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THE ACTION OF *sec*-ALIPHATIC AMINES ON BENZOFUROXANS

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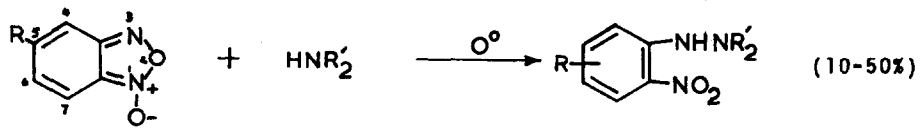
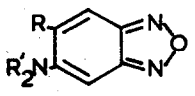
Various nucleophiles have been shown to react with benzofuroxans (1) by initial attack at the 3-position, offering synthetic routes to heterocycles[1] including quinoxaline, phenazine and benzimidazole derivatives. The useful reactions of nitrogen nucleophiles are limited to cases resulting in substitution in the homocyclic ring[2] or reduction to *o*-benzoquinone-dioxime and *o*-phenylenediamine[2]. We now report the ready interaction of benzofuroxans and cold, neat *sec*-aliphatic amines (2) to give *o*-nitrophenyl-



(1) (2) (3)

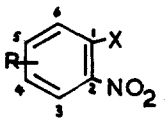
hydrazines (3) in fair yields. The hydrazines (3) are produced equally well with dialkylamines as with cyclic amines though with cyclic amines the rate of formation decreases with increasing ring size (Table 1).

The presence of substituents in the homocyclic ring markedly affects the course of the reaction. Thus, 5-nitrobenzofuroxan gave no definable products while the 5-chloro-derivative gave cleaner products and higher yields. However, with a 5-trifluoromethyl or 5-carbethoxy group present, the reaction takes a different course giving the ring aminated benzo-furazans (4). Conversely, the presence of electron donating substituents



(4)

(5)

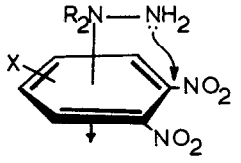


(6)

A; X = Cl
B; X = F
C; X = NO_2
D; X = NR'_2

(e.g. OMe) causes side-reactions. The nature of these by-products which also increase in quantity if the reaction mixture is warmed has not as yet been established but they probably arise from the attack of the homocyclic ring (*cf.* ref. 2).

Alternative routes to some of these hydrazines (3) were explored because of their potential synthetic use in cyclisation reactions. For instance, condensation in various solvents of *N*-aminopiperidine with *o*-chloro-, *o*-fluoro or 2,5-dichloronitrobenzene resulted predominantly in attack at the more basic (i.e. most substituted) nitrogen, yielding the corresponding *N*-(*o*-nitrophenyl)piperidine*. However, with electrophiles bearing at least two electron withdrawing substituents, (e.g. 2,4-dinitrohalobenzenes, *o*-dinitrobenzenes and 2-nitro-4-trifluoromethyl- or carbethoxy-chlorobenzene) the required hydrazine was the major product, often in good yield (Table 2). We attribute the different behaviour of these latter electrophiles to *indirect* nucleophilic substitution, after the formation of a charge transfer complex involving the most basic centre of the hydrazine with the highly electron-depleted π-ring system (e.g. 7). In accord with this principle the nucleo-



(7)

phile enters the most electrophilic site and the yield of hydrazine (3) increases with the increase of the 'π-acidity' of the benzene ring system.

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*The fate of the hydrazine NH_2 group in these reactions is at present not clear.

TABLE 1

Products from the action of bases (2) on benzofuroxans (1)

Reactants		Conditions		Product(s)
1; R=	2; R_2'=	Time(days)	Temp(^oC)	(%)
H	Me_2	5	20	3(5)
H	Et_2	5	20	3(10)
H	$(CH_2)_4$	3	0	3(44)
H	$(CH_2)_5$	5	0	3(48)
H	$(CH_2)_2O(CH_2)_2$	1	50	3(12)
H	$(CH_2)_2NMe(CH_2)_2$	5	20	3(10)
Cl	Et_2	7	0	3(29)
Cl	$(CH_2)_5$	4	0	3(50)
CF_3	$(CH_2)_5$	0.5	50	3(25) and 4(36)
COOEt	$(CH_2)_5$	4	20	

TABLE 2

Products from the action of hydrazines (5) on nitro-compounds (6)

Reactants			Conditions		Product(s)
Cpd.	R	5; R_2' =	Time(hr)	Temp(^oC)	(%)
6A	4-NO_2	Me_2	4	78*	3(75)
6A	4-NO_2	$(CH_2)_5$	3	78*	3(81)
6A	4-NO_2	$(CH_2)_2O(CH_2)_2$	6	78*	3(73)
6A	4-NO_2	$(CH_2)_6$	5	78*	3(57)
6A	4-CF_3	Me_2	2	100†	3(70)+6D(15)
6A	4-CF_3	$(CH_2)_5$	2	100†	3(58)+6D(trace)
6A	4-COOEt	Me_2	2	100†	3(67)+6D(18)
6B	H	Me_2	24	78*	3(5)+6D(80)
6B	H	Me_2	2	78*	6D(70)
6B	4-NO_2	$(CH_2)_5$	4	78*	3(83)

TABLE 2 Continued

Products from the action of hydrazines (5) on nitro-compounds (6)

Reactants			Conditions		Product(s)
Cpd.	R	5; R^1_2 =	Time(hr)	Temp(°C)	(%)
6C	H	Me_2	24	78	3(33)+6D(40)
6C	H	$(CH_2)_5$	60	78	3(9)+6D(12)
6C	5-Cl	Me_2	3	78	3(37)
6C	5-Cl	$(CH_2)_5$	6	78	3(42)
6C	5-Cl	$(CH_2)_2O(CH_2)_2$	8	78	3(26)
6C	5-Cl	$(CH_2)_6$	8	78	3(38)
6C	4-NO_2	Me_2	2	78	3(86)
6C	4-NO_2	$(CH_2)_5$	2	78	3(86)

*in refluxing ethanol

†in dimethylformamide

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