Tetrahedron Letters No. 24, pp 2103 - 2104, 1977. Pergamon Press. Printed in Great Britain.

NO OXYGEN EXCHANGE IN ALKALINE HYDROLYSIS OF n-HEXYL NITRITE

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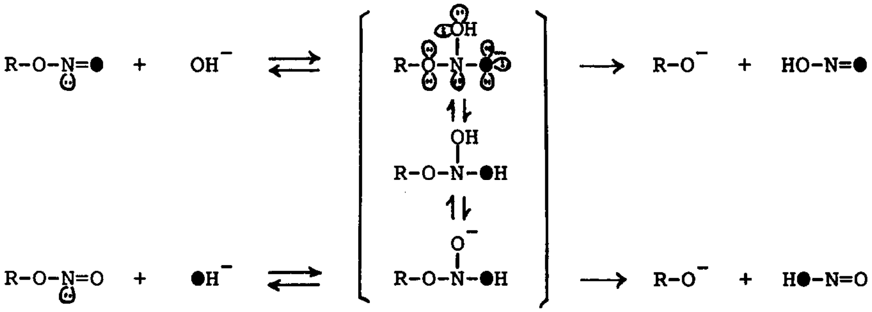
(Received in Japan 14 March 1977; received in UK for publication 5 May 1977)

Unlike numerous studies on nucleophilic substitution on sp^2 hybridized carbon, few systematic investigations on nucleophilic substitution on sp^2 hybridized trivalent nitrogen have been known.[1)] As a preliminary attempt, an alkaline hydrolysis of n-hexyl nitrite has been taken as a model for our systematic investigation on the nucleophilic substitution on sp^2 nitrogen. The addition-elimination mechanism for the alkaline hydrolyses of carboxylates was well established by Bender by means of ^{18}O-tracer.[2)] Recently, Kobayashi reported that a substantial amount of ^{18}O-label in OH^- is incorporated into nitroso oxygen of i-amyl nitrite after partial alkaline hydrolysis in DMSO-$H_2{}^{18}O$ and explained the result by Bender's addition-elimination mechanism.[3)] In our long experience of dealing ^{18}O-tracer experiments, however, we frequently encountered that accurate results could only be achieved when the original organic compounds are labeled with ^{18}O but not in the case when ^{18}O-enriched aqueous media such as ^{18}O-enriched acids and OH^- are used as the only ^{18}O-labeled components.

Addition-Elimination Mechanism



Thus, nitroso-^{18}O-labeled n-hexyl nitrite(1.336 atm %) was synthesized by treating an ether solution of n-hexyl alcohol with ^{18}O-enriched nitrous acid solution which was prepared by treating sodium nitrite with ^{18}O-enriched water$^{4)}$ and hydrolyzed in 61 % dioxane-water in several evacuated tubes ($[\text{nitrite}]_\circ$ = 0.06 M, $[\text{OH}^-]_\circ$ = 0.09 M) set in a thermostated bath from time to time. Since n-hexyl nitrite is unstable liquid and the purification of it is very difficult, the nitrite recovered at several time intervals was converted each time to nice crystalline dicyclohexyl-N-nitrosamine by treating with dicyclohexylamine. There is no loss of original ^{18}O-label in the nitroso group during the conversion of the nitrite to the nitrosamine. Then the nitrosamine was subjected to the routin ^{18}O-analysis.5) In any of several runs no oxygen exchange between n-hexyl nitrite and OH$^-$ was observed during the alkaline hydrolysis even up to 80 % completion of the reaction at both 45.0° and 55.1°C. Under the same conditions, the oxygen exchange was observed in the reaction of benzoates.2)

When we look at the tetrahedral intermediate, that of the nitrite is expected to be substantially less stable than that of the ester, due mainly to the repulsion between the lone pairs on the nitrogen and those on three vicinal oxygens, while there is no such repulsion in the tetrahedral addition intermediate of the carboxylate. Thus, the life time of the former would be much more shorter than the latter and not long enough for the proton transfer within the tetrahedral intermediate which is suggested to be very important for the oxygen exchange by Bender.2)

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