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Tertiary Amine *N*-Oxide XXXIII. Reaction of *α*,*N*-Diphenylnitrone with Acylating Reagents

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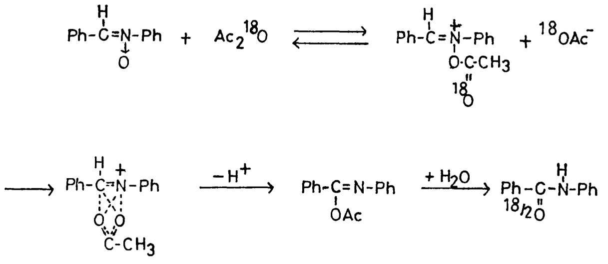
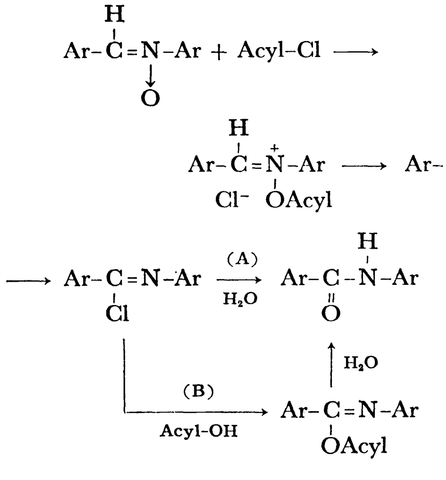
In the preceding paper of this series,[1] it was proposed on the ground of oxygen-^{18}O tracer experiments and kinetic studies that the mechanism of the reaction of aldonitrone with acetic anhydride cannot be represented by the intramolecular cyclic rearrangement alone as suggested by Umesawa,[2] but by the intramolecular rearrangement in which both the cyclic and sliding migrations of the acetoxy group take place concomitantly:



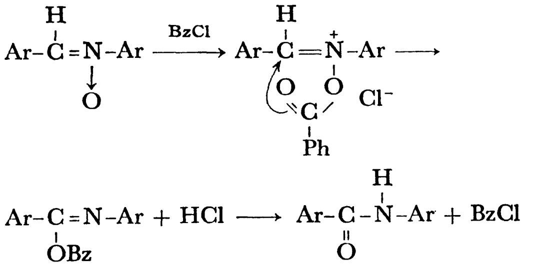
Krohenke[3] suggested that the rearrangement reaction of aldonitrone to amide proceeded *via* addition-elimination. According to his mechanism the reaction of aldonitrones with benzoyl chloride, benzenesulfonyl chloride, and phosphoryl chloride could be written as follows.



(2A)

(2B)

It was observed[2] that even less than one mol equivalent of acyl halide is sufficient to complete the reaction, and that in the reaction system there is not enough water to hydrolyze either the iminochloride or the acyloxyimine. Umesawa ruled out the two possibilities (2A and 2B) and postulated the following intramolecular cyclic rearrangement mechanism taking benzoyl chloride as an example.



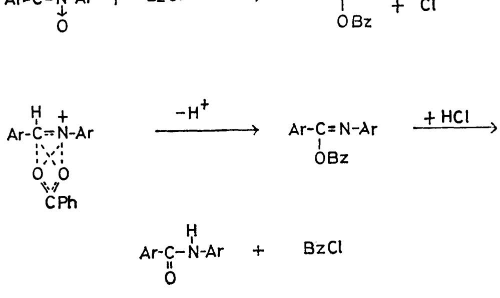
(3)

There are still controversies concerning the mechanistic interpretation of these rearrangement reactions.

In order to disclose the mechanistic picture of these reactions, we carried out ^{18}O-tracer experiments for the reactions of α,*N*-diphenylnitrone with benzoyl chloride, benzenesulfonyl chloride, and phosphoryl chloride enriched with excess ^{18}O.

Mechanism (3) would require the benzanilide to be completely scrambled with ^{18}O-distribution of all the oxygens incubated into the system when uniformly ^{18}O-labeled acyl halide is used, because, when the mechanism is operative the benzoyl chloride or other halides would be used repeatedly. Results of ^{18}O-analysis are given in Table 1. We see that the use of a greater amount of benzoyl chloride results in increasing incorporation of oxygen-^{18}O in benzanilide. The results are in line with the fact that benzoyl chloride in the system is used repeatedly, where the oxygen-^{18}O content in benzoyl chloride is diluted gradually with natural oxygen originated from the unlabeled nitrone.

Since benzoyl chloride can be recovered without decomposition, this reaction take place satisfactorily with only a catalytic amount of benzoyl chloride and affords benzanilide even when water is not present in the reaction mixture. Thus, the reaction likely proceeds through the initial formation of adduct and subsequent intramolecular cyclic or sliding transition state, as in the case for the reaction with acetic anhydride,[1] to give the **C**-benzoyloxyimine which is then attacked by chloride ion, rather than the cyclic rearrangement suggested by Umesawa.



(Successively used) (4)

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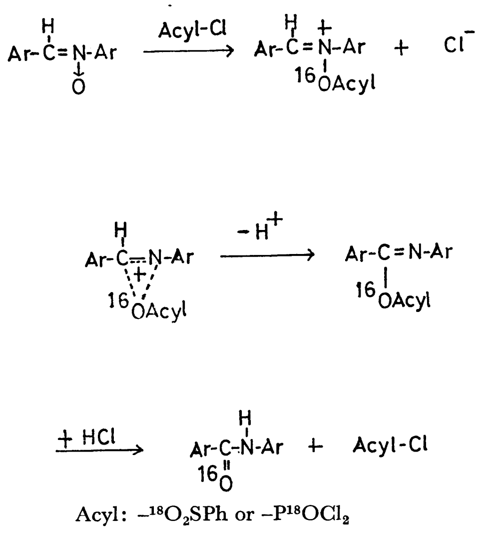
1) S. Tamagaki and S. Oae, *Tetrahedron*, **26**, 1795 (1970).
2) B. Umesawa, *Chem. Pharm. Bull.*, (Tokyo), **8**, 697, 967 (1960).
3) F. Krohenke, *Ann. Chem.*, **604**, 203 (1957).

Table 1. ^{18}O-analytical data for reaction of α,*N*-diphenylnitrone with various chlorides

Chloride	Solvent	Mole ratio, $\frac{\text{(chloride)}}{\text{(nitrone)}}$	^{18}O-excess atom %					
			chloride (used)	benzanilide				
				exptl.	theoretically calcd			
					a)	b)	c)	d)
BzCl	none	1.0	1.33	0.64	0.67	1.33	0	0.67
	$CHCl_3$	1.0	1.33	0.65	0.67	1.33	0	0.67
	$CHCl_3$	3.75	1.38	1.04	1.07	1.38	0	0.69
$C_6H_5SO_2Cl$	$CHCl_3$	1.0	1.00	0.01	0.50	1.00	0	0.50
	$CHCl_3$	1.0	1.00	0.00	0.50	1.00	0	0.50
$POCl_3$	$CHCl_3$	1.0	1.33	0.09	0.67	1.33	0	0.67

a) Chlorides were repeatedly used during the reaction.
b) Based on intramolecular cyclic mechanism
c) Based on intramolecular sliding mechanism
d) Based on scrambling mechanism

The other acyl chlorides, such as benzenesulfonyl and phosphoryl chlorides were treated in a similar way with α,*N*-diphenylnitrone. Data of ^{18}O-analysis show that the ^{18}O-results are not incompatible with all the previous mechanisms. The benzanilide obtained was found to contain no excess oxygen-18. Thus, the most reasonable mechanism for these reactions appears to involve the formation of the initial acyl adduct and the subsequent intramolecular sliding shift with no scrambling of the oxygens in the acyloxy group.



Acyl: $-^{18}O_2SPh$ or $-P^{18}OCl_2$

Experimental

Reaction with Benzoyl Chloride. To 3.0 g of α,*N*-diphenylnitrone without solvent or in chloroform, 2.14 g of benzoyl chloride was added portionwise under ice-cooling. The reaction mixture was then heated on a boiling water bath for 15 min. The mixture was cooled to room temperature and then solidified. The solids obtained were recrystallyzed from benzene or benzene-hexane.

This was identified as benzanilide by mixed melting point with the authentic sample, mp 163—164°C (lit, 163°C).

The yield was quantitative.

Reaction with Benzenesulfonyl Chloride. To a solution of 2.56 g α,*N*-diphenylnitrone in 7 cc of $CHCl_3$, 2.27 g of benzenesulfonyl chloride was added carefully.

The whole mixture was refluxed on a boiling water bath for 15 min. After it was cooled and an aqueous sodium hydrogen carbonate solution was added, the aqueous layer was extracted with chloroform. The solvent was evaporated to dryness. The residue was chromatographed on alumina eluted with benzene.

First elution product of pale yellow crystals, mp 155°C was recrystallized from benzene-hexane. Yield: 0.51 g(20%)

Reaction with Phosphoryl Chloride. To a solution of 3.20 g of α,*N*-diphenylnitrone in chloroform, 2.50 g of phosphoryl chloride was added. The column chromatographic treatment gave benzanilide, yield 6.5%.