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THE BENZIDINE-LIKE REARRANGEMENT OF N,O-DIARYLHYDROXYLAMINES

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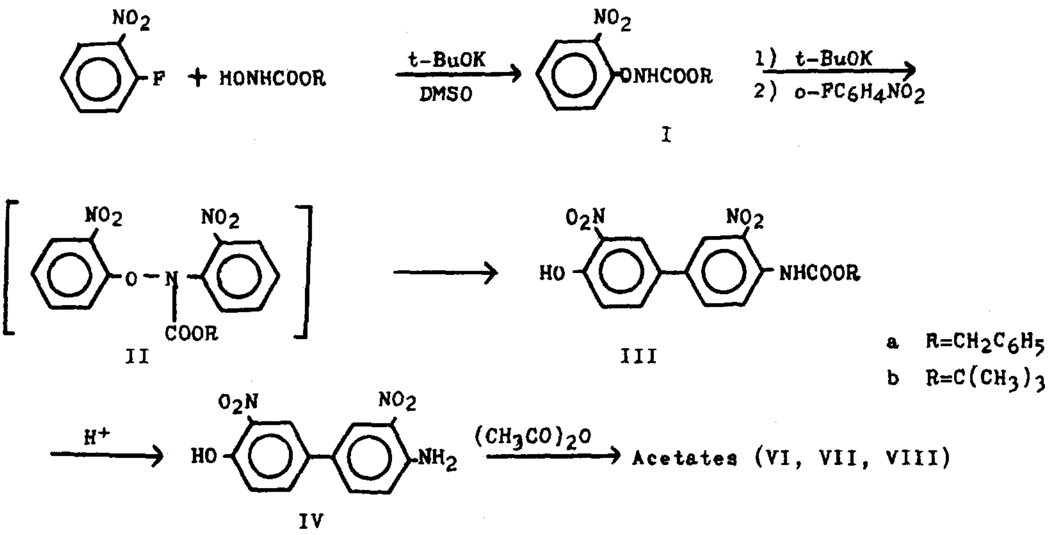
The prediction that N,O-diarylhydroxylamines should rearrange in the same manner as hydrazobenzenes was first made by Dewar (1) in 1963, but has not been demonstrated due to the unavailability of such compounds. Cox and Dunn (2) reported one case of biphenyl formation, for which a reasonable mechanism involves this type of rearrangement. We now wish to report a series of reactions which demonstrates the occurrence of the rearrangement and throws some light on its mechanism.

We have previously shown (3) that N-hydroxycarbamates react with nitrohalobenzenes to yield the corresponding N-phenoxycarbamates which could be transformedto O-phenylhydroxylamines. Now we tried to utilized the diarylation of N-hydroxycarbamates as a route to N,O-diarylhydroxylamines. For this purpose benzyl N-(o-nitrophenoxy)carbamate (Ia, m.p. 96°, prepared from benzyl N-hydroxycarbamate and o-nitrofluorobenzene) was treated with base and then with a secondequivalent of o-nitrofluorobenzen . The product (20%, m.p. 185°) had the right elemental analysis and molecular weight ($C_{20}H_{15}N_3O_7$) of the expected compound.IIa. However its infrared spectrum showed peaks at 3340 and 3250cm^{-1} (NH and OH respectively). Removal of the carbamate group (HBr in acetic acid) yielded the unprotected compound (m.p.295°,$C_{12}H_{19}N_3O_5$) which showed in the ir NH_2(3490, 3370cm^{-1}) and OH (3240cm^{-1}) absorptions. These data are inconsistent with the structure IIa and it appears that IIa rearranged spontaneously to the biphenyl IIIa, which then yielded 4-amino-4-hydroxy-3,3'-dinitrobiphenyl (IV). The same reaction sequence was observed starting with t-butyl N-hydroxycarbamate. Thus the reaction of Ib (m.p. 90-91°) with o-nitrofluorobenzene yielded the biphenyl IIIb (m.p. 194°) which was transformed into IV on treatment with trifluoroacetic acid.



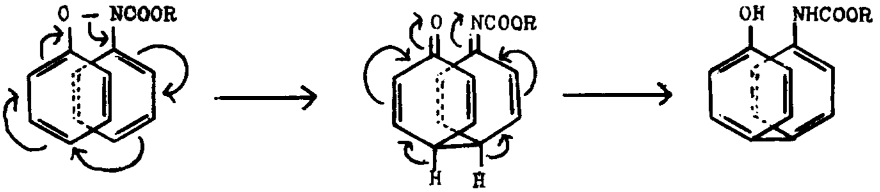
The NMR spectra are also in accord with structures III and IV. The spectrum of IV showed (DMSO-d_6) two doublets at δ 7.2 and 7.3 (1H each, H-5 and H-5'), two doublets of doublets at δ 7.8 and 7.9 (1H each, H-6 and H-6') and two doublets at δ 8.1 and 8.2 (1H each, H-2 and H-2'). $J_{2,6}=J_{2',6'}=2$Hz, $J_{5,6}=J_{5',6'}=8$Hz. The UV spectra also indicate the presence of the biphenyl linkage. Compound IV (in ethanol) absorbed at 273 nm ($\log\epsilon$ = 4.48) 407 (3.71).

A further confirmation was obtained from acetylation reactions. Treatment of III with acetic anhydride yielded a monacetate (V, m.p. 133°) with two carbonyl absorption at 1733 cm^{-1} (carbamate) and 1770 cm^{-1} (ester). Acetylation of IV yielded a mixture of three acetates. Their spectra are given in the table and confirm the presence of the hydroxy and the amino groups.

IR spectra

No.	compound	m.p.(°C)	OH	NH	C=O(ester)	C=O(amide)
VI	monoacetate	243-245	3240	3370	-	1708
VII	diacetate	242-243	-	3365	1762	1717
VIII	triacetate	169-170	-	-	1775	1740,1705

The formation of a biphenyl from I and o-nitrofluorobenzene can be rationalized by postulating the initial formation of the N,O-diphenylhydroxylamine II which rearranges to III by the following mechanism;



In contrast with the benzidine rearrangement of hydrazobenzenes, which requires protonation of both nitrogens (4), our reaction proceeds in non-acidic medium. The driving forces for the reaction are probably the high polarization of the N–O bond, assisted in this case by the electron withdrawing carbonyl group, and the big difference in bond energies between the cleaved N–O bond and the formed C–C bond. This difference is the basis of some other rearrangements recently reported by us (5-7) and by others(8-10).

Work is now in progress on rearrangements of p-substituted substances. Preliminary experiments showed the formation of both diphenyline and o-semidine-type products. Detailed results will be reported shortly.

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