

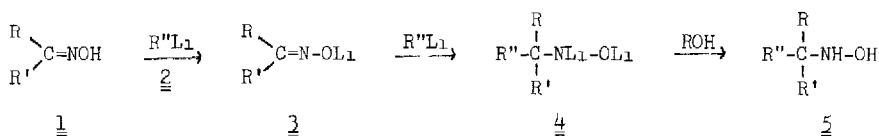
REACTIONS OF OXIMES WITH ORGANOLITHIUM COMPOUNDS, SYNTHESIS OF HYDROXYLAMINES

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Reactions of organolithium compounds and oximes can furnish hydroxylamines. Several successful additions are listed in the Table. Reactions generally were carried out at ambient tem-



perature with an organolithium compound and oxime in a molar ratio of 3:1 or 4:1. The solvent was hexane for reactions with *n*-butyllithium, 70:30 benzene:ether (v/v) for reactions with phenyllithium, and ether for reactions with methyllithium. Reactions were quenched with a small amount

Table. Preparation of Hydroxylamines from Oximes and Organolithium Compounds.

Oxime (<u>1</u>)	Organolithium Compound (<u>2</u>)	Hydroxylamine (<u>5</u>)	
		isolated yield (%)	mp or bp (°C)
benzophenone oxime	CH ₃ CH ₂ CH ₂ CH ₂ Li	63 ^{a, b}	bp 148-152 (0.3 torr)
benzaldehyde oxime	PhLi	63	mp 72-74 (lit ¹ 76)
" "	CH ₃ CH ₂ CH ₂ CH ₂ Li	46	mp 67.5-68.5
<i>p</i> -anisaldehyde oxime	"	40	mp 69-70
<i>trans</i> -cinnamaldehyde oxime	"	55 ^c	mp 87.5-89
camphor oxime	"	20 ^d	bp 90-100 (1.0 torr)
acetone oxime	"	17	bp 35-37 (0.10 torr)
butanal oxime	PhLi	20	mp 61-62
" "	CH ₃ Li	46 ^a	mp 54-55
" "	CH ₃ CH ₂ CH ₂ CH ₂ Li	36 ^a	bp 80-84 (0.1 torr) mp 32-33

^a Worked up without water.^b When worked up with water, 1,1-diphenyl-1-pentanol was isolated.^c Product of 1,2-addition.^d Reaction carried out at reflux temperature. The stereochemistry

of the product is unknown.

of methanol, followed either by addition of water and extraction with ether or by addition of ether and filtration to remove undissolved materials. The reactions were run on a small scale (typically 0.01-0.03 mole of oxime) and reaction conditions and workup procedures probably were not optimal, consequently, higher isolated yields certainly can be achieved in most of these reactions.

Hydroxylamines were not always observed. For example, camphor and benzophenone oximes were recovered in good yields from reactions with methylolithium or phenyllithium, even at reflux temperatures. The contrast to the successful isolation of addition products with *n*-butyllithium may be due to the inability of the less reactive methylolithium and phenyllithium to add to relatively hindered oximes. Acetophenone oxime was recovered from a reaction with *n*-butyllithium. The failure of this reaction probably was due to metalation of the methyl group (α -deuterioacetophenone oxime was isolated on quenching with D_2O), as observed earlier by Hauser for reactions in tetrahydrofuran.²

In other reactions, some hydroxylamine appeared to be formed but was accompanied by significant amounts of other compounds. For example, the crude product obtained from reaction of *t*-butyllithium and benzaldehyde oxime exhibited proton nmr absorptions attributable to the expected hydroxylamine.³ However, other compounds were present, and phenyl *t*-butyl ketone and the corresponding imine actually were isolated. In a reaction under more vigorous conditions than used for the reaction reported in Table 1, benzaldehyde oxime and *n*-butyllithium gave a more complex reaction mixture which included *trans*-1-phenyl-1-pentene, *n*-butyl phenyl ketone, and 5-(*N*-phenylamino)nonane. In these reactions, it is probable that precursor 4 of the hydroxylamines is formed, but then undergoes further reactions.

There are scattered reports⁴ of reactions of organolithium compounds and oximes that, instead of the hydroxylamines noted in this communication, furnish aziridines (and sometimes other products). These reactions may proceed by initial removal (by the organolithium compound) of an α -proton of the oxime, a step important in reactions of oximes with Grignard reagents⁵ and of derivatives of oximes in the Neber rearrangement.⁶ Alternatively, they may proceed by addition of the organolithium compound to form 4, followed by further reaction, one possibility being elimination of Li_2O to form a nitrene ($R-NLi-OLi \rightarrow R-N + Li_2O$).

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