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SYNTHESIS OF SILYLDIAZOKETONES FROM LITHIUM PENTAMETHYLDISILANYLDIAZOMETHANE WITH ACID CHLORIDES

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Lithium pentamethyldisilanyldiazomethane, prepared from pentamethyldisilanyldiazomethane and lithium diisopropylamide, reacts with acid chlorides to give pentamethyldisilanyldiazoketones in good yields.

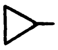
Silyl diazo compounds are potential sources of reactive silaethylenes via intramolecular rearrangement of silylcarbenes, and several silyl diazo compounds have been synthesized and studied.$^{1)}$ However, literature on the preparation of silyldiazoketones is very scarce because of the instability.$^{2)}$ We wish to report here preparation of stable pentamethyldisilanyldiazoketones in high yields.

Lithium salt of pentamethyldisilanyldiazomethane,$^{3)}$ prepared from pentamethyldisilanyldiazomethane and lithium diisopropylamide, reacted cleanly with acid chlorides to produce the corresponding pentamethyldisilanyldiazoketones in good yields. The reactions of the lithium salt with acetyl chloride, butyryl chloride, pivaloyl chloride, cyclopropanecarbonyl chloride, and 1-adamantanecarbonyl chloride gave satisfactory results (Table 1). A typical procedure for the preparation of pentamethyldisilanyldiazoketone is as follows (run 6). A solution of lithium diisopropylamide, prepared from diisopropylamine (900 μl, 6.39 mmol) and n-butyl lithium (15% hexane solution, 4.05 ml, 6.39 mmol) in diethyl ether (25 ml), was added to a solution of pentamethyldisilanyldiazomethane (1026 μl, 5.13 mmol) in diethyl ether (25 ml) at -30°C under argon atmosphere. The mixture was stirred at -30°C for 20 min. To the resulting solution was added dropwise a solution of 1-adamantanecarbonyl chloride (964 mg, 4.86 mmol) in diethyl ether (25 ml) at -60°C, then the mixture was warmed to 0°C and stirred for 1 h. The reaction mixture was treated with ice-water and extracted with diethyl ether. The ethereal extracts were dried over anhydrous sodium sulfate. Evaporation of the ether gave yellow solid which was washed with small amounts of hexane to give the pure disilanyldiazoketone (1400 mg, 86%), NMR(CCl_4,δ) 0.08(s,9H,$SiMe_3$), 0.17(s,6H,$SiMe_2$), and 1.55-2.23(m,15H,adamantyl CH); Mass m/e 306 (M^+-28).

However, the reaction of lithium pentamethyldisilanyldiazomethane with benzoyl chloride did not give satisfactory results because of the instability of the product, and diazoacetophenone was formed by the desilylation during work-up. Ethyl acetate also reacts with the lithium salt to produce the expected pentamethyldisilanyldiazoacetone in moderate yield (run 2). Our method presented here is undoubtedly simple and clean route for the preparation of pentamethyldisilanyldiazoketones.

We also tried the reactions of 1 eq. of lithium trimethylsilyldiazomethane with acid chlorides (1-adamantanecarbonyl chloride and pivaloyl chloride) at -60°C, and obtained the corresponding diazoketones instead of trimethylsilyldiazoketones. These diazoketones were presumably formed by the desilylation of trimethylsilyldiazoketones during work-up. In contrast to our observations, Aoyama and Shioiri reported the formation of 2-substituted 5-trimethylsilyltetrazoles by the reactions of 2 eq. of lithium trimethylsilyldiazomethane with methyl esters of carboxylic acids or benzoyl chloride.$^{4)}$

Table 1. Reaction of Lithium Pentamethyldisilanyldiazomethane with Acid Chlorides.

Run	Acid Chloride or Ester	Product$^{a)}$	Yield$^{b)}$ (%)	Bp (°C / mmHg)	$\nu(N_2)$ (cm^{-1})	$\nu(CO)$ (cm^{-1})
1	MeCOCl	$Me_3SiSiMe_2C(N_2)COMe$	69	66-68/2	2060	1635
2	MeCOOEt	$Me_3SiSiMe_2C(N_2)COMe$	59			
3	$Me(CH_2)_2COCl$	$Me_3SiSiMe_2C(N_2)CO(CH_2)_2Me$	88	67-68/1	2050	1630
4	Me_3CCOCl	$Me_3SiSiMe_2C(N_2)COCMe_3$	74	56-58/1	2060	1620
5	COCl	$Me_3SiSiMe_2C(N_2)CO$	53	79-81/1	2050	1620
6	Ad-COCl$^{c)}$	$Me_3SiSiMe_2C(N_2)CO$-Ad	86	Solid$^{d)}$	2055	1610

a) Products were collected by bulb-to-bulb distillation and all compounds were fully characterized by the usual spectroscopic properties.

b) Isolated yields. c) 1-Adamantanecarbonyl chloride.

d) This compound was gradually decomposed at above 85°C.

References

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