The Electronic Effect of the Phenylazoxy Group

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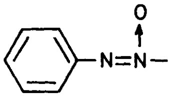
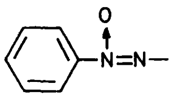
Hammett σ_m and σ_p values have been determined for the phenyl-*ONN*-azoxy and phenyl-*NNO*-azoxy groups by measuring the pK_a values of the phenylazoxybenzoic acids in 50% ethanol. The σ_p^+ value for phenyl-*ONN*-azoxy has been evaluated both from the rate of solvolysis of 4-phenyl-*ONN*-azoxyphenyldimethylcarbinyl chloride in aqueous acetone, and from the rate of bromination by acidified hypobromous acid. The two values obtained differ markedly, and the variations are interpreted in terms of differences in the geometry of the transition states for the two reactions.

The first compound to be synthesised with a phenylazoxy group was azoxybenzene, prepared by Zinin nearly 150 years ago by boiling nitrobenzene with alcoholic caustic potash.[1] There are two isomeric 'phenylazoxy' groups, differing in whether the oxygen is on the more distant or nearer of the nitrogens to the phenyl group. These are customarily referred to as phenyl-*NNO*-azoxy and phenyl-*ONN*-azoxy respectively, although in the past other terminologies have been used.



phenyl-*NNO*-azoxy



phenyl-*ONN*-azoxy

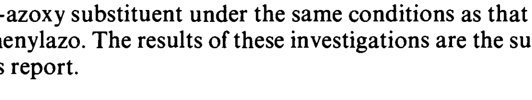
Surprisingly little is known about the electronic effect of these groups. The major reason for this would appear to be the considerable practical difficulties involved in obtaining pure samples of suitable compounds for study (most preparative methods yield mixtures of approximately equal amounts of the ONN and NNO isomers.).

The basic Hammett σ_m and σ_p constants are unknown (only two of the four phenylazoxybenzoic acids have ever been reported). Two groups of workers have reported σ_p^- values. Miller and his co-workers[2] measured the rates of the reaction of the two isomeric 1-chloro-2-nitro-4-phenylazoxybenzenes with sodium methoxide in methanol and derived σ_p^- values of $+0.616$ and $+0.772$ for phenyl-*ONN*-azoxy and phenyl-*NNO*-azoxy, respectively. Later, Jaffé and Ellerhorst,[3] based on the pK_a values of the dimethylanilinium ions, obtained ones of $+0.78$ and $+0.56$. The two sets of results were reconciled when it was found that the structures in the latter study were wrongly assigned.[4]

No σ_p^+ values have been reported. The electronic structure of the phenyl-*NNO*-azoxy substituent indicates that it is likely to be $-I$, $-R$ in all circumstances, with $\sigma_p^+ \approx \sigma_p$. On the other hand, results for electrophilic substitutions show that the phenyl-*ONN*-azoxy group is *ortho*/*para* directing and activating.[5] Since such a result is inconsistent with its reported σ_p^-, it must resemble a phenylazo in that it can be either $+R$ or $-R$ depending on the electronic demands placed on it. The only quantitative data available are those of Miller and his co-workers,[6] who measured the rate of chlorination of azoxybenzene by chlorine and chlorine acetate in acetic acid solution. Because no isomer distributions were determined, σ_p^+ values could not be calculated, but reasonable estimates for these lead to σ_p^+ values of *ca.* -0.2 and -0.3 respectively. Variation of σ_p^+ with electrophile has also been observed with the phenylazo substituent, and we have recently submitted for publication the results of an investigation into the reasons for the phenomenon.[7] The explanation proposed was based on the possibility of different mechanisms for the stabilisation of the transition state, which result from changes in transition-state geometries. For reactions involving highly reactive electrophiles, and also for the solvolysis of 4-arylazophenyldimethylcarbinyl chlorides, it was concluded that stabilisation of the transition state involved overlap with the azo π system; in reaction with weaker electrophiles there is a greater tendency for overlap to involve the lone pair on the adjacent nitrogen instead.

In the case of the phenyl-*ONN*-azoxy group, it is reasonable to conclude that the $+R$ effect involves participation by one of the lone pairs on the azoxy oxygen, a circumstance that requires that the azoxy π system be coplanar with the aromatic ring.

However, in view of the apparent variation in σ_p^+ found, participation by the nitrogen lone pair must be regarded as a serious alternative.



In the course of our azobenzene studies we had mastered the techniques involved, and obtained data on the standards needed, for evaluating σ and σ_p^+ constants for arylazo groups, and it seemed logical to take advantage of this and extend our investigation to determine these parameters for the phenyl-*ONN*-azoxy substituent under the same conditions as that used for phenylazo. The results of these investigations are the subject of this report.

Results and Discussion

σ_m and σ_p Values.—The σ_m and σ_p values for our two phenylazoxy groups were determined by measuring their pK_a values in 50% v/v ethanol–water and comparing these with values for a number of standards measured under the same conditions.[7] These measured pK_a values, together with the derived σ_m and σ_p values are given in Table 1.

The results lend strong support to the contention that phenyl-*NNO*-azoxy and phenyl-*ONN*-azoxy may be regarded as modified nitro and phenylazo groups respectively. In the case of phenyl-*NNO*-azoxy, comparison of the σ_m, σ_p, and σ_p^- values with the corresponding ones for nitro (σ_m $+0.74$, σ_p $+0.78$, $\sigma_p^- \approx +1.25$)[8] shows that the effect of replacing one of the oxygens in the latter by the less electronegative phenylimino group is to decrease σ_I by about one third and σ_R^- by about one half. Quantitatively, this relationship appears to be similar to

Table 1. pK_a Values for phenylazoxybenzoic acids and derived σ_m and σ_p constants[a]

Acid	pK_a (σ)
3-Phenyl-*ONN*-azoxybenzoic acid	5.17 (+0.24)
3-Phenyl-*NNO*-azoxybenzoic acid	4.79 (+0.50)
4-Phenyl-*ONN*-azoxybenzoic acid	5.12 (+0.27)
4-Phenyl-*NNO*-azoxybenzoic acid	4.70 (+0.56)
3,5-Dimethyl-4-phenyl-*ONN*-azoxybenzoic acid	5.43 (+0.17)[b]

[a] pK_a values are for 50% ethanol–water at 25 °C and $I = 0.1$. [b] This hindered σ value has been adjusted for the presence of the 3- and 5-methyl groups by substracting 0.13 from the original figure obtained.

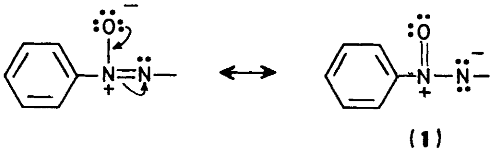
Table 2. Summary of σ_p^+ values for phenylazo and phenyl-*ONN*-azoxy groups

Reaction	σ_p^+ (azoxy)	σ_p^+ (azo)
Rate of substitution, ArH HOBr–HClO$_4$	−0.04[a]	+0.09[11]
Rate of solvolysis, 4-XC$_6$H$_4$CMe$_2$Cl, aqueous acetone	+0.06[b]	+0.17[7]
Rate of solvolysis, 3,5-Me$_2$-4-XC$_6$H$_2$CMe$_2$Cl, aqueous acetone	−0.08[c]	+0.01[7]

[a] Based on a third-order rate constant of 0.302 l^2 mol^{-2} s^{-1} and a measured *o*:*p* ratio of 0.92:1. [b] Based on k 1.21 × 10^{-3} s^{-1} in 80% acetone at 25 °C. [c] Based on k 2.06 × 10^{-3} s^{-1} in 87.5% acetone at 25 °C. This value has been corrected for the contribution from the methyl groups.

that between phenylazo and nitroso but a reliable comparison is hampered by a lack of reliable σ constants for the latter group.

In contrast, the close similarity between the σ_m, σ_p, and σ_p^- values of phenyl-*ONN*-azoxy, and phenylazo (σ_m +0.28, σ_p +0.34, σ_p^- +0.67)[5,7] is rather surprising. The introduction of the oxygen decreases σ_I by *ca.* 0.04 units and leaves σ_R and σ_R^- virtually unchanged. Yet studies in pyridine systems have shown that the conversion of the aza nitrogen into the *N*-oxide virtually doubles its $-I$ effect,[9] and the nitro group is considered to be more electron-withdrawing than nitroso.[10] We believe that the increase in the $-I$ character of the group which should have accompanied the conversion into the *N*-oxide has been more than offset by a resonance interaction that effectively increases the electron density on the adjacent nitrogen.

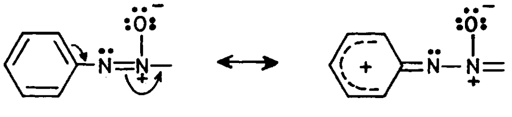


(1)

Since such an interaction is internal to the group it is manifested as a change in the inductive effect.

That the magnitudes of the $-R$ effects for phenyl-*ONN*-azoxy and phenylazo are also very similar is less surprising, as this also appears to be true in the pyridine system.[9]

σ_p^+ *Values*.—No attempt was made to evaluate a σ_p^+ value for the phenyl-*NNO*-azoxy substituent. While it is feasible for the group to exert a $+R$ effect by involvement of the phenyl ring



it was considered that any contribution to the stabilisation of an electron-deficient centre from this source was likely to be small. Investigations were, instead, confined to the phenyl-*ONN*-azoxy group. In view of the earlier indication that σ_p^+ for the latter might vary with the nature of the electrophile,[6] values were determined by the methods used for phenylazo.

These were (a) measurement of the rate of bromination using acidified hypobromous acid in 75% dioxane[11] and, (b) measurement of the rate of solvolysis of the aryldimethylcarbinyl chloride in aqueous acetone.[7] Additionally, when it turned out that these two methods yielded significantly different values, as had occurred for phenylazo, the solvolysis study was repeated using a modified substrate where coplanarity of the system was hindered by introducing methyl groups in the two ring positions on either side of the phenyl-*ONN*-group. The σ_p^+ constants obtained are listed in Table 2. To assist in the interpretation of the results for the hindered system, the pK_a value of the corresponding benzoic acid was also measured (see Table 1).

First, let us consider the results for the unhindered system. Perhaps the most striking feature is the degree to which the close parallel with phenylazo, already noted in the case of σ_m, σ_p, and σ_p^-, features also in the σ_p^+ values. The simplest interpretation of the σ_p^+ results is that phenyl-*ONN*-azoxy behaves essentially as a modified phenylazo, with the introduced oxygen enhancing the ability of the group to donate electrons [probably *via* contributions such as resonance form (**1**)], and the multiplicity of σ_p^+ values, like those observed for azobenzene arising from variations in transition-state geometries.[7]

The situation is not quite as straightforward as it appears, however, since, while the numerical values for the azoxy and azo series appear in line, the expected degree of hindrance in the two systems is very different. In the azobenzene system, interference with coplanarity arises as the result of interaction between a methyl and the lone pair on the more distant nitrogen.[12] In the azoxybenzene system this lone pair has been replaced by oxygen, a group that has much greater steric requirements. This means that the hindrance to coplanarity is much greater in the dimethylazoxybenzene than in the dimethylazobenzene system. In fact, that prevailing in the normal azoxy system should be comparable to that present in the hindered azo structure.

Let us now examine the results for the 3,5-dimethyl-4-phenyl-*ONN*-azoxy system in the light of the above considerations. The value for σ_p (+0.17) is virtually the same as that expected for the σ_I for the group, implying that for non-planar phenylazoxy σ_R is *ca.* 0. Such a result is only consistent with the relatively high σ_p^+ (−0.08) estimated for the hindered group if one accepts that it arises from offsetting $+R$ and $-R$ contributions to σ_p, and the latter, unlike the former requires some degree of overlap of the azoxy π system with the ring. Schaeffer and Miraglia have determined the pK_a of 4-acetamido-3,5-dimethylbenzoic acid and estimated that the acetamido group was twisted at an angle of 49° to the phenyl ring.[13] The steric requirements of a phenyl-*ONN*-azoxy group should be similar to the acetamido group, so at least some degree of overlap of the azoxy π system with the ring should be possible. Our σ_p value for the hindered system indicates that overlap must exist, although to a considerably lesser degree that in the unhindered one. There is some evidence it may not even be completely lost in the transition state for the solvolysis of the hindered substrate, since the σ_p^+ value derived for this system (−0.08) is considerably less negative than that estimated from the rates of chlorination of azoxybenzene.[6]

It should be pointed out that our σ_p^+ values for both the hindered azo and hindered azoxy systems might be influenced by the effect of the methyl groups on the solvation of the phenylazo and phenylazoxy substituents. Interference with solvation would certainly decrease the ability of the substituent to stabilise the system, but by how much it is difficult to say. One cannot therefore rule out the possibility that this could be the reason why σ_p^+ values obtained in the hindered systems are never as negative as those reported in the literature for both the phenylazo and phenylazoxy groups. However, this would not affect our basic interpretation of the behaviour of the system.

Experimental

A major difficulty encountered in the preparation of isomerically pure azoxybenzene derivatives is establishing when the products were free of the other isomer. The most satisfactory method for doing this was by ^{13}C n.m.r. spectrometry. Spectra were determined using solutions in $CDCl_3$ on a Varian model CFT-20 instrument and referenced to tetramethylsilane. In the spectra reported the numbering system used is based on that in use for azoxybenzene, *i.e.* C-1—C-6 refer to carbons in the ring more distant from the azoxy oxygen, and C-1′—C-6′ to those for the closer. The shifts for C-1′ were normally very weak and were rarely observed. The spectrum obtained for azoxybenzene was assigned as follows: δ 148.2 (C-1′), 144.0 (C-1), 131.3 (C-4′), 129.4 (C-4), 128.5 (C-3, C-5, C-3′, C-5′), 125.4 (C-2, C-6), and 122.2 p.p.m. (C-2′, C-6′). (*Note*: this assignment differs from that made in the literature.) Assignments for the various azoxybenzenes prepared were based on comparison of the spectrum obtained with these calculated based on the predicted effect of substituents on the azoxybenzene shifts.

Purification by chromatography was normally carried out using a Harrison Research Inc. Chromatotron centrifugally accelerated radial thin layer chromatograph, fitted with rotors coated with a layer of silica gel (PF_{254} type 60, Merck: EM Laboratories Inc.) of 2 mm thickness.

Preparation of Compounds.—(a) 3-*Phenylazoxybenzoic acids*. The two *meta*-acids were obtained by saponification of their ethyl esters. Both esters were isolated from a mixture of the two isomers prepared by oxidation of ethyl 3-phenylazobenzoate using 30% hydrogen peroxide in acetic acid.

3-Phenyl-*ONN*-azoxybenzoic acid. Crystallisation of the mixture of isomeric esters from ethanol yielded pure ethyl 3-phenyl-*ONN*-azoxybenzoate as pale yellow crystals, m.p. 83 °C; $\delta_C(CDCl_3)$ 165.9 (CO), 144.0 (C-3), 131.8 (C-4′), 131.2 (C-1), 130.2 (C-6), 129.1 (C-4), 128.8 (C-3′), 128.7 (C-5), 126.9 (C-2), 122.2 (C-2′), 61.2 (CH_2), and 14.5 p.p.m. (CH_3), C-1′ not observed.

Saponification with KOH in ethanol gave 3-*phenyl*-ONN-*azoxybenzoic acid*, m.p. 195—197 °C (Found: C, 64.6; H, 3.9; N, 11.6. $C_{13}H_{10}N_2O_3$ requires C, 64.5; H, 4.2; N, 11.6%).

3-Phenyl-*NNO*-azoxybenzoic acid. Evaporation of the mother liquor from the crystallisation of the *ONN*-ester gave a residue consisting of a 5:1 mixture of the *NNO*- and *ONN*-isomers. This mixture was repeatedly adsorbed onto a silica–polyethylene glycol-coated Chromatotron plate and eluted with light petroleum–ether, finally giving a sample of pure ethyl 3-phenyl-*NNO*-azoxybenzoate as a yellow oil, $\delta_C(CDCl_3)$ 165.3 (CO), 148.4 (C-3) 144.8 (C-1′), 132.4 (C-6), 131.6 (C-1), 130.0 (C-4′), 128.9 (C-5), 128.8 (C-3′), 126.4 (C-4), 125.7 (C-2′), 123.5 (C-2), 61.6 (CH_2), and 14.3 p.p.m. (CH_3).

Saponification of the ester by refluxing with potassium hydroxide in ethanol gave 3-*phenyl*-NNO-*azoxybenzoic acid*, m.p. 181—182 °C (Found: C, 64.6; H, 4.0; N, 11.5%).

(b) 4-*Phenylazoxybenzoic acids*. The successful separation of the two 4-phenylazoxybenzoic acids from an isomeric mixture had been previously reported.[14] Attempts to repeat this separation failed, as did all those to separate a mixture of ethyl 4-phenylazoxybenzoates. Both acids were prepared eventually from the appropriate 4-bromoazoxybenzenes *via* the nitriles.

4-Phenyl-*ONN*-azoxybenzonitrile. This was prepared from the bromo derivative by the method of Friedman and Shechter.[15] 1-Bromo-4-phenyl-*ONN*-azoxybenzene[16] (4.8 g) was heated with copper(I) cyanide (1.9 g) in dimethylformamide at 155—160 °C for 4 h. The mixture was worked up by the iron(III) chloride method. Recrystallisation of the crude product from ethanol gave 4-phenyl-*ONN*-azoxybenzonitrile (2.5 g), m.p. 112—113 °C, $\delta_C(CDCl_3)$ 147.8 (C-1′), 146.9 (C-1), 132.7 (C-4′), 132.6 (C-3), 128.9 (C-3′), 125.7 (C-2), 122.4 (C-2′), 118.4 (CN), and 112.0 p.p.m. (C-4).

Methyl 4-phenyl-*ONN*-azoxybenzoate. A solution of 4-phenyl-*ONN*-azoxybenzonitrile (3 g) in anhydrous ether (130 ml) and anhydrous methanol (30 ml) was saturated with hydrogen chloride and stored in the dark for 24 h. Evaporation of the solvent under reduced pressure gave the iminoester hydrochloride (yellow crystals, m.p. 213—215 °C). This was dissolved in 1:1 methanol–water (100 ml), concentrated hydrochloric acid (5 ml) was added, and the solution refluxed for 2 h. On chilling, a yellow solid precipitated. This was recrystallised from ethanol and proved to be pure methyl 4-phenyl-*ONN*-azoxybenzoate, m.p. 139—140 °C, $\delta_C(CDCl_3)$ 166.3 (CO), 147.3 (C-4), 132.0 (C-4′), 130.1 (C-2), 128.9 (C-3′), 125.1 (C-3), 122.4 (C-2′), and 52.2 p.p.m. (CH_3), C-1, C-1′ not observed.

4-Phenyl-*ONN*-azoxybenzoic acid. The above ester (1.0 g) was hydrolysed by refluxing a short time with alcoholic potassium hydroxide. Work-up gave 4-phenyl-*ONN*-azoxybenzoic acid (0.6 g), m.p. 242—244 °C (lit.,[14] 231 °C) (Found: C, 64.6; H, 4.2; N, 11.8. Calc. for $C_{13}H_{16}N_2O_3$: C, 64.5; H, 4.2; N, 11.6%).

4-Phenyl-*NNO*-azoxybenzonitrile. 4-Bromo-1-phenyl-*NNO*-azoxybenzene[16] (1.6 g) was converted into the nitrile by the same method as that used for the *ONN*-derivative, giving pale yellow plates (0.9 g), m.p. 120—122 °C, $\delta_C(CDCl_3)$ 143.5 (C-1), 132.9 (C-3′), 130.6 (C-4), 128.8 (C-3), 125.9 (C-2), 123.2 (C-2′), 117.6 (CN), and 115.2 p.p.m. (C-4′), C-1′ not observed.

4-Phenyl-*NNO*-azoxybenzoic acid. To a stirred solution of 4-phenyl-*NNO*-azoxybenzonitrile (800 mg) in ethanol (20 ml), 30% hydrogen peroxide (1 ml) and 25% sodium hydroxide (0.1 ml) were added and the solution was maintained at 45—50 °C for 2 h. On cooling and acidifying with 5% H_2SO_4, a precipitate was obtained. This was added to a solution of 25% sodium hydroxide (20 ml) in ethanol (50 ml) and the mixture refluxed for 90 min. The residue, after removal of the ethanol under reduced pressure, was acidified and extracted with ether. Evaporation of the ether gave a yellow solid which on crystallisation from ethanol gave yellow needles (550 mg), m.p. 261—263 °C (lit.,[15] 241 °C) (Found: C, 64.4; H, 3.9; N, 11.5%).

(c) 3,5-*Dimethyl*-4-*phenyl*-ONN-*azoxybenzoic acid*. Oxidation of ethyl 3,5-dimethyl-4-phenylazobenzoate by 30% hydrogen peroxide in acetic acid gave a mixture of the two azoxy derivatives in which the desired *ONN*-isomer was the major component (80%). Fractional crystallisation from pentane gave pure ethyl 3,5-dimethyl-4-phenyl-*ONN*-azoxybenzoate as yellow needles, m.p. 79—80 °C, $\delta_C(CDCl_3)$ 166.5 (CO), 146.8 (C-4), 132.4 (C-4′), 130.3 (C-3), 129.4 (C-2), 129.0 (C-3′), 128.8 (C-1), 122.5 (C-2′), 60.9 (CH_2), 17.5 (Me_2), and 14.4 p.p.m. (CH_3), C-1′ not observed. The ester was hydrolysed by potassium hydroxide in ethanol to give 3,5-*dimethyl*-4-*phenyl*-ONN-*azoxybenzoic acid*, m.p. 253—255 °C (Found: C, 66.5; H, 5.2; N, 10.3. $C_{15}H_{14}N_2O_3$ requires C, 66.7; H, 5.2; N, 10.4%).

(d) 3,5-*Dimethyl*-4-*phenyl*-ONN-*azoxyphenyldimethylcarbinyl chloride*. Oxidation of 3,5-dimethyl-4-phenylazophenyldimethylcarbinol by reaction with 3-chloroperbenzoic acid in chloroform at 20 °C for 17 h gave a mixture of the *ONN*- and

NNO-azoxy derivatives in a 4:1 ratio. This mixture was adsorbed onto a silica-coated Chromatotron plate. Elution with 5:1 light petroleum–ether gave a broad band, from the leading part of which was obtained a product that on crystallisation from carbon tetrachloride proved to be of isomerically pure 3,5-*dimethyl*-4-*phenyl*-ONN-*azoxyphenyldimethylcarbinol*, m.p. 108—109 °C, $\delta_C(CDCl_3)$ 147.7 (C-1), 141.4 (C-4), 132.1 (C-4′), 129.7 (C-3), 128.9 (C-3′), 124.3 (C-2), 122.6 (C-2′), 72.4 (COH), 31.7 (Me_2), and 17.9 p.p.m. (3,5-Me_2), C-1′ not observed (Found: C, 71.5; H, 7.1; N, 9.8. $C_{17}H_{20}N_2O_2$ requires C, 71.8; H, 7.1; N, 9.9%). The carbinol was converted into the carbinyl chloride as required for the kinetic studies by the following method.

To a stirred solution of the carbinol (100 mg) in methylene dichloride (5 ml), thionyl chloride (0.3 ml) was added and the solution stirred for 30 min. The solvent was then removed under reduced pressure and the excess of thionyl chloride removed under high vacuum. The purity of the carbinyl chloride was checked by ^1H n.m.r., but the identity was not checked by microanalysis.

(e) 4-*Phenyl*-ONN-*azoxyphenyldimethylcarbinyl chloride*. Oxidation of 4-phenylazophenyldimethylcarbinol gave a mixture of the azoxy isomers, but all attempts to separate them were unsuccessful. Attempted preparation *via* ethyl 4-phenyl-*ONN*-azoxybenzoate also failed when it was found that the inverse addition of an equimolar quantity of methylmagnesium iodide resulted in preferential attack at the azoxy function. However, it was discovered that 4-phenylazoxyacetophenone reacted with the Grignard reagent at the carbonyl carbon. Repeated fractional crystallisations of the isomeric mixture of 4-phenylazoxyacetophenones obtained by oxidation of 4-phenylazoacetophenone gave a pure sample of the *NNO*-isomer and a residue that consisted of a mixture that contained *ca.* 70% of the *ONN*-isomer. Further attempts to enrich this by either fractional crystallisation or chromatography were unsuccessful. Reaction of the *ONN*-enriched mixture with one equivalent of methylmagnesium iodide gave the mixed carbinols in similar proportions. These, when treated with thionyl chloride in methylene dichloride, gave a mixture of carbinyl chlorides, but it was found that when treated with anhydrous hydrogen chloride instead, only the *ONN*-isomer reacted. This product, consisting of a mixture of 4-phenyl-*ONN*-azoxyphenyldimethylcarbinyl chloride and 4-phenyl-*NNO*-azoxyphenyldimethylcarbinol, was used directly in the solvolysis studies, as there was no reason to believe that the presence of the carbinol was in any way likely to affect the results.

p*K and Solvolysis Measurements*.—The methods used have been described previously, and the σ values were calculated by the use of the data for the standards obtained at that time.[7]

Kinetics of Bromination of Azoxybenzene.—The method used was the same as that used previously for azobenzene.[11] The data were obtained in 75% dioxane–water, not 50% as reported earlier.

Acknowledgements

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