Smiles Rearrangement in Hydrazonyl Systems: Extension of a Recent 4*H*-1,3,4-Benzoxadiazine Synthesis

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Hydrazonyl aryl ethers derived from hydrazonyl halides $Ar_1CBr{=}NNHC_6H_3XY$ (2, 4) and (*a*) *o*- and *p*-nitrophenols or (*b*) pentachlorophenol undergo a facile base-catalyzed Smiles rearrangement to *N*-aroyl-*N'*,*N'*-diarylhydrazines typified by:

$$Ar_1C(OAr_2){=}NNHC_6H_3XY \rightarrow Ar_1CONHNAr_2C_6H_3XY$$

e.g. **6** → **7**, **8** → **9**, **10** → **11**.

If the 2-substituent X is Br or F and the 4-substituent Y is electron attracting, the *N*-aroyl-*N'*,*N'*-diarylhydrazines can be cyclized under basic conditions to 4-aryl-4*H*-1,3,4-benzoxadiazines by displacement of X, *i.e.* **7** → **13**, **9** → **14**. However, in the analogous cyclization of *N*-benzoyl-*N'*-(2,4-dibromophenyl)-*N'*-pentachlorophenylhydrazine (**11**), chlorine rather than bromine is displaced and the migrating ring ($Ar_2 = C_6Cl_5$) in **10** → **11** becomes the benzene ring of the benzoxadiazine, *i.e.* **11** → **15**.

Independent syntheses of two 4-aryl-4*H*-1,3,4-benzoxadiazines (**13***a* and **14**), from 7-bromo-2-phenyl-4*H*-1,3,4-benzoxadiazine (**5***a*) and *o*- and *p*-fluoronitrobenzene respectively, are reported.

Les ethers hydrazonyl aryle dérivés des halides hydrazonyl $Ar_1CBr{=}NNHC_6H_3XY$ (2, 4) et (*a*) *o*-, *p*-nitrophénol ou (*b*) pentachlorophénol subissent une simple réarrangement de Smiles à catalisation alkaline pour donner *N*-aroyle-*N'*,*N'*-diarylhydrazines tels que:

$$Ar_1C(OAr_2){=}NNHC_6H_3XY \rightarrow Ar_1CONHNAr_2C_6H_3XY$$

e.g. **6** → **7**, **8** → **9**, **10** → **11**.

Si le 2-substituant X est du Br ou du F et le 4-substituant Y est un groupe attirant les electrons, les *N*-aroyle-*N'*,*N'*-diarylhydrazines peuvent cycliser dans des conditions alkalines de façon pour donner 4-aryle-4*H*-1,3,4-benzoxadiazines par le déplacement du X, *i.e.* **7** → **13**, **9** → **14**. Cependant, dans le cyclisation analogue de *N*-benzoyl-*N'*-(2,4-dibromophényle)-*N'*-pentachlorophényl hydrazine (**11**), le chlore plûtot que le brome est déplacé et l'anneau migrateur ($Ar_2 = C_6Cl_5$) en **10** → **11** devient l'anneau benzoic de la benzoxadiazine, *i.e.* **11** → **15**.

On présente aussi les deux synthèses indépendantes de **13***a* et **14**, les 4-aryle-4*H*-1,3,4-benzoxadiazines à partir de 7-bromo-2-phényle-4*H*-1,3,4-benzoxadiazine (**5***a*) et *o*-, *p*-fluoronitrobénzene respectivements.

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A recent synthesis of 4*H*-1,3,4-benzoxadiazines employs various hydrazonyl bromides (**1**), where X = Br or F and Y = Br or NO_2, as starting materials (1). These are converted by reaction with sodium acetate to the corresponding *N*-acetyl-*N'*-aroyl-*N*-arylhydrazines (**3**), presumably by way of hydrazonyl acetates (**2**) though the latter are not isolated. Compounds **3**, on base treatment, give **4** by nucleophilic displacement of the substituent X; in some cases, a subsequent deacetylation (**4** → **5**) is observed under the reaction conditions (Scheme 1). This synthesis supplements the alternative synthesis due to Huisgen and Fleischmann (2).

In order to examine reactions of the type **2** → **3**, a less labile migrating group is required. To this end a number of phenoxy derivatives have been synthesized in which the electron deficiency of the phenoxy ring is controlled by choice of substituents. It was anticipated that if base-catalyzed rearrangement of these compounds were possible, it would lead to *N*-aryl derivatives analogous to **3**. Such an *O* → *N* aryl transfer would provide analogy for the *O* → *N* acyl transfer proposed in **2** → **3** and would represent a Smiles rearrangement (3) on a hydrazonyl skeleton as template. It was hoped further that some of these *N*-aryl derivatives

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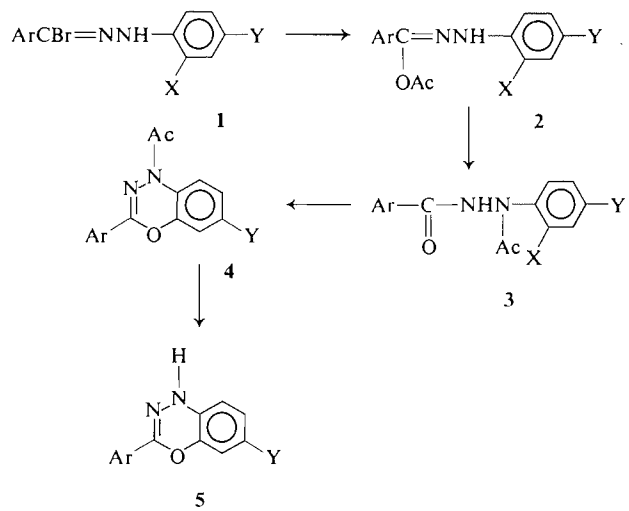


SCHEME 1

would be useful intermediates for syntheses of 4-aryl-4*H*-1,3,4-benzoxadiazines and so permit generalization (1) of the recent benzoxadiazine synthesis typified by **3** → **4**.

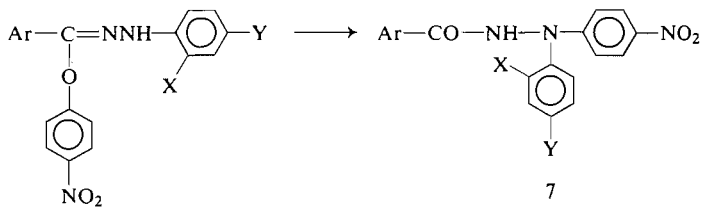
Certain of our observations, noted below, are germane to the thermal isomerisation (Chapman rearrangement) of aryl hydrazonyl ethers (aryl hydrazonates), which has recently been the subject of communications from other laboratories (4).

For convenience, the readily available nitrophenols have been principally used in this study. First, equivalent amounts of hydrazonyl bromide **1***a* and *p*-nitrophenol were stirred together in ethanol with added triethylamine at room temperature to give hydrazonyl *p*-nitrophenyl ether **6***a*. The latter rearranged smoothly in boiling ethanol–triethylamine to the corresponding hydrazide **7***a*. The mass spectra of **6***a* and **7***a* proved interesting. Only **6***a* lost the elements of *p*-nitrophenol on electron impact, an observation in agreement with structure **6***a* (*m/e* 350 for ^{79}Br isotope, 12% of base peak). Further examination of the mass spectrum of **6***a*, and correlation with that of **7***a*, permitted assignment of peaks at *m/e* 384 and 370 to the rearranged compound **7***a*, *i.e.* assignment after allowing for $O \rightarrow N$ aryl transfer. There was no evidence for reverse aryl migration in the mass spectrum of **7***a*.

Other hydrazonyl halides (**1***b–h*), similarly treated with *p*-nitrophenol and triethylamine, gave the corresponding hydrazonyl *p*-nitrophenyl ethers (**6***b–h*). Each of these ethers rearranged to the corresponding hydrazide **7** in refluxing ethanol–triethylamine, generally within a few minutes. Compounds (**6***d* and *f*) which contained electron-attracting groups in the *N*-aryl ring, required longer reaction times for complete rearrangement, reflecting the decreased nucleophilicity of the appropriate nitrogen atom in such compounds (Scheme 2).

Studies were then extended to *o*- and *m*- nitrophenols. It was found that *o*-nitrophenol and hydrazonyl halides (**1***a* and *g*) gave the corresponding hydrazonyl *o*-nitrophenyl ethers (**8***a* and *g*) and that these rearranged smoothly to the corresponding hydrazides (**9***a* and *g*) in boiling ethanol–triethylamine. Under similar conditions, the hydrazonyl aryl ether from **1***a* and *m*-nitrophenol was recovered, and more forcing conditions resulted in decomposition. The last compound examined was hydrazonyl aryl ether **10** from **1***a* and pentachlorophenol; this compound rearranged in boiling ethanol–triethylamine to give hydrazide **11**, though the latter compound was not obtained in an analytically pure condition (Scheme 3).

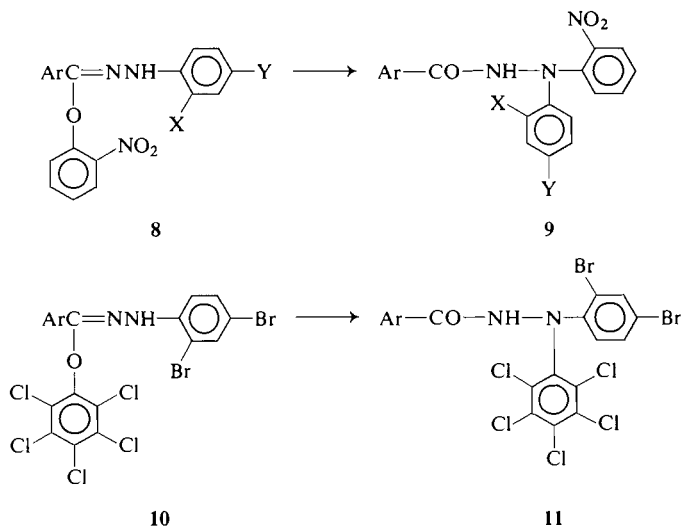
At this stage, in order to obtain some indication that the base-catalyzed rearrangement was intramolecular, the hydrazonyl ethers **6***g* and **8***a* were rearranged in admixture. Intramolecular rearrangement would give **7***g* and **9***a* respectively, whilst an intermolecular rearrangement, for example resulting from dissociation and recombination, would provide in addition **7***a* and **9***g*. The choice of compounds **6***g* and **8***a* was based



6 7

a Ar = C_6H_5; X = Y = Br
b Ar = *p*-$CH_3OC_6H_4$; X = Y = Br
c Ar = *p*-ClC_6H_4; X = Y = Br
d Ar = C_6H_5; X = Br; Y = CO_2Et
e Ar = C_6H_5; X = F; Y = Br
f Ar = C_6H_5; X = Br; Y = NO_2
g Ar = C_6H_5; X = Y = H (Cl instead of Br in **1**)
h Ar = $C_6H_5CH{:}CH{-}$; X = Y = H (Cl instead of Br in **1**)

SCHEME 2

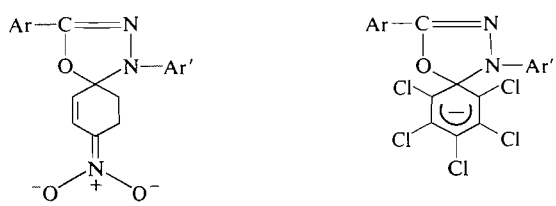


8 9 10 11

SCHEME 3

on similar reactivity, good yields on rearrangement, and ease of separation and identification of the possible products. The mixture produced by rearranging **6***g* and **8***a* in admixture under these conditions contained, within the limits of detection chromatographically, only **7***g* and **9***a*.

Our view is that these rearrangements are intramolecular and proceed through a five-membered cyclic transition state, *e.g.* **12** (Scheme 4). In the cases where the migrating group is *o*- or *p*-nitrophenyl, the transition state is stabilized by delocalisation involving the NO_2 group. No such delocalisation is possible in the case of *m*-nitrophenyl and, under the reaction conditions employed, no rearrangement occurs. In the case of pentachlorophenyl, the ring is sufficiently electron deficient for inductive stabilization of



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SCHEME 4

the minus charge on the migrating ring to allow rearrangement to proceed.

The thermally-induced or Chapman rearrangement of hydrazonyl aryl ethers to *N*-aroyl-*N'*,*N'*-diarylhydrazines, rather than the isomeric *N*-aroyl-*N*,*N'*-diarylhydrazines, is of some current interest (4).

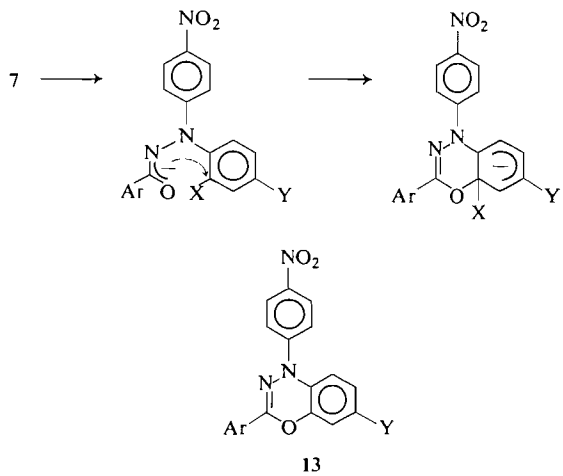
[1] $Ar_1C(OAr_2) = NNHAr_3 \rightarrow Ar_1CONHNAr_2Ar_3$

Rearrangement occurs readily at 200°. Our investigations have not encompassed these conditions but we have noted that no detectable rearrangement (t.l.c.) occurs, *e.g.*, during m.p. determination of **6***a* (118°). Part of the evidence for structural assignment to the products from thermal rearrangement of hydrazonyl aryl ethers comes from hydrolysis to the corresponding *N*,*N*-diarylhydrazines and it has been pointed out that this would provide a useful route to such hydrazines. Whilst this is undoubtedly true, it may be difficult to achieve hydrolysis successfully with more heavily substituted compounds (5). In particular, no success attended our efforts with **9***a* under normal conditions.

Extension of the previously reported 4*H*-1,3,4-benzoxadiazine synthesis (1) was the next objective. The cyclization of a series of the foregoing hydrazides (**7***a–f*) was effected by boiling with an equivalent amount of sodium hydroxide in dimethylformamide–triethylamine mixture for several hours. In most cases, the desired product (**13***a–f*) was isolated chromatographically, the yields ranging from 25–96%.

The presence of electron-withdrawing groups in the *N*-aryl rings and of electron-releasing groups in the *C*-aryl ring would be expected to aid the cyclization. This appears to be so, except for the case of **7***d*. However, in this case, competitive hydrolysis by sodium hydroxide of the ester function would replace an electron withdrawing ethoxycarbonyl group by carboxylate anion and cyclization would then be expected to take place reluctantly, if at all; the benzoxadiazine isolated (**13***d*, 25%) is that derived from the unhydrolyzed hydrazide **7***d* (Scheme 5).

Comparison of **7***a* with **7***e* shows that changing the leaving group from bromine to fluorine results in smoother cyclization and increased yield of the benzoxadiazine **13***a*. In fact **7***e* is converted entirely to benzoxadiazine **13***a* and the yield (96%) represents the material obtained after work-up. In view of this, the mechanism favored for the reaction **7** → **13** is analogous to



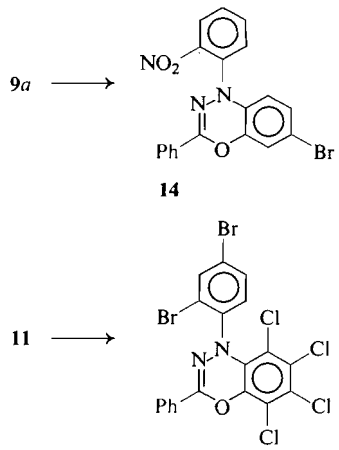
SCHEME 5

that proposed earlier for the cyclization **3** → **4**, except that the *p*-nitrophenyl substituent is not as labile as an acetyl group and is not removed under the reaction conditions, *i.e.* the reaction corresponding to **4** → **5** is not observed (1). The anionic species derived from **7**, or possibly the zwitterionic conjugate acid, is thought to attack the 2-position of the appropriate *N*-aryl ring to form the heterocyclic ring by nucleophilic displacement of halogen.

The structure of **13***a* was confirmed by an alternative synthesis. When **5***a* and *p*-fluoronitrobenzene were boiled together in acetonitrile–triethylamine for 4 h, **13***a* was obtained in 66% yield.

The cyclization of *N*-benzoyl-*N'*-(2,4-dibromophenyl)-*N'*-*o*-nitrophenylhydrazine (**9***a*) posed the alternatives of cyclization by displacement of bromine or by displacement of nitro group. When **9***a* was treated as for the foregoing hydrazides, only **14** was obtained; there was no evidence of other cyclized product (t.l.c.). This oxadiazine was also synthesized from **5***a* and *o*-fluoronitrobenzene.

The cyclization of *N*-benzoyl-*N'*-(2,4-dibromophenyl)-*N'*-pentachlorophenylhydrazine (**11**) posed similar alternatives. In earlier work on synthesis of 4*H*-1,3,4-benzothiadiazines (**6**) it had been noted that no benzothiadiazine formation occurred when compounds (**1**, X = Cl) were treated with potassium thioacetate, though reaction was successful when X = F, Br, or I. However, more heavily chlorinated aromatic rings do undergo nucleophilic displacement of chlorine, and the reactions are synthetically



SCHEME 6

useful (7). In the event, **11**, was cyclized to **15** by displacement of chlorine, with no evidence of other cyclized product (t.l.c.) (Scheme 6).

The present work establishes that aryl hydrazonyl ethers substituted such that the *O*-aryl ring is sufficiently electron deficient, undergo a facile base-catalyzed Smiles rearrangement to give the corresponding *N*-arylhydrazide, *e.g.* **6** → **7**, **8** → **9**, **10** → **11**. The *N*-arylhydrazides thus available are, for given substituents X and Y, eminently suitable intermediates for synthesis of 4-aryl-4*H*-1,3,4-benzoxadiazines. In many cases, the aryl group migrating in the Smiles rearrangement becomes the 4-aryl substituent in the benzoxadiazine finally produced, *e.g.* **6** → **7** → **13**, **8** → **9** → **14**. However, this is not necessarily so, as shown by the conversion **10** → **11** → **15** in which the aryl group migrating in the Smiles rearrangement is finally incorporated as the benzene ring of the benzoxadiazine ring system.

Experimental

General procedures follow those described previously (1). Mass spectra were determined with an AEI-MS30 double beam double focussing mass spectrometer, unless otherwise stated.

Hydrazonyl Halides: Preparation of **1***h* (*8*)

A mixture of *N*-cinnamoyl-*N'*-phenylhydrazine (12.0 g, 0.05 mol), phosphorus pentachloride (11.9 g, 0.055 mol) and dry ether (100 ml) was boiled under reflux for 78 h. The brown solution was cooled and treated with an ethereal solution of phenol until no further reaction was observed. Ethanol was then added and ether was removed by concentration *in vacuo*. The solid was filtered off and crystallized from ethanol to give *N*-α-*chlorocinnamylidene-N'-phenylhydrazine* (**1***h*) as plates (5.8 g, 45%), m.p. 150–151°.

Anal. Calcd. for $C_{15}H_{13}ClN_2$: C, 70.18; H, 5.07; N, 10.92. Found: C, 70.06; H, 5.08; N, 10.74.

Compound **1***h* gave an intense red coloration when heated with phenylhydrazine in ethanol.

Preparation of Hydrazonyl Aryl Ethers

As general procedure, the hydrazonyl halide (0.01 mol) and the phenol (0.01 mol) were stirred in ethanol (EtOH) or acetonitrile (MeCN) containing triethylamine (NEt_3, 0.02 mol) at room temperature, usually for 2 h. The product was collected by (*a*) filtration or (*b*) dilution of the reaction mixture with water followed by filtration, and then washed, dried and purified by crystallization.

Hydrazonyl Aryl Ethers from **1***a*

Compound **1***a* (9) (4.33 g), *p*-nitrophenol (1.39 g), EtOH (30 ml), and NEt_3 (2 ml) gave *N*-α-(*p-nitrophenoxy*)-*benzylidene-N'-(2,4-dibromophenyl)hydrazine* (**6***a*) (3.44 g, 70%) as yellow prisms, m.p. 100–101° or yellow needles, m.p. 117–118° (from ethanol); n.m.r. (CCl_4) δ 8.25 (s, NH), 8.3 (A) and 7.2 (B) (A_2B_2q, J = 8 Hz), and 7.9–7.35 (m, 8H); mass spectrum *m/e* 493/491/489 (M^+), 477/475/473, 463/461/459, 412/410, 411/409, 400/398/396, 354/352/350 ($M^+ - HOC_6H_4NO_2$), 344/342/340, 274/272, 252/250/248 ($Br_2C_6H_3NH$), 225/223/221, 171/169, 139 ($HOC_6H_4NO_2$), 105, 103, and 77. Low intensity peaks at *m/e* 388/386/384, 374/372/370, and 372/370/368 are attributable to rearranged material. A mass spectrum obtained using an AEI-MS902 spectrometer (200–300°) showed some differences, notably reduced intensity of peak *m/e* 354/352/350 and increased intensities of peaks due to rearranged material.

The compound did not undergo detectable rearrangement (t.l.c.) during m.p. determination.

Anal. Calcd. for $C_{19}H_{13}Br_2N_3O_3$: C, 46.44; H, 2.65; Br, 32.59; N, 8.55. Found: C, 46.5; H, 2.7; N, 8.6.

Compound **1***a* (2.0 g), *m*-nitrophenol (0.64 g), EtOH (25 ml) and NEt_3 (1 ml) gave the corresponding *hydrazonyl aryl ether* (1.24 g, 55%) as yellow prisms, m.p. 117–118° (from ethanol).

Anal. Found: C, 46.5; H, 2.9; Br, 32.5; N, 8.5.

Similarly, **1***a* (4.33 g), *o*-nitrophenol (1.39 g), EtOH (25 ml) and NEt_3 (2 ml) gave **8***a* (3.97 g, 81%) as yellow prisms, m.p. 106° or yellow needles, m.p. 122–124° (from ethanol).

Anal. Found: C, 46.6; H, 2.6; Br, 32.8; N, 8.6

Compound **1***a* (4.33 g), pentachlorophenol (2.66 g), EtOH (30 ml), and NEt_3 (1 ml) gave **10** (5.2 g, 84%) as colorless needles, m.p. 165° (from ethanol).

Anal. Calcd. for $C_{19}H_9Br_2Cl_5N_2O$: C, 36.86; H, 1.46; N, 4.53. Found: C, 37.1; H, 1.7; N, 4.7.

Hydrazonyl Aryl Ethers from **1**, *b–h*

Compound **1***b* (10) (4.64 g), *p*-nitrophenol (1.39 g), EtOH (25 ml), and NEt_3 (2 ml) gave **6***b* (4.73 g, 90%) as yellow needles, m.p. 143–144° (from ethanol – ethyl acetate).

Anal. Calcd. for $C_{20}H_{15}Br_2N_3O_4$; C, 46.06; H, 2.88; N, 8.06. Found: C, 45.99; H, 2.88; N. 8.03.

Compound **1***c* (1) (4.67 g), *p*-nitrophenol (1.39 g), EtOH (30 ml), and NEt_3 (2ml) gave **6***c* (4.4 g, 84%) as yellow needles, m.p. 151° (from *t*-amyl alcohol – benzene).

Anal. Calcd. for $C_{19}H_{12}Br_2ClN_3O_3$: C, 43.39; H, 2.28; N, 7.99. Found: C, 43.8; H, 2.5; N. 7.9.

Compound **1***d* (1) (2.13 g), *p*-nitrophenol (0.69 g), EtOH (20 ml), and NEt_3 (0.5 ml) gave **6***d* (1.49 g, 62%) as needles, m.p. 145° (from ethanol).

Anal. Calcd. for $C_{22}H_{18}BrN_3O_5$: C, 54.55; H, 3.72; Br, 16.53; N, 8.68. Found: C, 54.5; H, 3.7; Br. 16.7; N, 8.7.

Compound **1***e* (6) (3.72 g), *p*-nitrophenol (1.39 g), MeCN (30 ml), and NEt_3 (1ml) gave **6***e* (3.85 g. 90%) as yellow needles. m.p. 115° (from benzene–hexane).

Anal. Calcd. for $C_{19}H_{13}BrFN_3O_3$: C, 53.02; H, 3.02; N, 9.77. Found: C, 53.22; H, 3.14; N, 9.68.

Compound **1***f* (11) (3.99 g), *p*-nitrophenol (1.39 g), EtOH (30 ml), and NEt_3 (1 ml) gave **6***f* (3.8 g, 83%) as yellow plates, m.p. 192° (from toluene).

Anal. Calcd. for $C_{19}H_{13}BrN_4O_5$: C, 49.89; H, 2.84; Br, 17.51; N, 12.25. Found: C, 50.0; H, 3.0; Br, 17.3; N, 12.4.

Compound **1***g* (8) (2.3 g), *p*-nitrophenol (1.39 g), EtOH (60 ml), and NEt_3 (2 ml) gave, after 3 h, **6***g* (1.2 g, 36%) as yellow needles, m.p. 138–139° (from ethanol) (lit. (4*c*) m.p. 134°).

Anal. Calcd. for $C_{19}H_{15}N_3O_3$: C, 68.47; H, 4.50; N, 12.61. Found: C, 68.68; H, 4.59; N, 12.43.

Similarly, **1***g* (2.3 g), *o*-nitrophenol (1.39 g), EtOH (60 ml), and NEt_3 (2 ml) gave, after 3 h, **8***g* (1.5 g, 45%) as yellow needles, m.p. 122–123° (from ethanol).

Anal. Found: C, 68.12; H, 4.44; N, 12.65.

Compound **1***h* (1.4 g), *p*-nitrophenol (0.75 g), EtOH (25 ml) and NEt_3 (1 ml), stirred overnight, gave **6***h* (0.5 g, 25%) as pale orange needles, m.p. 182–183° (from ethanol).

Anal. Calcd. for $C_{21}H_{17}N_3O_3$: C, 70.19; H, 4.74; N, 11.70. Found: C, 70.06; H, 4.85; N, 11.52.

N-Aroyl-N′,N′-diarylhydrazines by Smiles Rearrangement of Hydrazonyl Aryl Ethers

As general procedure, the hydrazonyl aryl ether in 1:1 EtOH–NEt_3 mixture was boiled under reflux for 15 min. In some cases, the product separated on cooling; otherwise solvents were removed *in vacuo* and the product was crystallized.

Compound **6***a* (0.5 g, 0.001 mol) in EtOH (5 ml) and NEt_3 (5 ml) gave *N-benzoyl-N′-(2,4-dibromophenyl)-N′-p-nitrophenylhydrazine* (7*a*) (0.34 g, 68%) as prisms, m.p. 215–216° (from benzene); i.r. (KBr) 1645 cm^{-1} (C=O); n.m.r. (DMSO-d_6) δ 11.4 (s, NH), 8.0 (A) and 6.65 (B) (A_2B_2q, J = 9Hz), and 7.9–7.3 (m, 8H); mass spectrum *m/e* 493/491/489 (M^+), 477/475/473, 463/461/459, 412/410, 411/409, 395/393, 388/386/384 (M^+ – PhCO), 374/372/370 (M^+ – PhCON), 372/370/368 (M^+ – $PhCONH_2$), 344/342/340, 342/340/338, 309/307, 263/261/259, 246/244, 199, 166, 121, 106, 105, 104, 103 and 77.

Anal. Calcd. for $C_{19}H_{13}Br_2N_3O_3$: C, 46.44; H, 2.65; Br, 32.59; N, 8.55. Found: C, 46.3; H, 2.6; N, 8.4.

Similarly, **8***a* (0.5 g) in EtOH (5 ml) and NEt_3 (5 ml) gave **9***a* (0.32 g, 64%) as yellow needles, m.p. 200–201° (from benzene–hexane).

Anal. Found: C, 46.4; H, 2.9; Br, 32.8; N, 8.8.

The isomeric hydrazonyl *m*-nitrophenyl ether did not rearrange under these conditions, even after 2 h, nor when boiled under reflux in 2,6-lutidine for 1 h. Under more vigorous conditions (DMF–NEt_3) decomposition ensued.

Compound **6***b* (3 g) in EtOH (15 ml) and NEt_3 (15 ml) gave **7***b* (2.5 g, 83%) as cream needles, m.p. 235° (from ethanol – ethyl acetate).

Anal. Calcd. for $C_{20}H_{15}Br_2N_3O_4$: C, 46.07; H, 2.88; Br, 30.71. Found: C, 46.04; H, 3.01; Br, 30.89.

Compound **6***c* (0.5 g) in EtOH (5 ml) and NEt_3 (5 ml) gave **7***c* (0.32 g, 64%) as cream needles, m.p. 235° (from reaction mixture).

Anal. Calcd. for $C_{19}H_{12}Br_2ClN_3O_3$: C, 43.39; H, 2.28; N, 7.99. Found: C, 43.4; H, 2.4; N, 8.0.

Compound **6***d* (0.5 g) in EtOH (5 ml) and NEt_3 (5 ml) gave, after 2 h, **7***d* (0.31 g, 62%) as pale yellow prisms, m.p. 119° (from benzene–hexane).

Anal. Calcd. for $C_{22}H_{18}BrN_3O_5$: C, 54.55; H, 3.72; Br, 16.53; N, 8.68. Found: C, 54.7; H, 3.9; Br. 16.5; N, 8.6.

Compound **6***e* (2.15 g) in MeCN (15 ml) and NEt_3 (15 ml) gave **7***e* (1.9 g, 88%) as needles, m.p. 214–216° (from benzene).

Anal. Calcd. for $C_{19}H_{13}BrFN_3O_3$: C, 53.02; H, 3.02. Found: C, 53.15; H, 3.10.

Compound **6***f* (0.5 g) in EtOH (5ml) and NEt_3 (5 ml) gave, after 2 h. **7***f* (0.41 g, 82%) as yellow prisms, m.p. 286° (trituration with boiling hexane–toluene).

Anal. Calcd. for $C_{19}H_{13}BrN_4O_5$: C, 49.89; H, 2.84; Br, 17.51; N, 12.25. Found: C, 50.2; H, 2.8; Br, 17.7; N, 12.35.

Compound **6***g* (0.5 g) in EtOH (10 ml) and NEt_3 (5 ml) gave, after 1 h, **7***g* (0.3g, 60%) as cream needles, m.p. 173–174° (from benzene) (lit. (4*c*) m.p. 178–180°).

Anal. Calcd. for $C_{19}H_{15}N_3O_3$: C, 68.47; H, 4.50; N, 12.61. Found: C, 68.85; H, 4.45; N, 12.61.

Similarly, **8***g* (0.5 g) in EtOH (10 ml) and NEt_3 (5 ml) gave, after 1 h, **9***g* (0.3 g, 60%) as yellow needles, m.p. 171–172° (from benzene).

Anal. Found: C, 68.24; H, 4.38; N, 12.60.

Compound **6***h* (0.3 g) in EtOH (15 ml) and NEt_3 (5 ml) gave, after 2 h. **7***h* (0.17 g, 57%) as yellow needles, m.p. 155–156° (from benzene, then from ethanol).

Anal. Calcd. for $C_{21}H_{17}N_3O_3$; C, 70.19; H, 4.74; N, 11.70. Found: C, 70.38; H, 4.89; N, 11.79.

Compound **10** (0.5 g) in EtOH (5 ml) and NEt_3 (5 ml) gave, after 1 h, **11** (0.4 g, 80%) as needles, m.p. 248–249° (from hexane).

Anal. Calcd. for $C_{19}H_9Br_2Cl_5N_2O$ (mol. wt. 618.5): C, 36.86; H, 1.46; N, 4.53. Found (620, vapor pressure, acetone): C, 39.2; H, 1.9; N, 4.5.

Rearrangement of 6g and 8a in Admixture

T.l.c. (silica gel, $CHCl_3$) of reference mixtures of **7***g* (R_f 0.33), **7***a* (R_f 0.39), **9***g* (R_f 0.51), and **9***a* (R_f 0.60) showed that **7***a* and **9***g* were each detectable in mixtures containing **7***g* (49.5% w/w), **7***a* (0.5%), **9***g* (0.5%), and **9***a* (49.5%).

A mixture of **6***g* (0.3 g) and **8***a* (0.3 g) in EtOH (15 ml) and NEt_3 (5 ml) was boiled under reflux for 1 h and the mixture of rearranged products was isolated by evaporation of solvents *in vacuo*. T.l.c. showed that **7***g* and **9***a*, but not **7***a* and **9***g*, were present. The mixture was chromatographed to yield **9***a* and **7***g*; these compounds were identified after crystallization by correlation (i.r., t.l.c., mixture m.p.) with reference samples. The eluates collected between **9***a* and **7***g* were evaporated and examined by t.l.c.; there was no indication of the presence of **7***a* or **9***g*.

Attempted Debenzoylation of 9a

Attempts to debenzoylate **9***a* by hydrolysis (24 h

reflux with 1:1 ethanol – concentrated HCl) or by ethanolysis (12 h reflux with 5–6% ethanolic sodium ethoxide) were unsuccessful; **9***a* was recovered.

Preparation of Substituted 4H-1,3,4-Benzoxadiazines from N-Aroyl-N′,N′-diarylhydrazines

As general procedure, equivalent amounts of the *N*-aroyl-*N′*,*N′*-diarylhydrazine and sodium hydroxide were dissolved in a mixture of dimethylformamide (DMF) and NEt_3 and boiled under reflux for 6 h. The solution was cooled, poured into excess 5% acetic acid, and the solid was collected, washed with water, and dried. Except where directly crystallized, the crude products were chromatographed on Florisil (toluene as eluant) and the fraction containing the fluorescent product was collected.

Compound **7***a* (4.91 g, 0.01 mol), sodium hydroxide (0.4 g, 0.01 mol), DMF (25 ml), and NEt_3 (5 ml) yielded *7-bromo-4-p-nitrophenyl-2-phenyl-4H-1,3,4-benzoxadiazine* (**13***a*) (1.2 g, 29%) as yellow-orange needles, m.p. 221–222° (from benzene). The yield was improved in a subsequent experiment (79%, 10 h).

Anal. Calcd. for $C_{19}H_{12}BrN_3O_3$: C, 55.61; H, 2.93; N, 10.24. Found: C, 54.97; H, 2.90; N, 10.09.

Compound **7***e* (2.15 g), sodium hydroxide (0.2 g), DMF (25 ml), and NEt_3 (5 ml) also gave **13***a* (2.0 g, 97%) as needles, m.p. 221–222° (direct crystallization from benzene); mixture m.p. (with above sample) 221–222°.

Compound **7***b* (1.3 g), sodium hydroxide (0.1 g), DMF (15 ml) and NEt_3 (5 ml) gave **13***b* (0.8 g, 73%) as orange needles, m.p. 179–180° (from ethanol – ethyl acetate).

Anal. Calcd. for $C_{20}H_{14}BrN_3O_4$: C, 54.55; H, 3.18; Br, 18.18. Found: C, 54.26; H, 3.35; Br, 18.48.

Compound **7***c* (2.6 g), sodium hydroxide (0.2 g), DMF (25 ml), and NEt_3 (5 ml) gave **13***c* (0.8 g, 36%) as yellow needles, m.p. 267–268° (from benzene).

Anal. Calcd. for $C_{19}H_{11}BrClN_3O_3$: C, 51.29; H, 2.47; N, 9.45. Found: C, 51.29; H, 2.54; N, 9.80.

Compound **7***d* (1.21 g), sodium hydroxide (0.1 g), DMF (15 ml), and NEt_3 (2 ml) gave **13***d* (0.26 g, 25%) as yellow-orange prisms, m.p. 217° (from toluene).

Anal. Calcd. for $C_{22}H_{17}N_3O_5$: C, 65.51; H, 4.22; N, 10.42. Found: C, 65.66; H, 4.14; N, 10.31.

Compound **7***f* (4.57 g), sodium hydroxide (0.4 g), DMF (25 ml), and NEt_3 (5 ml) gave **13***f* (2.3 g, 62%) as red prisms, m.p. 288° (direct crystallization from DMF).

Anal. Calcd. for $C_{19}H_{12}N_4O_5$: C, 60.64; H, 3.19; N, 14.89. Found: C, 60.56; H, 3.31; N, 14.73.

Compound **9***a* (4.91 g), sodium hydroxide (0.4 g), DMF (25 ml), and NEt_3 (5 ml) gave **14** (1.1 g, 27%) as red needles, m.p. 163° (from benzene–hexane).

Anal. Calcd. for $C_{19}H_{12}BrN_3O_3$: C, 55.61; H, 2.93; Br, 19.51. Found: C, 55.49; H, 2.84; Br, 19.58.

Compound **11** (3.09 g), sodium hydroxide (0.2 g), DMF (15 ml), and NEt_3 (5 ml) gave **15** (1.8 g, 62%) as yellow needles, m.p. 215–216° (from benzene–hexane).

Anal. Calcd. for $C_{19}H_8Br_2Cl_4N_2O$ (mol. wt. 582): C, 39.16; H, 1.37; N, 4.81. Found (577, vapour pressure, benzene): C, 39.45; H, 1.45; N, 4.82.

Alternative Syntheses of 13a and 14 from 5a (1)

Compound **5***a* (1) (0.3 g), *p*-fluoronitrobenzene (0.14 g), NEt_3 (5 ml), and MeCN (15 ml) were boiled together under reflux for 4 h. Solvents were removed *in vacuo* and the residue was washed with water and dried. Crystallization from benzene gave **13***a* (0.24 g, 60%), m.p. and mixture m.p. 221–222°.

An analogous experiment in which *o*-fluoronitrobenzene (0.14 g) replaced the *p*-isomer gave, after crystallization from hexane–toluene, **14** (0.20 g, 50%), m.p. and mixture m.p. 162–163°.

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