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LETTERS TO THE EDITOR

TRANSFORMATION OF 2,3-BUTADIENEAMIDES TO N-[2(5H)-FURANYLIDENE]AMINES CATALYZED BY SILVER ACETATE

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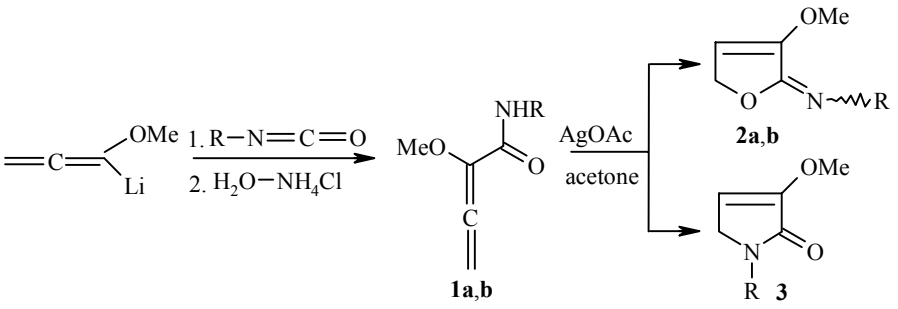
The reaction of lithiated 1,2-dienes with isocyanates was first accomplished in our laboratory as a simple, convenient pathway to 2,3-butadieneamides [1], which are synthetic intermediates and promising precursors for new heterocycles.

We have found that N-alkyl-2-methoxy-2,3-butadieneamides **1**, which are readily obtained by the reaction of α-lithiated 1-methoxyallene with isocyanates such as propyl and isopropyl isocyanates [2], are transformed smoothly and almost quantitatively in the presence of 14-16 mass % AgOAc in acetone at 20-45°C over ~0.2-1.5 h into 1-alkyl-N-[3-methoxy-2(5H)-furanylidene]amines **2a** and **2b**, which had been unknown and difficult to prepare by other means. Gas-liquid chromatographic analysis indicated that the conversion was 90-100%. Isomeric 1-alkyl-3-methoxy-1,5-dihydro-2H-pyrrol-2-ones **3**, whose formation might have been expected, were not identified among the reaction products.



This reaction may be carried out in a single preparative step without distillation of the intermediate amides **1**. Thus, we have developed a fundamentally new convenient synthesis of N-[2(5H)-furanylidene]amines by the reaction of carbanions of 1,2-dienes with isocyanates.

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N-[3-Methoxy-2(5H)-furanylidene]-1-propaneamine (2a). A solution of *n*-BuLi (0.1 mol) in hexane (65 ml) was added to a solution of methoxyallene (10 g, 0.14 mol) in THF (60 ml) at -100°C and the temperature was permitted to rise to -60°C. The mixture was then recooled to -100°C and a solution of propyl isocyanate (8.5 g, 0.1 mol) in THF (15 ml) was added dropwise maintaining the temperature at from -85 to -80°C. Then, concentrated aqueous NH_4Cl (100 ml) was added at about -30°C. The organic layer was separated and the aqueous solution was extracted with ether. The organic fraction was washed with water and dried over $MgSO_4$. The solvents were removed to give 14 g (~90%) of 2-methoxy-N-propyl-2,3-butadieneamide (**1a**). Gas-liquid chromatographic analysis indicated that the product was obtained in ~100% purity. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 6.44 (1H, s, NH); 5.85 (2H, d, CH_2=); 3.50 (3H, s, OMe); 3.29 (2H, m, NCH_2); 1.56 (2H, m, CH_2); 0.93 (3H, t, Me).

A mixture of 2,3-butadieneamide **1a** (7.7 g, 0.05 mol) and AgOAc (1.5 g, 0.0087 mol) in acetone (20 ml) was stirred for 1 h at room temperature. Gas-liquid chromatographic analysis indicated that the conversion of **1a** was 15.5%. Then the mixture was heated at 40-45°C for about 10 min. Gas-liquid chromatographic analysis indicated that the conversion of **1a** was then 91%. Acetone was removed at reduced pressure. Ether and aqueous lithium bromide were added to the residue. The organic layer was separated and passed through a neutral alumina column. Removal of ether at reduced pressure gave 6.4 g (83.1%) of compound **2a**. Gas-liquid chromatographic analysis indicated that the product purity was about 100%. Distillation gave 3.5 g (45.5%) of compound **2a**. Gas-liquid chromatographic analysis indicated that the product purity was 98.3%; bp ~85°C (~0.5 mm), n_D^{20} 1.4900. IR spectrum (neat), ν, cm^{-1}: 740, 760, 900, 950, 980, 1000, 1010 sh, 1050, 1130, 1140 sh, 1190, 1250, 1350, 1370 sh, 1460, 1650, 1700, 2850 sh, 2870, 2940, 2960, 3020 sh, 3100. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 5.61 (1H, t, CH=); 4.78 (2H, d, OCH_2); 3.77 (3H, s, OMe); 3.31 (2H, t, NCH_2); 1.64 (2H, m, CH_2); 0.93 (3H, t, Me). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 156.49 (N=C); 149.66 (OC=), 104.44 (CH=), 70.50 (OCH_2), 57.68 (OMe), 48.86 (NCH_2), 24.12 (CH_2), 12.11 (Me). ^{15}N NMR spectrum (40.56 MHz, $CDCl_3$), δ, ppm: 164.96. Found, %: N 8.59. $C_8H_{13}NO_2$. Calculated, %: N 9.03.

N-[3-Methoxy-2(5H)-furanylidene]-2-propaneamine (2b). N-Isopropyl-2-methoxy-2,3-butadieneamide (**1b**) was obtained analogously in ~90% yield. Gas-liquid chromatographic analysis indicated that the product purity was 98.8%. ^{1}H NMR spectrum (90 MHz, CCl_4), δ, ppm: 6.35 (1H, s, NH); 5.78 (2H, s, CH_2=); 4.03 (1H, m, NCH); 3.44 (3H, s, OMe); 1.16 (6H, d, CMe_2).

A mixture of 2,3-butadieneamide **1b** (7.7 g, 0.05 mol) and AgOAc (1.3 g, 0.0076 mol) in acetone (20 ml) was stirred at room temperature for about 1.5 h. Gas-liquid chromatographic analysis indicated that the conversion of **1b** was about 100%. Acetone was distilled off. Ether and aqueous NaCl were added to the residue. The layers were separated. The ethereal solution was passed through an alumina column. The solvent was removed on a rotary evaporator. Distillation of the residue gave 4.5 g (58.4%) of compound **2b**. Gas-liquid chromatographic analysis indicated that the product purity was 97%; bp 80-82°C (0.5 mm Hg), n_D^{20} 1.4870. IR spectrum (neat), ν, cm^{-1}: 740, 760, 800 sh, 950, 980, 1000, 1050, 1110, 1150, 1170 sh, 1190 sh, 1260, 1350, 1360, 1380, 1460, 1650, 1700, 2850, 2870, 2940, 2970, 3020 sh, 3100. ^{1}H NMR spectrum (400 MHz, acetone-d_6), δ, ppm, *J* (Hz): 5.82 (1H, t, *J* = 2.2, CH=); 4.75 (2H, d, *J* = 2.2, OCH_2); 3.86 (1H, m, NCH); 3.70 (3H, s, OMe); 1.04 (6H, m, *J* = 6.4, CMe_2). ^{13}C NMR spectrum (100 MHz, acetone-d_6), δ, ppm: 155.13 (N=C), 150.66 (OC=), 106.19 (CH=), 70.98 (OCH_2), 57.75 (OMe), 47.37 (NCH), 24.34 (2Me). ^{15}N NMR spectrum (40.56 MHz, $CDCl_3$), δ, ppm: 148.60. Found, %: N 8.29. $C_8H_{13}NO_2$. Calculated, %: N 9.03.

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REFERENCES

1. N. A. Nedolya, L. Brandsma, and B. A. Trofimov, *Zh. Org. Khim.*, **33**, 615 (1997).
2. N. A. Nedolya, L. Brandsma, N. I. Schlyakhtina, V. P. Zinov'eva, and A. I. Albanov, in: *Proceedings of the First Eurasian Meeting on Heterocyclic Chemistry*, Suzdal, Russia (2000), p. 43.