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OXYGEN-18 TRACER STUDY OF THE REARRANGEMENT OF O-BENZOYL-N-(p-TOLUENESULFONYL)ARYLHYDROXYLAMINES

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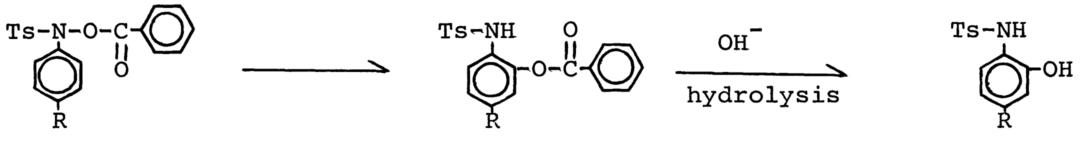
O-Benzoyl-N-(p-toluenesulfonyl)arylhydroxylamines (I) were found to rearrange thermally giving o-acyloxy-p-toluenesulfonanilides (II) in quantitative yields. An intramolecular concerted cyclic process has been suggested for the rearrangement on the basis of ^{18}O tracer study. The solvent and the substituent effects on the mechanism of this novel 1,3-acyloxy migration were also examined.

Several modes of 1,3-migration of acyloxy group, namely, oxygen-bridged ion-pair,1) intimate ion-pair,2,3) solvent-separated ion-pair4) and dissociated ion-pair,5) have been suggested for the rearrangements of heteroaromatic and aromatic amine oxides with acylating agents, on the basis of ^{18}O tracer experiments.

During the study of the nucleophilic displacement reaction on nitrogen atom with acyloxy group as leaving group,6) we have found that O-benzoyl-N-(p-toluenesulfonyl)-arylhydroxylamines (I) rearrange thermally to give o-acyloxy-p-toluenesulfonanilides (II) in quantitative yields. The usual ^{18}O tracer study indicates the reaction to proceed via a rather exclusive cyclic rearrangement.

In this communication, we wish to present the ^{18}O tracer data to verify the mechanism of this novel rearrangement.

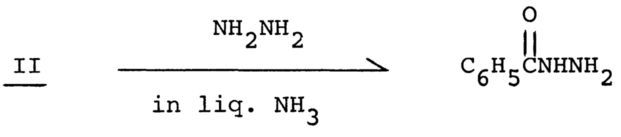


I   II   III

Ts = p-$CH_3C_6H_4SO_2$-   R = CH_3, H, Cl

I was heated in dimethyl sulfoxide (DMSO) or in other solvent at 110-120°C under nitrogen atmosphere until completion of the rearrangement. The structure of the product II was confirmed by comparison of the physical properties of III which was obtained upon alkaline hydrolysis of II, with those of the authentic sample.

Oxygen-18 tracer experiment was carried out with carbonyl-^{18}O labeled I to investigate the effects of the sulfonyl group and the substituent R on the aniline ring on the 1,3-migration of the benzoyloxy group. The isotope analysis of the starting material was done with both benzamide prepared from the starting ^{18}O-labeled benzoyl chloride and benzhydrazide IV formed by hydrazinolysis of the labeled I. Product II was cleaved by treating it with hydrazine, in the same procedure employed for the hydrazinolysis of I to give IV which was subjected to the ^{18}O analysis in order to know ^{18}O distribution in the product. These results are collected in the Table.



$$\mathrm{II} \xrightarrow[\text{in liq. } NH_3]{NH_2NH_2} C_6H_5\overset{\overset{O}{\|}}{C}NHNH_2$$

IV

Inspection of the result suggests that the isotope labeling in the carbonyl oxygen of the starting material I was achieved without any oxygen scrambling. (line 1 and 2) The same data also show that there was no oxygen exchange reaction during the hydrazine cleavage of II. Since there are no possibilities of oxygen exchange reactions both in the migration and the hydrazinolysis, comparison of the isotope contents of those hydrazides IV obtained from I and II clearly indicates the isotope distribution in the carbonyl and phenolic oxygens of the product II.

The ^{18}O amount of the hydrazide IV, obtained from the product II, appeared to be almost natural regardless of the nature of the solvent used. This observation suggests strongly the mechanism of the rearrangement to involve an intramolecular concerted cyclic migration.

The similar cyclic process was once deemed widely to account for many 1,3-migrations of acyloxy groups in heterolytic rearrangements.7) Detailed studies with the use of ^{18}O tracer technique on these rearrangements, however, ruled out such a mechanism8) except for the Cope-like rearrangement of 2-butenyl trifluoroacetate in gas phase.9)

Uneven distribution of ^{18}O in the resulting ester, in which the etheral oxygen

Table. ^{18}O Analytical Result of the Thermal Rearrangement of I at 110-120°C.

Compound	Substituent R	Solvent	^{18}O excess atom %
$PhCONH_2$ a)	-----	-----	1.31
$PhCONHNH_2$ b)	H	-----	1.31
$PhCONHNH_2$ c)	H	DMSO	0.02
	Cl	DMSO	0.03
	CH_3	DMSO	0.07
	H	Benzene	0.03
	H	$ClCH_2CH_2Cl$	0.04
	H	CH_3CN	0.03

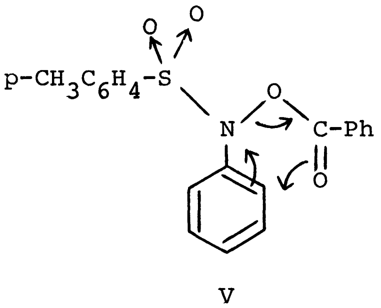
a) derived from PhCOCl, used for the preparation of I.

b) obtained from the reaction of I with NH_2NH_2 in liq. NH_3.

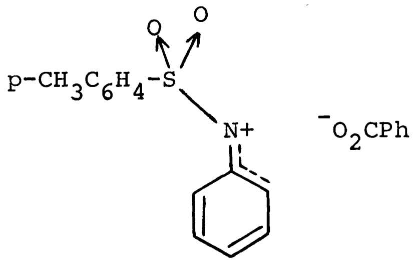
c) derived from II with the given R which was obtained by thermal rearrangement of I in the given solvent.

picked up more ^{18}O than that of carbonyl, was also observed in the rearrangement of 2-picoline and quinaldine N-oxides with the labeled acetic anhydride and ascribed to the conformational preference of the intermediate, anhydrobase.[10)]

Here again, due to the steric and electronic repulsions of the oxygens of the sulfonyl and the carbonyl groups, the rearrangement of I would undergo from the favorable conformation V, presumably via the attack of the carbonyl oxygen on the ortho-carbon of the aniline ring.



V



VI

Another factor to rationalize the rather exclusive cyclic mechanism is the strong electron withdrawing nature of the sulfonyl group attached to the nitrogen atom to suppress the heterolytic cleavage of the N-O bond and favor the internal nucleophilic attack of carbonyl oxygen on the ortho-carbon. Thus, the stepwise mechanism involving the intermediate VI would be very unfavorable.

Stabilizing the anilino cation intermediate VI, however, would increase the contribution of the ion-pair mechanism via VI. In fact, the introduction of an electron-releasing p-methyl group which is known to stabilize anilino cation 11) resulted in a small, but partial (ca. 10%) scrambling of ^{18}O in the resulting ester (line 5 of the Table).

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