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PREPARATION AND PHOTOCHEMICAL BEHAVIOUR OF 2,3,4,5,6-PENTAFLUOROPHENYLAZO-BENZENE AND -4'-METHOXYBENZENE

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SUMMARY

Pentafluoronitrosobenzene reacts readily with aniline and with p-methoxyaniline to give the corresponding 2,3,4,5,-6-pentafluoroazobenzenes (1a and 1b) in good yield. Minor components detected by n.m.r. spectroscopy in the analytically pure products are shown by a combination of lanthanide-induced shift studies and photochemical reactions to be the cis-azo compounds; these cis-azo compounds are unusually stable in the dark, with half lives ranging from 19h to > 100 days at room temperature.

INTRODUCTION

Pentachloronitrosobenzene reacts with various amines to give the corresponding azobenzenes [1], and the reaction of trifluoronitrosomethane with amines also gives azo-compounds in good yield [2]. The reaction of nitrosobenzenes with

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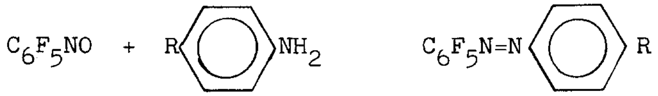
aminofluorobenzenes has also been reported [3]. In each case the product appears (or is assumed) to be exclusively the trans-isomer. We report here the preparation of 2,3,4,5,6-pentafluorophenylazobenzene (1a) and of the 4'-methoxy compound (1b), and a study of their photochemistry and of their n.m.r. spectra in the presence of a lanthanide shift reagent.

RESULTS AND DISCUSSION

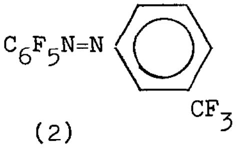
Pentafluoronitrosobenzene, prepared by oxidation of pentafluoroaniline with performic acid [4], reacted with aniline in a mixture of toluene and glacial acetic acid at 40-75 °C, following the procedure described by McBee et al. for reactions with pentachloronitrosobenzene [1], to give 2,3,4,5,6-pentafluorophenylazobenzene (1a) in 65% yield. p-Anisidine similarly gave the corresponding 4'-methoxy-compound (1b) in 45% yield after only 1h at



(1)

a: R = H; b: R = OMe

reflux in glacial acetic acid. These reactions are thus considerably more rapid than those reported for the preparation of 4-amino-2,3,5,6-tetrafluorophenylazobenzene and its 4'-alkyl analogues from 2,3,5,6-tetrafluorophenylenediamine and the hydrocarbon nitroso-benzenes [3], presumably because the amino-groups of the tetrafluorodiamine are so much less nucleophilic. In accord with this, the reaction of pentafluoronitrosobenzene with 3-trifluoromethylaniline gave only a low yield of the azo-compound (2).



(2)

Azo-compounds (1a and b) were obtained analytically pure by a combination of column chromatography and recrystallisation but although the ^1H n.m.r. spectrum of a freshly prepared sample of (1a) showed the expected pair of complex bands in 3:2 ratio at 7.6 and 8.0 δ for the aromatic hydrogens, a similar pattern of low intensity was also visible at 7.5 and 7.0 δ. The ^{19}F n.m.r. spectrum showed six groups of peaks, which could be assigned on the basis of their intensities and multiplicities to two C_6F_5 groups present in 9:1 ratio. The second component showed more obviously in the ^1H spectrum of (1b), where two overlapping p-disubstitution patterns of different intensities could be seen, together with a second weak singlet in the OCH_3 region. Again the ^{19}F spectrum showed the presence of two C_6F_5 group, with intensities corresponding to those of the ^1H bands.

The nature of the second component was clarified by successive additions of $Eu(fod)_3$ to the n.m.r. samples (see Table 1). The major bands in the ^1H spectra of (1a and b)

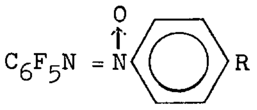
TABLE 1

N.m.r. Spectra and LIS Chemical Shifts [a]

Compound	MR[b]	2,6F	3,5F	4F	2',6'-H	3',5', (4')-H	4-OMe
cis-1a	0	-68·2[c]	-81·9[c]	-77·1[c]	7·0	7·4	
	0·537	-66·9	-81·4	-76·5	8·0	7·6	
trans-1a	0	-71·3[d]	-83·6[d]	-74·5[d]	8·0	7·6	
	0·537	-71·3	-83·6	-74·5	8·0	7·6	
cis-1b	0	-68·8	-81·6	-77·8	6·96	6·76	3·74
	0·882	-63·6	-80·0	-76·1	10·12	7·77	4·25
trans-1b	0	-71·7	-83·8	-75·9	7·84	6·90	3·84
	0·882	-71·7	-83·8	-75·9	7·96	7·00	3·93
4-$MeOC_6H_4Br$	0	-	-		7·27	6·66	3·76
	0·882	-	-		7·37	6·87	3·99

[a] ^{19}F shifts in p.p.m from external trifluoroacetic acid, ^{1}H shifts from internal TMS;CCl_4 solvent. Positive values are to high frequency of reference. [b] Mole ratio of $Eu(fod)_3$ to total substrate. [c] In hexane ^{19}F shifts are -69·5, -83·8, and -79·2 p.p.m. [d] In hexane -72·5, -85·7, -76·6 p.p.m.

were unaffected, but the weaker bands moved to higher frequency. The minor bands of (1a) merged with the major bands at a mole ratio (LSR : substrate) of 0·54, and resolution was lost on further addition of $Eu(fod)_3$, but with (1b) the movement could be followed to a higher concentration of $Eu(fod)_3$. In parallel with the movement of bands in the ^{1}H spectra, small shifts in the bands of the weaker AA'MXX' patterns in the ^{19}F spectra showed that the high frequency band in each case was due to fluorines *ortho* to the site of complex formation with the lanthanide. The positions of the bands of the major AA'MXX' patterns remained unchanged for both (1a and b). Azoxy-compounds are reported to complex to lanthanide shift reagents *via* the oxygen [5]. The possibility that the minor components were the azoxy-compounds (3), which might be formed by oxidation of the azo-compounds (1a and b) either in the course of reaction or during work-up, was discounted when zero shifts were found in the ^{1}H and ^{19}F spectra of the known azoxy-compound (4) [6]. The electron-withdrawing effect of the perfluoroaromatic group evidently reduces the availability of the oxygen lone pair so that complex formation with the lanthanide does not occur. The shifts induced in the aromatic hydrogens of the minor component of (1b) are not due to complex formation at the methoxyl oxygen, being much larger than those shown by p-bromoanisole (Table 1).



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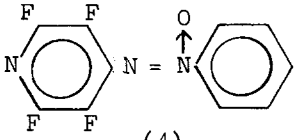

(4)

Several authors have noted that *cis*-azo compounds show lanthanide-induced shifts, but the *trans*-isomers do not [7], and the minor components in the reaction products (1a and b) are thus assigned the *cis*-azo structure. There are comparatively few reports of lanthanide-induced shifts in ^{19}F spectra; those reported [8] are mostly similar in magnitude to those found in the present work, where electron withdrawal by the fluorines reduces the availability of the lone pair for complex formation.

The observation of both cis- and trans-isomers of (1a and b) was contrary to our expectation, since most reports suggest that the more stable trans-isomer is formed exclusively. McBee *et al.*, for instance, report that simple para-disubstitution patterns were found in the ^{1}H n.m.r. spectra of the azobenzenes they prepared from pentachloronitrosobenzene and 4-substituted anilines [1]. However, it is by no means easy to detect concentrations of 10-15% of the cis-isomer other than by n.m.r., and even with this technique, clear separation of the bands from the two isomers, as has been found here, may not always be achieved, depending on the substituents present. In this respect, the greater separation of the bands in the ^{19}F spectra of the C_6F_5 groups is a considerable advantage.

Since the well-separated signals in the n.m.r. spectra of (1a and b) allowed easy independent estimation of the concentrations of cis- and trans- isomers in a given sample, in contrast to the u.v. spectroscopic method, where the bands of the two isomers overlap substantially, the photochemical behaviour of (1a and b) has been examined briefly.

Samples of (1a and b) kept in the dark for prolonged periods, either in the solid state or in solution in carbon tetrachloride, showed no signals due to the cis-isomer. U.v. irradiation, *in vacuo* or in the presence of air, in soda-glass n.m.r. tubes, of solutions of (1a or b) in carbon tetrachloride or hexane showed a rapid increase of the cis-isomer to a photo-equilibrium concentration which depended somewhat on the compound and the solvent (See Table 2). Irradiation in silica n.m.r. tubes gave similar results for hexane solutions, but led to extensive decomposition of carbon tetrachloride solutions. Irradiation of solid (1a) resulted in no detectable isomerisation.

When the irradiated solutions were kept in the dark, the concentration of the cis-isomer fell again, but, particularly in hexane solutions, decay to the trans-isomer at room temperature was very slow. Approximate half-lives for the reversion cis ⟶ trans are give in Table 2. No other products were detected in the mixtures; the isomerisation/reversion sequence could be repeated without any other change, providing conclusive evidence that the second component found in the initial products is the cis-isomer.

TABLE 2

Equilibrium Concentrations and Half-lives for cis-Azo Compounds

Compound	Solvent	% cis[a]	$t_{\frac{1}{2}}$(20 °C)	$t_{\frac{1}{2}}$(55 °C)
$C_6F_5N_2Ph$	CCl_4	50	100 days	25 h
(1a)	Hexane	42	>100 days	2·7 days
	EtOH	-[b]	>100 days	6 days
$C_6F_5N_2C_6H_4OMe$	CCl_4	38	19 h	
(1b)	Hexane	50[c]	25 days	19 h

[a] Photo-equilibrium concentration in soda-glass n.m.r. tubes. [b] Sample irradiated in hexane, solvent removed and replaced by EtOH for decay study. [c] In silica, equilibrium concentration was 35-38% cis-isomer.

The stability of cis-(1a) is considerably greater than that of cis-azobenzene (log A and E_a values reported [9] imply a half-life in n-heptane at 20 °C of ca. 6 days). Fletcher et al. noted [3] that the cis-isomer of 4-amino-2,3,5,6-tetrafluorophenylazobenzene relaxed to the trans-isomer 'remarkably slowly'; although their reported 10% decay in 4 h (estimated from changes in intensity of u.v. absorption) implies a half-life of ca. 25 h, comparable with the fastest of the decay rates observed at room temperature for (1a and b), it is much slower than the rate for non-fluorinated azo-benzenes containing a free amino group. The effect of the polyfluorophenyl group is thus clearly stabilisation of the cis-isomer, but the mechanism by which this takes place is not clear.

Although these irradiation experiments were carried out with mercury discharge lamps, we have found that solutions of the trans-azo compounds show appreciable conversion to the cis-isomers after a few hours exposure in glass apparatus to (Manchester) sunlight. It is thus not necessary to propose that the reaction of pentafluorophenylnitrosobenzene with aniline and 4-methoxyaniline resulted in the direct formation of both cis- and trans-azo compounds. Presumably unintentional irradiation of the reaction products, together with the high stability of the cis-isomers and their ease of detection by ^{19}F n.m.r. spectroscopy, allowed their unexpected initial observation.

U.v. spectra. The u.v. spectra of the pure trans-isomers are readily obtained, and since the isomer ratio in a mixture can be derived from the n.m.r. spectrum, the u.v. spectrum of the cis-isomer can be obtained by difference, as illustrated in Fig. 1 for (1a). The spectra for trans-(1a and 1b) are similar to those reported for trans-azobenzene [9] and trans-4-methoxyphenylazobenzene [10] respectively, and that of cis-(1a) corresponds to that reported [9] for cis-azobenzene, with the added appearance in cis-(1a) of a weak maximum at 340 nm.

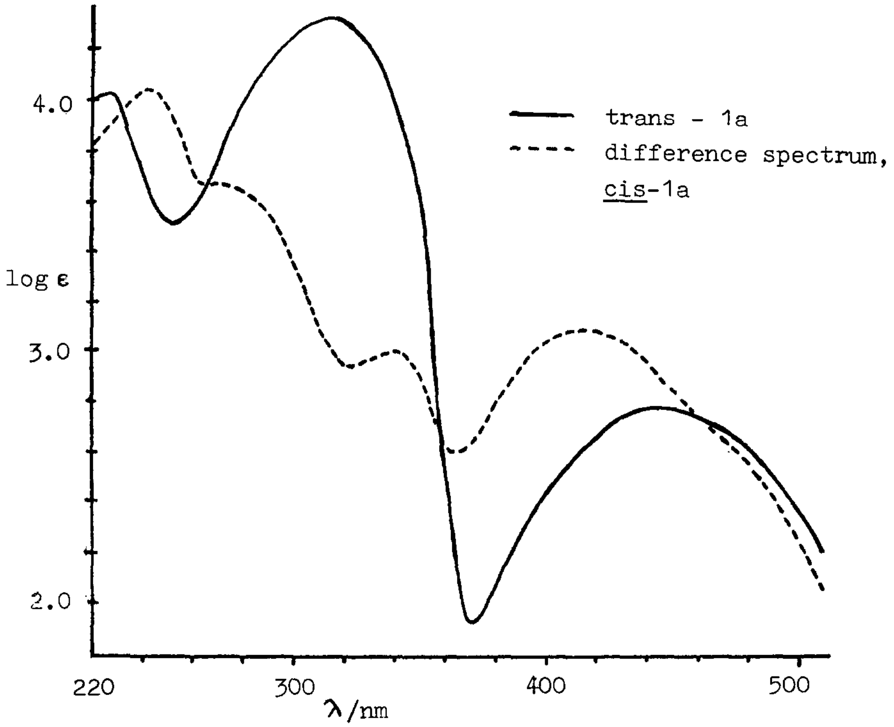

Fig 1. U.v. spectra of (1a)

EXPERIMENTAL

Pentafluoronitrosobenzene was prepared by oxidation of pentafluoroaniline with performic acid [4]. N.m.r. spectra were recorded on Perkin Elmer R10 and R12 B (60.0 MHz for ^1H, 56.46 MHz for ^{19}F) or R32 (90.0 MHz for ^1H, 84.69 MHz for ^{19}F) Spectrometers. U.v. spectra were measured on a Cary 118X recording spectrophotometer. Irradiations were with Hanovia UVS 500 medium pressure mercury arc lamps.

Preparation of 2,3,4,5,6-pentafluorophenylazobenzene (1a)

Pentafluoronitrosobenzene (1.0 g, 5.1 mmol) and aniline (0.51 g, 5.5 mmol) were heated together in a mixture of toluene (48 ml) and glacial acetic acid (2 ml), the temperature being raised in steps from 40 °C to 75 °C over 30 h. The solvent was removed, and chromatography on alumina gave an orange fraction which was recrystallised from ethanol to give 2,3,4,5,6-pentafluorophenylazobenzene (nc) (0.90 g, 65%) initially as a mixture of cis- and trans-isomers, m.p. 88-89 °C, but subsequently obtained as the pure trans-isomer, m.p. 89 °C.

Analysis: Found: C, 53.0; H, 1.6; F, 35.0; N, 10.2%. $C_{12}H_5F_5N_2$ requires C, 52.9; H, 1.8; F, 34.9; N,10.3%

Preparation of 2,3,4,5,6-Pentafluorophenylazo-4'-methoxybenzene

Pentafluoronitrosobenzene (1.52 g, 7.7 mmol), p-methoxyaniline (1.1 g, 9.0 mmol) and acetic acid were heated under reflux (1 h). Water was added and the precipitated solid was chromatographed on alumina. The orange product was recrystallised from ethanol to give 2,3,4,5,6-pentafluorophenylazo-4'-methoxybenzene (nc) (1.05 g, 45%), initially as a mixture of *cis*- and *trans*-isomers m.p. 98-99 °C, from which the pure *trans*-isomer (λ_{max}/nm, log ε: 427, 3.15; 346, 4.31; 244, 4.13) was subsequently obtained.

Analysis: Found: C, 51.9; H, 2.5; F, 31.3; N, 9.2%, $\underline{M}^+$, 302. $C_{13}H_7F_5N_2O$ requires C, 51.7; H, 2.3; F, 31.4; N, 9.3%; $\underline{M}$, 302.

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