CH_2.CH_2-$) was made and allowed to decompose in benzene, since it is known[9] that a phenyl propionyl cation (XXV) readily cyclizes to 1-hydrindone (XXVI). However, the cyclic ketone (XXVI) was not formed even when anhydrous aluminium chloride was added to aid ring-closure.

Recent mechanistic studies of the acylarylnitrosamine rearrangement by Hey[2] and Huisgen[10] tend to support a non-ionic S_Ni(intramolecular) rather than an ionic S_Ni



[7] H. J. Van Opstall, *Rec. Trav. Chim.* **52**, 901 (1933).
[8] E. Berliner, M. J. Quinn and P. J. Edgerton, *J. Amer. Chem. Soc.* **72**, 5305 (1950).
[9] H. Burton and P. G. F. Praill, *Quart. Rev.* VI, 302 (1952).
[10] R. Huisgen and L. Krause, *Liebigs Ann.* **574**, 157 (1951).

pathway for this transformation. This interpretation is based on the insensitivity of the rate of this reaction to changes in the solvent polarity and in the nature of the aryl substituent (R in I), though the variation of the acyl group (R′ in I) has a pronounced effect on the rate[10] possibly more compatible with intermediate acylium ion formation (S_N1). In the light of Hey's and Huisgen's work acyl fluoride formation is conveniently accounted for by a bimolecular nucleophilic attack (S_N2) of a fluoride anion provided by the ion pair (XXVII) on the carbonyl carbon atom in the nitrosocompound (XXVIII) as set out (XXVII) → (XXIX). It is to be expected that the strongly nucleophilic fluorine ion competes successfully with the oxygen of the nitroso-group for possession of the carbonyl carbon atom, causing deacylation in preference to diazoester rearrangement. This reaction course would produce the observed acyl fluoride and the diazoanhydride (XXIX) which is known to be a precursor of aryl radicals.[11] The final products would thus be indistinguishable from those formed by the starting material.

EXPERIMENTAL

Preparation of nitrosocompounds

(a) The required acylarylamine (2 g) was dissolved in a mixture of acetic acid and acetic anhydride (20 ml each) to which some fused sodium acetate had been added.[1] A 20% solution containing an excess of nitrosylchloride in acetic anhydride was added dropwise with stirring over 0·5 hr. On pouring the reaction mixture on to crushed ice (250 g) the yellow nitrosocompound separated. It was washed with cold water and dried in a vacuum desiccator. The benzoyl compound of *4-amino-4′-fluorobiphenyl*, m.p. 241–242°. (Found: C, 78·0; H, 5·0; N, 5·0. $C_{19}H_{14}FNO$ requires: C, 78·4; H, 4·8; N, 4·8%) gave on nitrosation *4′-fluoro-3-nitro-4-biphenylyl benzamide*, m.p. 176–178°. (Found: C, 67·8; H, 4·1; N, 8·3. $C_{19}H_{13}FN_2O_3$ requires: C, 67·9; H, 3·9; N, 8·3%. Fluorine present). Hydrolysis in a mixture of ethanol and conc sulphuric acid gave *4-amino-4′-fluoro-3-nitrobiphenyl* as pale-orange needles, (pet ether b.p. 60–80°). (Found: C, 62·0; H, 3·9; N, 12·1; $C_{12}H_9FN_2O_2$ requires: C, 62·2; H, 4·2; N, 12·3%. Fluorine present). Reduction in ethanol with Raney nickel and hydrogen and addition of diacetyl to an ethanolic solution of the diamine furnished a yellow compound. Its purification by sublimation and recrystallization (aqueous ethanol) gave *6-(p-fluorophenyl)-2,3-dimethylquinoxaline* as white needles, m.p. 117° (Found: N, 10·8. $C_{16}H_{13}FN_2$ requires: N, 11·1%. Fluorine present).

(b) With sparingly soluble acylarylamines anhydrous pyridine (up to 10% of the total volume) was added to the reaction mixture prior to running in nitrosyl chloride. Sodium acetate was omitted in this modification. Results of the preparations (a) and (b) are given in Table 1.

Mixed decompositions of acylphenylnitrosamines

(a) The nitrosocompound of N-phenylacetamide, N-*p*-chloro-, N-*p*-methyl, and N-*m*-methylphenylacetamide were each (1·5–2·0 g) added to a benzene solution (200 ml, 0·5%) of either 1-fluoro-2-nitro- or 1-fluoro-2,4-dinitrobenzene or picrylchloride. The reaction mixture was allowed to stand at room temp (1 day) and decomposition completed by heating on a water-bath to 60° (3 hr). No ionic fluorine (zirconium-alizarin method)[12] or chlorine in the case of picryl chloride was detected.

No halogen replacement occurred when solutions (0·5% or 1%) of the above halonitrocompounds in aqueous acetic acid (10%) were allowed to stand at room temp for one week.

(b) The above nitrosocompounds (ca. 1 part by wt) were each made to decompose for 5 days in benzene (100 ml) containing N-nitroso-*p*-fluorophenylbenzamide (ca. 2 parts by wt) as described under (a). The reaction mixture gave a positive test for fluorine ions. Acidic material was removed from the reaction mixture with an aqueous solution of sodium hydrogen carbonate and the solvent driven off *in vacuo*. Steam distillation of the residue followed by ether extraction of the distillate gave after ether removal a low melting solid which was analysed by column and gas-liquid chromatography. It contained 4-acetoxybiphenyl (2–17%) in every case. From the distillation residue 4-benzoyloxybiphenyl was obtained by sublimation and identified by mixed m.p.

[11] E. Bamberger, *Ber. Dtsch. Chem. Ges.* **29**, 446 (1896); Th. Kauffmann, H. O. Friestad, and H. Henkler, *Liebigs Ann.* **634**, 64 (1960).

[12] Feigl, *Spot tests* II, *Organic Applications* p. 67. Elsevier (1954).

TABLE 1. PREPARATION OF ACYLARYLNITROSAMINES R.N(NO).CO.R′

R	R′	Yield (%)	M.P. (dec.)	Method
p-FC_6H_4-	C_6H_5-	98·5	68°	b
p-FC_6H_4-	H	86	68·5	a
m-FC_6H_4-	C_6H_5-	50·5	58	b
m-FC_6H_4-	Me	17	44	b
p-BrC_6H_4-	Me	78·5	80	b
p-ClC_6H_4-	Me	66	77	a
C_6H_5	Me	92·5	53	a
C_6H_5-	C_6H_5-	78	76	a
C_6H_5-	C_6H_5-	98	76	b
C_6H_5-	$C_6H_5 . CH_2 . CH_2$	89	78	a
o-$Me.C_6H_4$-	Me	—	oil	a
m-MeC_6H_4-	Me	—	oil	a
p-MeC_6H_4-	Me	84	73	a
p-$NO_2.C_6H_4$-	Me	53	61	b
p-$F.C_6H_4.C_6H_4$-	Me	87	84	a
p-$F.C_6H_4.C_6H_4$-	C_6H_5-	89	83	b
o-$CF_3.C_6H_4$-	Me	84	45	a
4-F-naphthyl-1	Me	68	66	a
4-F-naphthyl-1	Me	86	64	b
4-F-naphthyl-1	C_6H_5-	90	71	a
4-F-naphthyl-1	H	96	60	a
4-Cl-naphthyl-1	Me	87	65	b
4-Cl-naphthyl-1	C_6H_5-	80	semi-solid	b
4-Br-naphthyl-1	Me	88	73	a
4-Br-naphthyl-1	C_6H_5-	83·0	72·5	b

(c) A benzene solution (100 ml) of N-(*p*-fluorophenyl)-N-nitrosobenzamide (2 g) containing 0·5 ml acetic acid was kept at room temp for 5 days. The reaction mixture was then extracted with aqueous sodium carbonate solution (5%; 3 × 10 ml), washed with water and dried ($MgSO_4$). The aqueous extract yielded benzoic acid (0·41 g) on acidification. Evaporation of the benzene under red. press. gave a red residue (1·46 g) which was steam distilled. The steam volatile material obtained by ether extraction of the distillate was heated for 2 hr with aqueous sodium hydroxide (15%) but no 4-hydroxybiphenyl was produced. It contained 4-fluorobiphenyl (0·66 g) m.p. 69–72° undepressed on admixture with an authentic sample (m.p. 74–75°). G.L.C. analysis showed also absence of 4-acetoxy- and 4-hydroxybiphenyl.

The distillation residue (0·7 g) was shown to be impure 4-benzoyloxybiphenyl, m.p. 143–145°, raised to 150° on admixture with authentic specimen.

A similar result was obtained when the reaction mixture contained 1 ml acetic acid.

Analysis of mixed decomposition products

(a) *Column chromatography*. A solution (0·5%; 100 ml) of the steam volatile products from the mixed decompositions (cf. b) in pet ether (b.p. 40–60°) was passed through a column (50 cm × 2 cm) of magnesium carbonate (B.D.H. chromatographic purity) and developed with further portions of the same solvent. The first portions (200 ml) contained 4-fluorobiphenyl followed by other substituted biphenyls with 4-acetoxybiphenyl being in the last percolates. The products obtained after evaporation of the solvent were recrystallized (pet ether; b.p. 40–60°) and identified by mixed m.p. with authentic samples.

On an alumina column (activated alumina, type H. P. Spence, Widnes, Lancs.) 4-acetoxybiphenyl was quickly and completely hydrolysed to 4-hydroxybiphenyl which was strongly retained. On this basis a quantitative estimation of 4-acetoxybiphenyl in all mixed decompositions was made as follows:

A 0·5% solution of the steam volatile reaction products in light petrol (b.p. 40–60°; 100 ml) was passed down an alumina column (30 cm × 2 cm) and more of this solvent (200–400 ml) used for elution until the percolate was free from solid material. The column material was then extracted with hot ethanol in a soxhlet and 4-hydroxybiphenyl obtained by evaporation of the solvent weighed. For results see Table 2.

(b) *Gas-liquid chromatography.* A Pye-Argon instrument was used for all analyses. Steam volatile materials from (b) was dissolved in acetone and the sample (0·05–0·1 μl) run on a 4-foot column (4 mm internal diameter) packed with celite (50–100 mesh) containing 20% w/w silicone E.301 elastomer as stationary phase. The flow rate was 40 cc/min of argon and optimum working temp for biphenyl separation around 200°. Since peak heights and corresponding concentrations of 4-acetoxybiphenyl were found to be non-linear calibration factors were applied. All peaks were positive (except that of 4-nitrobiphenyl which was negative) and symmetrical, and coincided with those observed for authentic material. Percentages were estimated by making up known mixtures and comparing areas under each curve. G.L.C. results and relative retention times are given in Table 2.

Decomposition of an acylbiphenylnitrosamine

N-(4-Fluoro-4′-biphenylyl)-N-nitrosoacetamide (3·5 g) obtained by nitrosation of the acetyl-compound[13] was set aside in benzene (300 ml) for 5 days. An aqueous extract of the reaction mixture

TABLE 2. MIXED DECOMPOSITIONS OF ACYLARYLNITROSAMINES IN BENZENE (100 ml)

Composition of mixture (g)	Products R.C_6H_4.C_6H_5			
	R	Yield (g)[a]	(%)[b]	Retention volume[c]
p-$FC_6H_4N(NO)Bz$(0·8)	4-F-	0·33	44	1
	4-BzO-	0·3	—	—
PhN(NO)Ac(1·6)	4-H-	0·31	43	1·14
	4-AcO[d]	0·02	3	3·50
p-F.$C_6H_4N(NO)Bz$(1·0)	4-F	0·42	36	1
	4-BzO	0·37	—	—
p-CHl.$C_6H_4N(NO)Ac$(2·0)	4-Cl	0·58	62	1·66
	4-AcO[d]	0·03	2	3·55
p-F.$C_6H_4N(NO)Bz$(0·9)	4-F	0·35	27	1
	4-BzO	0·41	—	—
p-Me.$C_6H_4N(NO)Ac$(1·8)	4-Me	0·58	70	1·44
	4-AcO[d]	0·04	3	3·55
p-F.$C_6H_4N(NO)Bz$(0·7)	4-F	0·20	40	1
	4-BzO	0·25	—	—
p-NO_2.$C_6H_4N(NO)Ac$(1·0)	4-NO_2	0·3	56	4·33
	4-AcO[d]	0·02	4	3·55
p-F.$C_6H_4N(NO)Bz$(1·5)	4-F	0·22	29	1
	4-BzO	0·22	—	—
m-Me.$C_6H_4N(NO)Ac$(3·0)	3-Me	0·33	54	1·40
	4-AcO[d]	0·13	17	3·40

[a] Obtained by column chromatography except for 4-benzoyloxybiphenyl.

[b] Relative composition of biphenyls in mixture obtained by G.L.C. analysis.

[c] Relative retention volume based upon 4-fluorobiphenyl being taken as unity.

[d] Estimated as 4-hydroxybiphenyl.

[13] T. Van Hove, *Bull. Acad. Roy. Belg.* (5), **8**, 513 (1922).

did not contain ionic fluorine. The benzene solution was extracted with an aqueous solution of sodium hydroxide and the solvent then removed. On trituration of the residue with ether some acetyl compound (1·1 g) was left behind. The ethereal solution after evaporation yielded 4-fluoro-*p*-*ter*phenyl (0·57 g) white needles from ethanol, m.p. 215–215·5°. Burawoy[14] reports m.p. 215°.

Decomposition of N-o-*trifluoromethylphenylacetamide*

Reduction of *o*-nitrotrifluoromethylbenzene[15] in ethanol with Raney nickel and hydrogen gave the amine which on conversion into the acetyl-compound had m.p. 96°. Its nitroso compound, m.p. 45° (1·3 g) was allowed to stand in dry benzene (100 ml) for 3 days. Decomposition occurred to the extent of 97% (titration of free acetic acid) but no ionic fluorine was present.

Decomposition of acylnaphthylnitrosamines

(a) *Fluorine substituted compounds.* 1-Fluoro-4-nitronaphthalene, m.p. 80°, was prepared by Schiemann's method[16] and reduced with iron and ammonium chloride[17] to the amine in 90% yield. Its *acetyl* compound had m.p. 181°. (Found: C, 70·4; H, 4·9. $C_{12}H_{10}FNO$ requires: C, 70·9; H, 5·0%. Fluorine present), its benzoyl derivative m.p. 196° and its *formyl* derivative m.p. 149°. (Found: C, 69·25; H, 4·4; N, 7·4. $C_{11}H_8FNO$ requires: C, 69·3; H, 4·2; N, 7·4%. Fluorine present). The formyl and acetyl compound (2–3 g) were each made to decompose in a benzene solution contained in a two-necked flask fitted with inlet tube and condenser. The gases from the decomposition were passed through a delivery tube attached to the top of the condenser into two ice cooled traps in series containing aniline (2 g) dissolved in dry benzene (100 ml). Nitrogen was used via the inlet tube as a carrier gas. Formanilide and acetanilide respectively were formed in the traps. There was no formation of anilides when a blank test using formic or acetic acid was arranged under the conditions of the reaction. From the decomposition products of the benzoyl derivative benzoyl fluoride, b.p. 153°, was obtained by fractional distillation. The residue was steam distilled and gave 1-fluoronaphthalene, b.p. 216°.

(b) *Chlorine substituted compounds.* By an experimental procedure similar to (a) N-(4-chloro-1-naphthyl)-N-nitrosobenzamide and -acetamide gave benzoyl chloride and acetyl chloride. Chlorine replacement amounted to ca. 10% in each case (estimated as AgCl).

(c) *Bromine substituted compounds.* Bromine replacement (estimated as AgBr) was found to be 18% in the 4-bromo-analogues of the compounds mentioned in (b).

Attempts at producing acylium cations

(a) Decomposition of N-(phenyl)-N-nitroso-β-phenylpropionamide (2·5 g) in dry benzene (100 ml) with or without addition of aluminium chloride gave only biphenyl on steam distillation of the reaction mixture.

(b) N-*Naphthyl-β-phenylpropionamide* obtained from 1-naphthylamine and β-phenyl propionyl chloride as white needles, m.p. 138° (Found: C, 82·5; H, 6·1; N, 5·2. $C_{19}H_{17}NO$ requires: C, 82·9; H, 6·2; N, 5·1%) was nitrosated and the product treated as in (a). No 1-hydrindone was produced.

Decomposition of various acylphenylnitrosamines

(a) After a 4% solution of N(*p*-fluorophenyl)-N-nitrosobenzamide in benzene (100 ml) had been kept for 5 days at room temp it yielded benzoyl fluoride, b.p. 153°, (0·17 g) on fractional distillation. A blank test in which benzoic acid and anhydrous hydrogen fluoride were allowed to interact in dry benzene did not yield benzoyl fluoride.

(b) The corresponding chloro- or bromo-compound suffered no halogen replacement.

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