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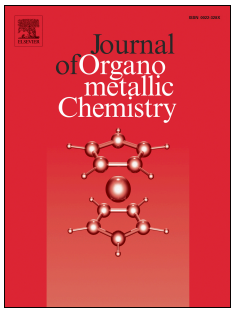

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Reactivity of 2-benzylpyridyl lithium toward benzonitrile derivatives: addition versus elimination

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Abstract

This work investigated the reactivity of 2-benzylpyridyl lithium (2-Pyr)C(Ph)(R)Li (R = $SiMe_3$, **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 $[\{(2\text{-Pyr})C(Ph)C(Ar)N(SiMe_3)\}Li]_2$ (**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 $-SiMe_3$ group to form a dimeric pyridyl-1-aza-allyl-lithium then followed by acidic hydrolysis. The MeOLi elimination reaction between **Li2** and *p*-$MeO(C_6H_4)CN$ resulted in formation of 4-(2-benzylpyridyl)benzonitrile **6**. The reaction of **Li2** with *p*-$Me(C_6H_4)CN$ 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