

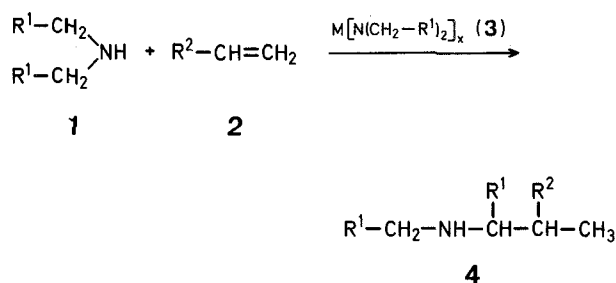
Catalytic C-Alkylation of Secondary Amines with Alkenes

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The alkylation of ammonia or amines with alkenes is a subject of considerable current interest. The *N*-alkylation has been studied by several groups^{1,2,3}, but no expedient catalytic processes have been found, except for reactions with ethene^{4,5,6}. Also, the *C*-alkylation of amines with 1-alkenes has been carried out via a radical process^{7,8,9}, resulting in the linear alkylation products.

We now report on the *C*-alkylation of secondary amines **1** with 1-alkenes **2** by means of a particular catalytic system **3**, yielding the branched products **4** with a high selectivity.



In a typical example, 1-hexene (**2**; $\text{R}^2 = n\text{-C}_4\text{H}_9$) and dimethylamine (**1**; $\text{R}^1 = \text{H}$) in toluene solution reacted in the presence of $\text{Nb}[\text{N}(\text{CH}_3)_2]_5$ ¹⁰ at 160 °C or $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ ¹¹ at 200 °C, giving the corresponding **4** as the only product, which could be isolated by distillation. The reaction is unusually slow, since it takes not less than 24 h to reach optimal yield; most of the product, however (~70%), was formed within the first hour.

The reaction appeared to be general; in fact, other alkenes reacted analogously, i.e. on the C atom in the position 2. Most of the experimental work was done with dimethylamine, but also other secondary amines reacted similarly on the C atom α to the nitrogen; the corresponding complexes $\text{M}[\text{N}(\text{CH}_2\text{R})_2]_x$ were conveniently used. No reaction was observed using the same catalytic systems **3** with primary or tertiary amines.

The yields depend on the particular alkene and the amine used; the best yields are obtained with lower alkenes and dimethylamine.

Other possible catalysts were checked; among these, $\text{Zr}[\text{N}(\text{CH}_3)_2]_4$ ¹² was found to be active, while use of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ ¹², $\text{V}[\text{N}(\text{CH}_3)_2]_4$ ¹³, $\text{Mo}[\text{N}(\text{CH}_3)_2]_4$ ¹⁴, and $\text{Sn}[\text{N}(\text{CH}_3)_2]_4$ ¹⁵ afforded only traces of product. Replacing toluene with other solvents (tris[*n*-butyl]amine, tetrahydrofuran, 1-hexene) did not affect the final yield.

The Table lists the type and the quantity of the products obtained, expressed both in terms of mol of product per mol of catalyst, as calculated from G.L.C. peaks, and of percentage yield calculated with respect to the alkene, as found on isolating the product by distillation.

The catalysts undergo a more or less rapid deactivation, depending on the reaction conditions; for example, they be-

Table. Catalytic C-Alkylation of Secondary Amines **1** with Alkenes **2** in the Presence of $M[N(CH_2---R^1)_2]$, (**3**)^a

R ¹ in 1 and 3	R ² in 2	M in 3	Yield [%] ^b of 4	Complex [mol/l]	Catalytic turnover ^c	b.p. [°C]/torr of 4	Lit. b.p. [°C]/torr	Purity [%]
H	<i>n</i> -C ₄ H ₉	Nb	10 12	0.03 0.08	8 4	105-107/0.2	131/11 ¹⁶	90
H	<i>n</i> -C ₄ H ₉	Ta	20 ^d 38 ^d	0.03 0.08	16 14			
H	<i>n</i> -C ₄ H ₉	Zr	18	0.08	6			
H	H	Nb	28 ^c	0.03	20	62-64/760	62-64/760 ¹⁷	85
H	CH ₃	Nb	21	0.03	15	76-78/760	76-78/760 ¹⁷	90
CH ₃	H	Nb	13 ^c	0.03	9	98/760	98/760 ¹⁸	90

^a Reaction conditions: **1**: 4 mol/l; **2**: 2 mol/l; temperature: 160 °C; time: 24 h; solvent: toluene. Products identified by ¹H-N.M.R. and mass spectrometry.

^b Yield of distilled product.

^c From G.L.C. peak integration.

^d Temperature: 200 °C; time: 150 h.

^e Pressure: 20 atm; volume gas: 50 ml; volume solution: 20 ml.

come unactive after a very short heating in toluene, unless an excess of dimethylamine is present. Probably there are many reasons for this deactivation: e.g. with Nb[N(CH₃)₂]₅, the negative effect found for the complex concentration on the catalytic turnover, is suggestive of some degree of complex association, probably giving inactive polymeric species. In addition, the dry residues obtained after evaporation of the reacted solution were unactive, and gave methylamine and 1-amino-2-methylhexane after basic hydrolysis. This suggests that the unactive complex be of an imidic type.

N-Methyl-*N*-(2-methylhexyl)-amine (**4**; R¹ = H, R² = *n*-C₄H₉):

Strictly anhydrous reagents are employed (dimethylamine over lithium dimethylamide). Into a glass tube, containing toluene (13 ml), 1-hexene (**2**; R¹ = *n*-C₄H₉; 3.5 g, 0.04 mol), Ta[N(CH₃)₂]₅ (**3**; M = Ta, *x* = 5; 0.6 g, 0.015 mol), is distilled dimethylamine (**1**; R¹ = H; 3.6 g, 0.08 mol) under anhydrous conditions. The tube is sealed and the sealed tube is inserted into a high-pressure apparatus, together with some of the liquid reagents to equilibrate the pressure on the walls of the tube. The bomb is heated at 200 °C for 150 h. After cooling, the solution is fractionally distilled through a silver-plated Widmer column, length 200 mm, \varnothing 10 mm, 5 trays to give the product **4**; yield: 2.0 g (38% based on **2**); b.p. 105-107 °C/0.2 torr; purity 90% (by G.L.C. on Chromosorb 103).

¹H-N.M.R. [C₆D₆/Eu(DPM)₃ shift reagent]: (s, 3H, CH₃NH); (m, 2H, NHCH₂CH); [m, 1H, CH₂CH(CH₃)CH₂]; (m, 2H, CHCH₂CH₂); [d, 3H, CH(CH₃), *J* = 7 Hz]; (m, 2H, CH₂CH₂CH₂); (sext., 2H, CH₂CH₂CH₃, *J* = 7.5 Hz); (t, 3H, CH₂CH₃, *J* = 7.5 Hz).

M.S.: *m/e* = 129 (M⁺).

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