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HYDRAZINES AND AZO COMPOUNDS FROM O-DIPHENYLPHOSPHINOYL ARYLHYDROXYLAMINES

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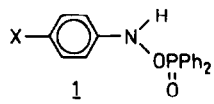
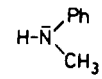
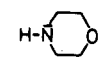
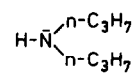
Summary: The reactions of the O-diphenylphosphinoylhydroxylamines **1a-d** with the amines **2-4** lead to the hydrazines **5** and the symmetrical azo compounds **6**. **5** are formed via electrophilic amination; the azo compounds **6** do not result from the corresponding phenylnitrene intermediates.

In the course of our investigations of model reactions on the carcinogenesis of aromatic amines[1] we studied the behaviour of the acceptor substituted O-diphenylphosphinoyl hydroxylamines **1a-d**[2] towards N-methylaniline **2**, morpholine **3** and di-n-propyl amine **4**, respectively.



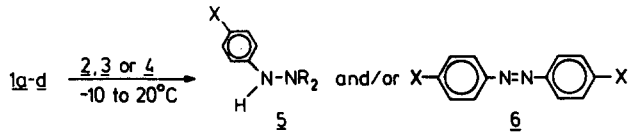
1

1	X	σ_p^-
a:	$COCH_3$	0.84
b:	CN	0.88
c:	SO_2CH_3	0.98
d:	NO_2	1.24

	Amines	pk_B
2		9.15
3		5.70
4		3.09

The acceptor qualities of the substituents X (σ_p^- [3]) increase from **1a** to **1d**, and the basicities of the amines (pk_B[4]) from **2** to **4**. The reactions which were performed employing 1 mmol **1** and 2.5 mmol amine in 25 ml THF at -10°C led only to the hydrazines **5**[2] and the symmetrical azo compounds **6**[2]. The yields are listed in Table 1.

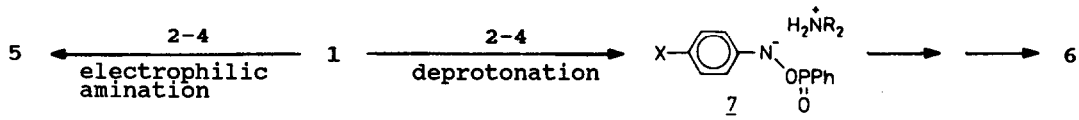
The formation of the hydrazines **5** models the electrophilic amination of bionucleophiles by the "ultimate carcinogen" of an aromatic amine[5]. The decreasing yields of the hydrazines **5** together with the increasing amounts of the azo compounds **6** on going from **1a** to **1d** and **2** to **4**, respectively, suggest a competition between the nucleophilic attack of the amines **2-4** at the electrophilic nitrogen atoms of **1a-d** to give the hydrazines **5**, and a reaction channel starting with the deprotonation of **1a-d** and finally leading to the symmetrical azo compounds **6**.



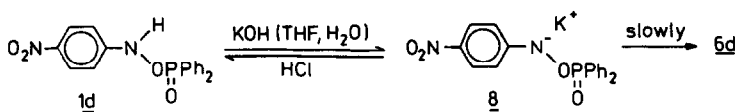
5 6

Table 1. Yields of 5 and/or 6 in the reactions of **1a-d** with **2**, **3** and **4**, respectively.

1	2, 3 or 4	5[%]	6[%]	1	2, 3 or 4	5[%]	6[%]
a	2	71	-	c	2	77	-
	3	23	70		3	15	80
	4	-	91		4	-	92
b	2	75	-	d	2	95	-
	3	20	70		3	8	80
	4	-	93		4	-	90

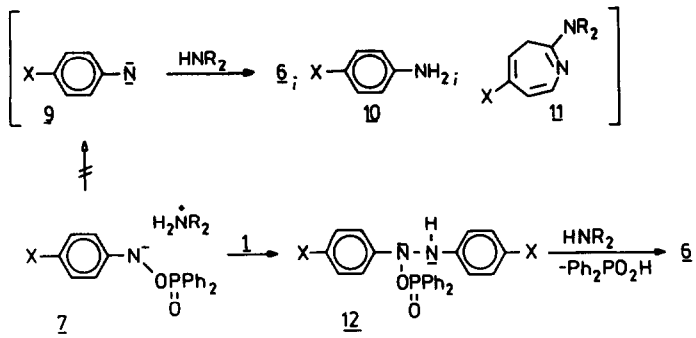


Deprotonation of **1a-d** with amines should give the ammonium salts **7**. The formation of **7** is supported by the reaction of the p-nitro-substituted yellow (λ_{max} = 335 nm) **1d** with potassium hydroxide in THF/H_2O to give the corresponding dark red (λ_{max} = 485 nm) K^+ salt **8**, which on protonation with HCl leads back to **1d**. The facile formation and the stability of this salt, of course, are due to the excellent stabilization of the negative charge by the p-nitro substituent[6].



What is the mechanism of the formation of the azo compounds **6**? One could imagine that the "nitrenoids" **7** transform via α-elimination of $Ph_2PO_2^-$ $H_2N^+R_2$ into the substituted phenylnitrenes **9**. Aryl nitrenes are known from photochemical and thermal reactions of aryl azides to give symmetrical azo compounds of the type[7] **6**. The formation of **6** from arylnitrenes such as **9**, however, is generally accompanied by the formation of the corresponding anilines **10** and 3-H-azepines[7] **11**, which are <u>not</u> observed in the reactions of **1**

with the amines **2-4**. Thus, the "nitrenoids" **7** under the reaction conditions do not transform into the nitrenes **9**. That substituted phenylnitrenes of the type **9** indeed are formed by α-elimination under mild conditions from nitrenoids if a better leaving group ($CH_3SO_3^-$) is involved, is shown in ref. 8 (following communication).



Concerning the formation of the azo compounds **6** it is therefore assumed that the "nitrenoids" **7** are aminated[9] by the aminating reagents **1** to give the intermediates **12** which in the presence of the amines **2-4** should easily eliminate[15] Ph_2PO_2H to give **6**.

The formation of symmetrical aryl azo compounds in reactions suggesting the intermediate formation of arylnitrenes[16] thus not necessarily requires these intermediates.

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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, F. Bosold, S. Schröder, Angew. Chem., submitted.
2. **1a-d** as well as the hydrazines **5** and the azo compounds **6** are fully characterized by elementary analyses and 300 MHz nmr spectra. Details will be reported in the forthcoming full paper.
3. L.A. Cohn, W.M. Jones, J. Am. Chem. Soc. 85, 3397, 3402 (1963), cited in D.J. Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York, London, 1965, p. 58.
4. R.T. Morrison, R.N. Boyd, Organic Chemistry, Second Edition, Allyn & Bacon Inc., Boston, 1966, p. 720, 743.
5. See, e.g., a. J.A. Miller, Cancer Res. 30, 559 (1970); b. E. Kriek, Biochim. Biophys. Acta 335, 177 (1974); c. E. Miller, Cancer Res. 38, 1479 (1978); d. E.C. Miller, J.A. Miller, Cancer (Amsterdam) 47, 2327 (1981).
6. According to the UV/VIS spectrum **1d** is completely transformed into **8** at pH9. On standing at room temperature the potassium salt **8** slowly (ca.1 h) transforms into the azo compound **6d**.