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Reactivity of 2-benzylpyridyl lithium toward benzonitrile derivatives: addition versus elimination

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Abstract

This work investigated the reactivity of 2-benzylpyridyl lithium (2-Pyr)C(Ph)(R)Li (R = SiMe₃, **Li1**; R = H, **Li2**) toward benzonitrile derivatives. Based on the different products, the reaction between lithium salts and nitriles might involve in addition, elimination and bimolecular coupling pathways, respectively. Treatment of **Li1** with ArCN (Ar = Ph, *p*-Tolyl, *o*-Tolyl, *p*-OMePh) yielded an addition intermediate pyridyl-1-aza-allyl-lithium [{(2-Pyr)C(Ph)C(Ar)N(SiMe₃)}Li]₂ (**1**, Ar = Ph) and its corresponding hydrolysis product 2-benzylpyridyl-ketone **2–5**, respectively, in which the reaction involved in a 1,3-shift of –SiMe₃ group to form a dimeric pyridyl-1-aza-allyl-lithium then followed by acidic hydrolysis. The MeOLi elimination reaction between **Li2** and *p*-MeO(C₆H₄)CN resulted in formation of 4-(2-benzylpyridyl)benzonitrile **6**. The reaction of **Li2** with *p*-Me(C₆H₄)CN in the presence of TMEDA generated a 1:2 hydrolysis adduct 2-benzylpyridyl-enaminone **7**, however, in the absence of TMEDA it afforded a coupling product of bimolecular nitriles, 1-(4-methylphenyl)-2-cyanophenyl-ethanone **8**. We speculated the reaction mechanisms in sequence. The crystal structures of **1** and **5–8** were analyzed.

Keywords: 2-benzylpyridyl lithium; nitriles; addition; elimination; bimolecular coupling; silyl group migration.

1. Introduction

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