Additions and Corrections

2004, Volume 23

Christian Lorber,* Robert Choukroun, and Laure Vendier: Hydroamination of Alkynes Catalyzed by Imido Complexes of Titanium and Vanadium.

Pages 1848−1849. We reported the hydroamination of 1-hexyne with *tert*-butylamine by catalyst **5**, inadvertently inverting the regioisomer Markovnikov:anti-Markovnikov ratios. Accordingly, the text and Table 3 (row 10) must be corrected as M:anti-M = 1:99. We thank Dr. Sven Doye for bringing this to our attention.

Subsequent investigation led us to determine that the GC columns we used were unreliable in measuring the regioisomer ratio in the case of the benzylamine substrate, which gives very low yields of imine products. Therefore, imine products were only poorly separated (and multiple side products gave peaks in the same region of the chromatogram), which led to a misinterpretation of the regioselectivity. The crude products were reduced with $NaBH_3(CN)/ZnCl_2$ in THF, and the corresponding amines were analyzed by GC and compared with authentic samples. In this case, the ratio M:anti-M was found to be ca. 7:3 with catalyst **5**. Low yields of imine/amine products (ca. 15%) as well as formation of several side products with similar retention times did not allow a precise determination of this ratio. For the same reason, this value could not be confirmed by ^{1}H NMR spectroscopy. With catalyst **3**, we were not able to determine the regioselectivity because the yield of imine products is too low (<5%). Table 3 (rows 7, 8, and 10) should be corrected as shown. We regret these mistakes.

Table 3. Intermolecular Hydroamination of 1-Hexyne with Various Primary Amines in the Presence of $[V(\mu_2\text{-NPh})(NMe_2)_2]_2$ (3) or $[Ti(NPh)(NHPh_2)]$ (5)[a]

Catalyst	Amine	Time (h)[b]	Yield Imine (%)[c]	Selectivity (M:AM)[d]	Alkyne Recovery (%)
3	$PhCH_2NH_2$	24	<5	n.d.	57
5	$PhCH_2NH_2$	24	15	7:3[e]	52
5	^{t}BuNH$_2$	4	59	1:99	5

[a] Conditions: Catalyst 0.2 mmol (except for the dimer **3**: 0.1 mmol), 1-hexyne 2 mmol, amine 3 mmol (except for ^{t}BuNH$_2$: 6 mmol), toluene 5 g, 80 °C. Reaction conditions are not optimized. [b] The reaction time has not been minimized. [c] Yields were obtained by GC analysis vs dodecane internal standard. [d] Ratio Markovnikov:anti-Markovnikov imine products by GC. [e] Ratio M:AM by GC analysis after reduction of the imine products.

OM049461+

10.1021/om049461+
Published on Web 08/12/2004