# The Synthesis of Formazans from *ortho*-Substituted Arylidene Arylhydrazines

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Formazans, *ortho*-substituted in the *C*-aryl ring, have been prepared in two ways. These involve (*a*) coupling a highly electrophilic diazonium salt with an *ortho*-substituted benzylidene arylhydrazine and (*b*) replacement of bromine of a hydrazidic bromide by phenylhydrazine.

FORMAZANS are normally formed by the reaction of arylidene arylhydrazones with diazonium salts. This reaction involves, as a first step, the formation of a *bis*-(arylazo)-methane intermediate,[1] resulting from diazonium ion attack at the methine carbon, and large substituents in the *ortho*-position of the aromatic aldehyde ring may hinder formazan formation for steric reasons.[2] Thus, attempts to prepare formazans from 2-chlorobenzaldehyde phenylhydrazone[3] and 2,6-dichlorobenzaldehyde phenylhydrazone[4] failed, and in Nineham's[5] and in Putter's[6] compilations no formazans with *ortho*-substituents in the *C*-aryl ring (with the exception of *o*-hydroxy and *o*-nitro-groups for which special reasons may apply) are listed.

Our kinetic studies of the reaction of benzenediazonium ion with arylidene arylhydrazines[2] showed that *ortho*-substituents in the arylidene ring did indeed decrease the rate of the coupling reaction. However, the order of decrease was such that it suggested that use of a diazonium salt an order of magnitude more reactive than benzenediazonium chloride should overcome the steric effect and yield formazans. We have now confirmed this since *p*-nitrobenzenediazonium ion, a more electrophilic agent than benzenediazonium ion[7] reacted with a number of *o*-substituted arylidene arylhydrazines in pyridine solution to give the appropriate formazans (Table). Thus, the effect of the *o*-substituent is such that a barrier, rather than a total prohibition, to formazan formation is provided.

The analogous reaction of bromine with hydrazones, giving the hydrazidic bromides (I), is not effectively subject to steric hindrance, the rates of bromination even for 2,6-disubstituted aldehyde hydrazones being correlated merely using electronic parameters.[8] These *N*-(aryl)-*o*-substituted benzhydrazidic bromides (I) react with phenylhydrazine to give the *o*-substituted formazans (III).*

The conditions which optimised the yield of the formazan in this case involved stirring the hydrazidic bromide in 95% ethanol with an excess of phenylhydrazine for 36 hr. at ambient temperature. At higher temperatures the solvoltyic decomposition of the hydrazidic bromide (*e.g.*, with water resulting in the formation of benzhydrazides[10]) competes with the replacement reaction. The initial products formed were the hydrazidines (II) of which only one (X = Cl) was actually

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* The reaction of hydrazidic halides with substituted hydrazines has been reported in two cases, see ref. 9.

[1] A. F. Hegarty and F. L. Scott, *Chem. Comm.*, 1966, 622.

[2] A. F. Hegarty and F. L. Scott, *J. Org. Chem.* 1967, **32**, 1957.

[3] F. R. Frichter and J. Frolich, *Chem. Zentr.*, 1903, **11**, 426.

[4] A. W. Nineham, D. L. Pain, and R. Slack, *J. Chem. Soc.*, 1954, 1568.

[5] A. W. Nineham, *Chem. Rev.*, 1955, **55**, 355.

[6] R. Putter, 'Houben-Weyl Methoden der Organischen Chemie,' Thieme, Stuttgart, 1965, vol. 10/3, p. 633.

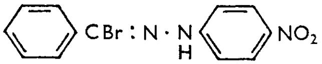
[7] H. Zollinger, *Helv. Chim. Acta*, 1953, **36**, 1730.

[8] A. F. Hegarty and F. L. Scott, *J. Chem. Soc.*, 1966, 1031.

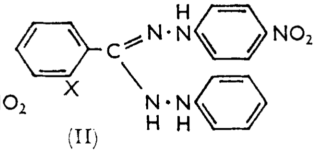
[9] H. von Pechmann, *Ber.*, 1894, **27**, 320; F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, 1925, 975.

[10] F. L. Scott and J. B. Aylward, *Tetrahedron Letters*, 1965, 841.

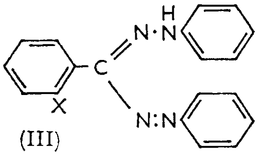
isolated. These were generally precipitated together with some formazan from the reaction mixture. Then without their separation, mere crystallisation of the mixture from boiling 95% ethanol sufficed to give the



(I)



(II)



(III)

pure formazan. The same formazans (see Table) were prepared by this second (replacement) route as those by the coupling route (above).

Formazans containing a *p*-nitro-group have been reported to be very dark in colour (*e.g.*, greenish-black [11]) However, the formazans with *o*-substituents (III) prepared here show an interesting gradation in colour, lightening in the series X = H, F, Cl, or Br from greenish-black to bright red for 1-*p*-nitrophenyl-3-(2′,6′-dichlorophenyl)-5-phenylformazan.* This colour change presumably reflects the increasing steric hindrance to coplanarity with the consequent decrease in π-orbital overlap caused by the more bulky substituents.

$ArC(N{:}NPh){:}N{\cdot}NH{\cdot}C_6H_4{-}NO_2{-}p$

| Ar | M. p. | Found (%) C | Found (%) H | Found (%) N | Formula | Required (%) C | Required (%) H | Required (%) N |
|---|---|---|---|---|---|---|---|---|
| Ph | 198—199° * | 67·2 | 4·7 | 20·25 | $C_{19}H_{15}N_5O_2$ | 67·05 | 4·45 | 20·6 |
| 2-$ClC_6H_4$ | 178—180 | 59·8 | 3·9 | 18·55 | $C_{19}H_{14}ClN_5O_2$ | 60·1 | 3·7 | 18·4 |
| 2-$BrC_6H_4$ | 184—185 | 54·2 | 3·55 | 16·7 | $C_{19}H_{14}BrN_5O_2$ | 53·8 | 3·35 | 16·5 |
| 2-$FC_6H_4$ | 165 | 62·65 | 3·95 | 18·75 | $C_{19}H_{14}FN_5O_2$ | 62·8 | 3·9 | 19·3 |
| 2,6-$Cl_2C_6H_3$ | 222—223 | 55·25 | 3·4 | 16·4 | $C_{19}H_{13}Cl_2N_5O_2$ | 55·1 | 3·15 | 16·9 |

* Lit.,[14] m. p. 199—200°.

The scope of the bromide-replacement procedure is limited by two factors inherent in the bromination reactions in which the hydrazidic bromides are formed, namely, (*a*) bromine may be introduced into the aromatic ring of the hydrazine group, unless this has been deactivated [12] (as *e.g.*, with a *p*-nitro-group used here) and (*b*) the bromination reaction is subject to at least one of the same limitations as formazan formation in that it fails with *N*-disubstituted hydrazones.[13]

## EXPERIMENTAL

Experimental details are provided for examples of both the replacement route (A) and the coupling route (B) to 1-*p*-nitrophenyl-3-(*o*-substituted phenyl)-5-phenylformazans; the experimental details are presented for only one such compound.

1-p-*Nitrophenyl*-3-o-*chlorophenyl*-5-*phenylformazan* (III; X = Cl).—*Route* (*A*). A slurry of *o*-chlorobenzaldehyde *p*-nitrophenylhydrazone (2·76 g., 0·01 mole) was stirred in glacial acetic acid (40 ml.) at room temperature and bromine (0·6 ml., 0·012 mole) in glacial acetic acid (10 ml.) was added during 3 hr.[8] The precipitated hydrazidic bromide was filtered off and washed thoroughly with water and crystallised, m. p. 170° (acetic acid). The hydrazidic bromide was then suspended in 95% ethanol (25 ml.) at room temperature while phenylhydrazine (3 ml.) was added dropwise. The yellow solid dissolved rapidly to give a bright red solution. A red solid began to precipitate after stirring for 6 hr. and this was collected after a further 30 hr. This had m. p. 156—157° and corresponded analytically to the hydrazidine (II; X = Cl) (Found: C, 59·4; H, 4·2; N, 18·4. $C_{19}H_{16}ClN_5O_2$ requires C, 59·8; H, 4·2; N, 18·35%). Its infrared spectrum showed a sharp N–H stretching band at 3·0 μ.

Three crystallisations from 95% ethanol gave the darker formazan, m. p. 178° (see Table). The overall yield of the formazan was 48%.

*Route* (*B*). *p*-Nitroaniline (1·38 g., 0·01 mole) was dissolved at 50° in constant boiling hydrochloric acid (3·3 ml.) (*d* 1·18), diluted with an equal volume of water. The warm solution was poured on ice chips (15 g.) and sodium nitrite (0·76 g., 0·011 mole) was added dropwise rapidly to the fine yellow precipitate. The solid dissolved and the solution of *p*-nitrobenzenediazonium chloride was added, during 20 min., to a stirred solution of *o*-chlorobenzaldehyde phenylhydrazone (2·30 g., 0·01 mole) in pyridine (20 ml.) at 0°. On the first addition the solution became momentarily yellow and then rapidly deep red. A viscous oil separated which solidified when the pyridine solution was stored overnight in a refrigerator. The solid was collected and washed thoroughly with warm water. Several crystallisations from aqueous ethanol gave the formazan (2·34 g., 62%), m. p. 178—180°. A mixture melting point between this material and a sample prepared above as described by method (*A*), showed no depression and the infrared spectra of both compounds were identical.

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* The nomenclature used is that proposed by Nineham, see ref. 5.

[11] M. Busch and R. Schmidt, *J. prakt. Chem.*, 1931, **131**, 182.

[12] A. F. Hegarty and F. L. Scott, *J. Chem. Soc.*, 1966, 672.

[13] J. M. Burgess and M. S. Gibson, *Tetrahedron*, 1962, **18**, 1001.

[14] O. W. Maender and G. A. Russell, *J. Org. Chem.*, 1966, **31**, 442.