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FORMATION OF ACCEPTOR SUBSTITUTED PHENYLNITRENES VIA α-ELIMINATION UNDER MILD CONDITIONS

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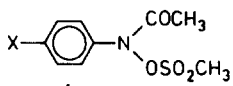
Summary: The acceptor substituted **1a-d** and **2d** react with n-butylamine to give **5**, **6** and **7**. This strongly suggests the intermediate formation of substituted phenylnitrenes via α-elimination.

As part of our studies[1] of model reactions on the carcinogenesis of aromatic amines[2] we investigated the reactions of the p-substituted O-(methylsulfonyl)-phenylhydroxamic acids **1a-d**[3] and of p-nitrophenyl-O-(methylsulfonyl)-hydroxylamine **2d** with n-butylamine. Only with X = NO_2 we were able to isolate besides the more stable hydroxamic acid derivative **1d** the (generally much more labile) hydroxylamine species **2d**.



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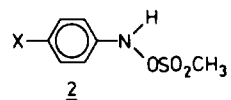

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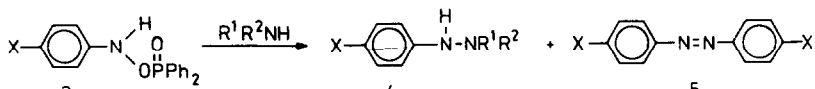
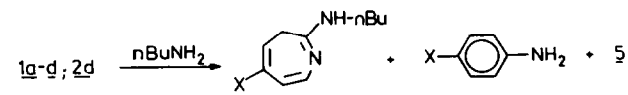
1 **a**: X = CH_3OCO; **b**: X = CH_3CO; **c**: X = CN; **d**: X = NO_2

Since the reactions of the related O-(diphenylphosphinyl)phenylhydroxylamines **3b-d**[1b] and of others[1a,b] with primary and secondary amines, respectively, gave hydrazines **4** and symmetrical azo compounds **5** we anticipated these products also from the reactions of **1a-d** and **2d** with amines.



3 **4** **5**

However, no hydrazines **4** have been observed in the reactions of **1a-d** and **2d** with n-butylamine. Instead, we isolated only the 3-H-azepines **6** and the anilines **7** together with the symmetrical azo compounds **5**.



6 **7**

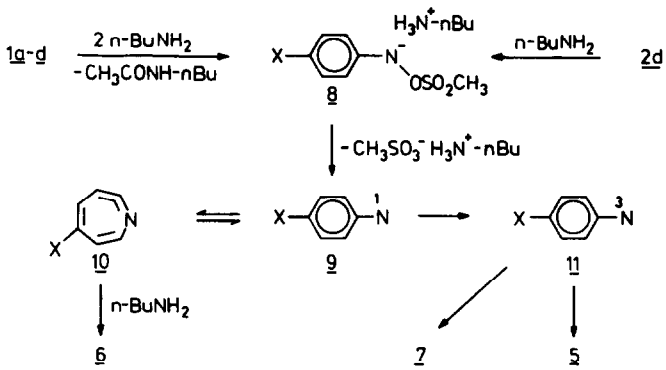
The thermal conditions of the 100 mM reactions of **1a-d** and **2d**, respectively, in n-butylamine as the solvent, and the yields of **6**, **7** and **5** are given in Table 1.

Table 1. Yields of **6**, **7** and **5** in the reactions of **1a-d** and **2d**, respectively, with n-butylamine at various temperatures[4]

1 or 2	T[°]	azepines 6 [%]	anilines 7 [%]	azo compounds 5 [%]
1a	20	93	-	-
1b	20	8	44	25
	78	47	15	20
1c	-30	9	49	23
	20	30	3	67
	78	51	2	44
1d	-30	-	90	7
	78	-	94	2
2d	-30	-	60	30
	78	-	15	22[a]

[a] In this reaction tar is formed, too.

These products, the 3-H-azepines **6**, anilines **7** and symmetrical azo compounds **5**, of course, are strongly indicative of arylnitrene intermediates as observed in a plethora of investigations on the photolysis and thermolysis of arylazides in the presence of amines[5]. In the present case the reactions should start via deacetylation of **1a-d**[6], and deprotonation of **2d**, respectively, to give the nitrenoids **8**. In contrast to the "nitrenoids" formed on deprotonation of **3** (see the preceding communication) the nitrenoids **8** should be much more prone to α-elimination because $CH_3SO_3^-$ is a much better leaving group than $Ph_2PO_2^-$. α-Elimination of $CH_3SO_3^-H_3N^+$-nBu thus should lead to the singlet nitrenes **9**.



Singlet nitrenes like **9** are known to be in equilibrium with the corresponding dehydroazepines **10** the formation of which is generally more favorable at higher temperatures[5,7]; the dehydroazepines **10** are trapped by amines to give

the 3-H-azepines[5,8] **6**. This pathway competes with the intersystem crossing reaction which transforms the singlet nitrenes **9** into the triplet nitrenes **11** from which the anilines **7** and the symmetrical azo compounds **5** are formed. The anilines **7** could either result from H-abstraction[5] or via electron transfer reactions[9]. The formation of the azo compounds **5** from nitrenes is "not completely understood"[5b].

The following details of Table 1 are especially supportive for the intermediate formation of the singlet **9** and the triplet nitrenes **11**, respectively:

1. In the reactions of **1b** and **1c** the amounts of 3-H-azepines **6b** and **6c**, respectively, increase as the temperature is raised which is in agreement with the above mentioned general observations[5,7].
2. The reaction of the p-methoxycarbonyl substituted **1a** with n-butylamine at 20°C leads exclusively to the 3-H-azepine **6a**; neither aniline **7a** nor azo compound **5a** have been detected. This result compares well with that of the photolysis of p-dimethylamidophenyl azide if one accepts similar substituent effects in both cases: In the presence of diethylamine at 20°C the corresponding 3-H-azepine is similarly formed in "nearly quantitative yield"[10]. Thus, in both cases the same intermediates, that is the singlet nitrenes, should dominate.
3. Neither in the photochemical reactions of p-nitrophenylazide in the presence of amines nor in the reactions of **1d** or **2d** with n-butylamine 3-H-azepines like **6d** have been observed. Because of the comparatively fast intersytem crossing reaction only the products formed from the triplet nitrene **11d** - **7d** and **5d** - are found in both cases[5,11,12]. It is worth mentioning that because of the fast formation of the triplet nitrene **11d** p-nitrophenylazide is widely used as a photolabelling agent in biological macromolecules[13]. The results reported in this work suggest a similar use for **1d** and **2d**.

Finally, it should be mentioned that arylnitrenes have been prepared before by α-elimination or related reactions, as, e.g., in the deoxygenation of arylnitro or arylnitroso compounds with phosphorous(III) reagents[14]. The formation of nitrene intermediates occurs, however, mostly at temperatures >100°C as this is the case in the thermolysis of N,O-disilylated phenylhydroxylamines[15]. In the reaction of N-chloro aniline with n-butyllithium at -100°C a nitrene intermediate apparently has also been formed[16,17].

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1. a. G. Boche, R.H. Sommerlade, F. Bosold, Angew. Chem. 98, 563 (1986); Angew. Chem. Int. Ed. Engl. 25, 562 (1986); b. G. Boche, C. Meier, W. Kleemiß, preceding communication; c. G. Boche, F. Bosold, S. Schröder, Angew. Chem. , submitted.
2. See ref. 5 in the preceding communication.