Diphenylamines and Quinone Di-imines from Base-catalysed Reactions of 2-(Alkoxyamino)diaryl Sulphones: Evidence against a Nitrene Mechanism

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Summary Reaction of 2-(alkoxyamino)diaryl sulphones with sodium alkoxides at 20° results in loss of alkoxy-groups and furnishes diphenylamine derivatives and quinone di-imines; trapping experiments and comparison with reactions designed to generate *o*-(phenylsulphonyl)-aryl nitrenes indicate that a nitrene mechanism is unlikely.

WE showed earlier[1,2] that reactions of 2-(hydroxyamino)-diaryl sulphones (1; $R^1 = H$) with base yielded azoxy-derivatives in which phenylsulphonyl groups had been replaced by hydrogen or by hydroxy-groups. Mechanisms involving nucleophilic oxygen in the –NHOH group were postulated and it was of interest to extend our studies to *O*-alkyl derivatives. We now report that base-catalysed reactions of 2-(alkoxyamino)diaryl sulphones (1; R^1 = Me or Et) give a new range of products.

It was soon apparent that the alkoxyamino-derivatives were sensitive to alkoxides and could not be prepared in the presence of an excess of base. Slow addition of potassium t-butoxide in t-butyl alcohol to a mixture of 2-hydroxyaminodiaryl sulphones and the requisite alkyl iodide afforded, however, the alkoxyamines (1; R^1 = Me or Et, R^2 = H or Cl) in yields of 45—57%. I.r. absorption at 3200 cm^{-1} indicated that *O*- rather than *N*-alkylation had occurred, and this was confirmed by reduction of the products to the corresponding primary amines.

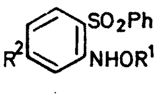
Treatment of 2-(methoxyamino)diphenyl sulphone (1; R^1 = Me, R^2 = H) with sodium methoxide in methanol at 20° or of the ethoxy-derivative (1; R^1 = Et, R^2 = H) with sodium ethoxide in ethanol resulted in the loss of the alkoxy-groups and formation in each case of the diphenylamine derivative (2; $R^1 = R^2$ = H) (35—40%), the azoxy-compound[2] (3; R = H) (18—21%), and 2-nitrodiphenyl sulphone (5—6%). The structure of the diphenylamine was investigated by spectroscopic and chemical methods and confirmed by synthesis.

The reaction was applied also to the substituted sulphones (1; R^2 = Cl), and the corresponding diphenylamine (2; R^1 = Cl, R^2 = H) (35%) was obtained by addition of sodium methoxide to the methoxyamino-derivative (1; R^1 = Me, R^2 = Cl) and to the ethoxyamino-compound (1; R^1 = Et, R^2 = Cl). The structure of the diphenylamine was established by unambiguous synthesis. In the reactions of the chloro-sulphones with base, yellow crystalline products were also isolated. The compound from the methoxyamino-derivative (1; R^1 = Me, R^2 = Cl) had a molecular formula of $C_{20}H_{16}Cl_2N_2O_4S$, M^+ 450, and the presence of a phenylsulphonyl group was indicated by a peak at (M − 141) in the mass spectrum and by i.r. absorption at 1310 and 1160 cm^{-1}. The n.m.r. spectrum showed singlets at τ 5·8 (3H) and 6·36 (3H) attributed to methoxy-groups.

On catalytic reduction, two molecules of hydrogen were absorbed leading to loss of a methoxy-group and formation of the diphenylamine (4). The structure of this compound was established by spectroscopic studies and by synthesis. On the basis of these observations, the yellow compound obtained from the methoxyaminodiaryl sulphone (1; R^1 = Me, R^2 = Cl) was formulated as the quinone di-imine (5; R = Me).

The yellow compound, $C_{21}H_{18}Cl_2N_2O_4S$, obtained from reaction of the ethoxyamino-derivative (1; R^1 = Et, R^2 = Cl) with sodium methoxide was apparently the quinone di-imine (5; R = Et). The n.m.r. spectrum indicated the presence of an ethoxy-group [quartet at τ 5·54 (2H) and triplet at 8·62 (3H)]. The aryl methoxy-groups in the two quinone di-imines clearly arise by displacement of a phenylsulphonyl group by methoxide.

The most striking feature of these alkoxide-catalysed reactions leading to diphenylamines and quinone di-imines is the ready cleavage of N–O bonds; this also occurs with triethylamine as the base, although less readily. A possible mechanism involves formation of nitrenes by α-elimination, and we considered that the aryl nitrene (6), like sulphonyl nitrenes, $RSO_2\ddot{N}$:,[3] might be sufficiently electrophilic to form diphenylamines by addition to an aryl nucleus. Indeed, Abramovitch and Scriven[4] have shown very recently that diphenylamines are formed by thermolysis of aryl azides containing electron-attracting substituents. In order to test the hypothesis, the reaction of the methoxyamino-sulphone (1; R^1 = Me, R^2 = Cl) with sodium methoxide was repeated in the presence of cyclohexene, but the diphenylamine and quinone di-imine were obtained as before and no products resulting from trapping of a nitrene were detected.



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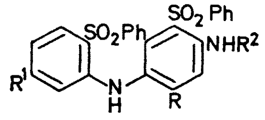

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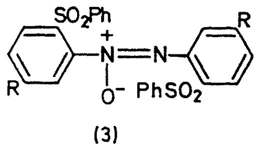

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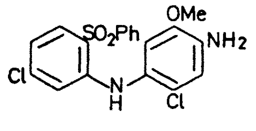

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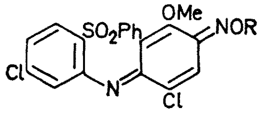

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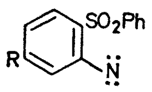

(6)

We have also studied the following two methods of generating the phenylsulphonyl nitrene (6) and compared the products with those obtained from methoxyamino-sulphones (1; R^1 = Me or Et) . (a) Bunyan and Cadogan[5] showed that reaction of triethyl phosphite with nitrosobenzene furnished azoxybenzene (21%), probably *via* addition of phenyl nitrene to a nitroso-group. Application of the reaction to 4-chloro-2-nitrosodiphenyl sulphone in the absence or in the presence of the methoxyamino-compound (1; R^1 = Me, R^2 = Cl) furnished the azoxy-derivative (3; R = Cl) (3—9%) but no diphenylamine or quinone di-imine. (b) The results of Lwowski and Maricich[6] on *N*-sulphonoxyurethans suggested that the nitrene (6) might be generated more readily if the alkoxy-groups in sulphones (1) were replaced by good leaving groups. Accordingly, the hydroxyamino-sulphone (1; R^1 = H, R^2 = Cl) was treated with *p*-bromobenzenesulphonyl chloride and triethylamine and yielded 5,5′-dichloro-2,2′-bisphenylsulphonylazobenzene (16%) and 2-amino-4-chlorodiphenyl sulphone (7%) as the only recognised products. These compounds are the expected products from the sulphonyl nitrene (6; R = Cl) derived from the unstable *p*-bromophenylsulphonyloxyamine (1; R^1 = *p*-$BrC_6H_4SO_2$, R^2 = Cl).

The results indicate that diphenylamines and quinone di-imines are not formed *via* sulphonyl nitrene (6). An alternative mechanism involves nucleophilic displacement of an *N*-methoxy-group to give alkoxyamino-diphenylamines (2; R^2 = OMe or OEt) that could serve as common intermediate for diphenylamines (2; R^2 = H) and quinone di-imines (5). This and other possible routes are under investigation.

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