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DIMERIZATION OF ORGANOLITHIUM DERIVATIVES

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SUMMARY

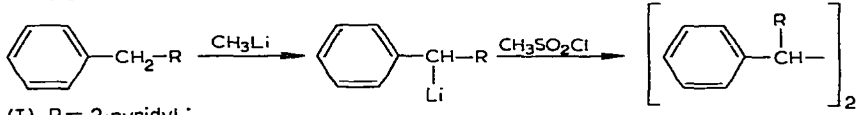
Reactions of benzylic-type lithium derivatives with methanesulfonyl chloride gave high yields of dimeric products. The mechanism probably involves formation, by halogen–lithium exchange, of a benzylic chloride which subsequently reacts with a second mole of the organolithium reagent.

INTRODUCTION

Dimerization of organolithium compounds has been attempted with various reagents and among these air[1], iodine[2], and bromine[3] have shown some success. We want to report on the dimerization of three benzylic-type lithium derivatives in high yields using methanesulfonyl chloride.

RESULTS AND DISCUSSION

An ether solution of 2-benzylpyridine (I) reacted rapidly with methyllithium at room temperature to give a deep red solution of the lithium derivative. Addition of the organometallic compound to methanesulfonyl chloride caused an exothermic reaction with formation of a precipitate. This was shown by elemental analysis and spectroscopic evidence to be 1,2-diphenyl-1,2-di(2-pyridyl)ethane (II), m.p. 240–241°; furthermore, thin layer chromatography indicated that the product was actually a mixture of the diastereomers. The yield was 79%. Compound (II) had previously been prepared in low yield by dimerization of (I) with sulfur or selenium[4]. By the two-step procedure 4-benzylpyridine (III) gave 1,2-diphenyl-1,2-di(4-pyridyl)ethane (IV), m.p. 242–243°, as a mixture of diastereomers in 72% yield. Recently, Traynelis and Yamauchi[5] reported the isolation of both *meso* and *d*, *l* forms of (IV). The utility of our method was further demonstrated by the dimerization of fluorene to 9,9′-bifluorene (V) in 65% yield.



(I), R = 2-pyridyl ;
(III), R = 4-pyridyl;

(II), R = 2-pyridyl ;
(IV), R = 4-pyridyl

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We believe the first step in the reaction of the lithium derivative with methanesulfonyl chloride to be a chlorine–lithium interconversion with formation of the respective benzylic-type chloride, which then couples with a second mole of the lithium reagent to give the dimer. Support for such a mechanism is provided by the recent observation[6] that halogen–metal exchange is the predominant path in the reaction of α-toluenesulfonyl chloride with phenyllithium.

The procedure will probably be of general use for the dimerization of lithium derivatives in cases where a benzylic-type chloride would be formed by the halogen–metal exchange reaction.

EXPERIMENTAL

1,2-Diphenyl-1,2-di(2-pyridyl)ethane (II)

To a solution of 16.9 g (0.1 mole) of 4-benzylpyridine in 100 ml of anh. ether was added dropwise with stirring 50 ml of methyllithium (2.05 *M*). The dark red solution was then stirred for an additional 1/2 h and then added dropwise to a stirred solution of 11.5 g (0.12 mole) of methanesulfonyl chloride in 50 ml of anh. ether. The addition took place at such a rate that a gentle reflux was maintained. The reaction mixture was left stirring at room temperature over night. Water was added, the solid material filtered and washed well with ether and water. The white product was dried at 50° (0.1 mm) leaving 13.3 g (79%) of the dimer (II), m.p. 230–233°. Recrystallization from ethanol–benzene gave a pure sample, m.p. 240–241° (lit[4]. m.p. 244–245°); UV λ_{max} (methanol) 271.5 nm (log ε 3.88), 265 (3.99), 262 infl. (3.97); mass spectrum *m/e* (% relative abundance): 336 (41.5), 258 (19), 245 (47.2), 180 (5), 169 (43.4), 168 (100), 167 (73.6), 139 (6.6). (Found: C, 85.48; H, 6.16; N, 8.27. $C_{24}H_{18}N_2$ calcd.: C, 85.68; H, 5.99; N, 8.33%.)

1,2-Diphenyl-1,2-di(4-pyridyl)ethane (IV)

This compound was prepared by the same procedure as described above for compound (II). Using 16.9 g (0.1 mole) of 4-benzylpyridine 12.1 g (72%) of the dimer (IV) was obtained, m.p. 235–240°. Recrystallization from ethanol/benzene gave a pure sample, m.p. 242–243° (lit.[5] m.p. 219.5–221° and 270–272°); UV λ_{max} (methanol) 271.5 nm (log ε 3.87), 265 (3.96), 262 infl. (3.95); mass spectrum *m/e* (% relative abundance): 336 (17), 258 (11.3), 245 (30), 180 (3), 169 (45.3), 168 (100), 167 (56.6), 139 (2.8). (Found: C, 85.70; H, 6.16; N, 8.26. $C_{24}H_{18}N_2$ calcd.: C, 85.68; H, 5.99; N, 8.33%.)

9,9'-Bifluorene (V)

(V) was prepared by the same procedure as described for compound (II). From 8.3 g (50 mmoles) of fluorene 5.4 g (65%) of (V) was obtained; m.p. 245–246°, undepressed by mixed m.p. with an authentic sample.

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