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Preliminary communication

Trimethylsilylation of carbenoids generated in situ from allyl and benzyl halides

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Abstract

Efficient procedures for the trimethylsilylation of the transient carbenoids $H_2C{=}CHCH(X)Li$ and $Ph(CH(X)Li$ (X = Cl or Br) are described.

The pioneering investigations of Köbrich et al. [1] in the field of carbenoids have stimulated further research which has resulted in a number of useful synthetic applications [2]. The significance of the products obtained in the reactions lies in the fact that the derivatives obtained usually contain one or more halogen atoms which make them amenable to further synthetic operations.

In spite of the considerable progress in synthetic techniques and the availability of a variety of basic reagents, each with its specific properties, a number of interesting carbenoids have resisted attempts at generation and subsequent functionalization. For the generation of carbenoids from allyl and benzyl halides, bases like lithium diisopropylamide and lithium tetramethylpiperidide [3] seem the best choice, since their C-nucleophilicity (i.e. tendency to undergo allylation or benzylation) is moderate. However, these carbenoids are powerful nucleophiles, which are very likely to couple with the reactive substrates.

Addition at $\backsim -100\,^{\circ}C$ of benzyl chloride or benzyl bromide to a solution of lithium diisopropylamide (LDA) in tetrahydrofuran (THF), followed by, quenching with trimethylchlorosilane (Me_3SiCl), gave only the products $PhCH_2CH(X)Ph$ (X = Cl or Br) resulting from the very fast subsequent reaction of the carbenoids PhCH(X)Li with benzyl halide. Despite several approaches, including varying the rate of addition of $PhCH_2X$, using tetramethylethylenediamine in order to enhance the kinetic basicity of LDA, etc., the desired silyl derivatives $PhCH(X)SiMe_3$ were formed in traces only. Excellent yields of these compounds were obtained, however, when the mixture of benzyl halide and a slight (molar) excess of Me_3SiCl was added to a well-cooled solution of LDA in THF and hexane. Silylation of benzyl chloride was also accomplished with excellent yields by adding a solution of LDA in THF to a mixture, kept at $-25\,^{\circ}C$, of benzyl chloride, a 10 to 20% molar excess of Me_3SiCl,

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and THF. Allyl bromide was converted into the silyl derivative $H_2C{=}CH{-}CH(Br){-}SiMe_3$ by a similar procedure carried out at $-60\,^{\circ}C$. In the absence of Me_3SiCl the transient carbenoid reacted with allyl bromide to form $H_2C{=}CHCH(Br){-}CH_2CH{=}CH_2$.

Allyl chloride, LDA, and Me_3SiCl did give the expected compound $H_2C{=}CHCH(Cl)SiMe_3$, but owing to its high volalility no satisfactory separation from the hexane and THF could be achieved. From prenyl chloride and phenyl bromide $(CH_3)_2C{=}CHCH_2X$ (X = Cl or Br), LDA, and Me_3SiCl, complicated mixtures were obtained which did not contain the expected products.

The successful results in our trapping experiments with Me_3SiCl show that the benzyl and allyl halides react much faster with LDA than does Me_3SiCl, and that trimethylsilylation of the carbenoids occurs more readily than the allylation or benzylation.

$$RCH_2X \xrightarrow[THF/hexane]{LDA} RCH(Li)X \begin{cases} \xrightarrow{RCH_2X} RCH(X)CH_2R \\ \xrightarrow{Me_3SiCl} RCH(X)(SiMe_3) \end{cases}$$

Analogous trapping experiments with allylic chlorides, LDA and alkyl bromides have been reported by McDonald [4]. Recently, Mirsadeghi and Rickborn [5] succeeded in intercepting with Me_3SiCl unstable enolates generated by use of Li-TMP. Mauzé, Miginiac and coworkers [6–8] generated carbenoïds derived from allylic chlorides by treating the lead compounds $Ph_3PbCH_2CH{=}C(Cl)R$ with butyllithium.

Experimental

1. Trimethylsilylation of the carbenoids from benzyl chloride and benzyl bromide. a. A mixture of 0.10 mol of benzyl chloride or bromide, 0.12 mol of Me_3SiCl, and 50 ml THF was added dropwise during 20 min to a solution of 0.10 mol of LDA in 70 ml of THF and 70 ml of hexane maintained between -100 and $-110\,^{\circ}C$. After an additional 15 min (at $-100\,^{\circ}C$) the cooling bath was removed and the temperature allowed to rise to $-20\,^{\circ}C$. Water (100 ml) was added, and after separation of the layers three extractions with diethyl ether were carried out. The combined organic solutions were washed with dilute (2 *N*) hydrochloric acid and the water. After drying over $MgSO_4$, the solution was concentrated in vacuo, and the remaining liquid distilled through a 20-cm Vigreux column to give: $PhCH(SiMe_3)Cl$, b.p. 60–65 °C/0.6 mmHg, n_D^{20} 1.5171, in 84% yield, and $PhCH(SiMe_3)Br$, b.p. 70–75 °C/0.3 mmHg, n_D^{20} 1.5386, in 72% yield. The ^1H NMR spectra (20% v/v solutions in CCl_4, internal standard CH_2Br_2, δ 4.91 ppm) showed the following signals: $PhCH(Cl)SiMe_3$: 7.31, 4.44 and 0.31 ppm and $PhCH(Br)SiMe_3$: 7.31, 4.39 and 0.31 ppm.

b. A solution of 0.10 mol of LDA in 50 ml of THF and 70 ml hexane (placed in the dropping funnel) was added dropwise during 15 min to a mixture of 0.12 mol of benzyl chloride, 0.15 mol of Me_3SiCl and 50 ml of THF, maintained between -25 and $-30\,^{\circ}C$. After an additional 15 min water was added and the product was isolated in 91% yield as described above.

2. Trimethylsilylation of the carbenoid from allyl bromide. A solution of 0.10 mol of LDA in 50 ml of THF and 70 ml of hexane (placed in the dropping funnel) was

added during 15 min to a mixture of 0.20 mol (excess) of allyl bromide, 0.15 mol (excess) of Me_3SiCl, and 50 ml of THF, maintained at ~ −60 °C. After an additional 15 min water (100 ml) was added, followed by a mixture of 15 ml of 36% hydrochloric acid and 200 ml of water. After shaking and separation of the layers, four extractions with pentane were carried out. The combined organic solutions were dried over $MgSO_4$, and most of the solvent was distilled off at atmospheric pressure through a 40 cm Vigreux column. Careful distillation of the remaining liquid gave $H_2C{=}CHCH(SiMe_3)Br$, b.p. 42–44 °C/15 mmHg, n_D^{20} 1.4698, in 75% yield. ^1H NMR: (20% v/v solution in CCl_4, CH_2Br_2, δ 4.91 ppm as internal standard): $H_2C{=}CH$ (δ 4.9–6.3 ppm, m); CH_2 (δ 3.67 ppm, d) and Me_3Si (δ 0.16 ppm, s).

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References

1 G. Köbrich, Angew. Chem., 84 (1972) 557.
2 H. Siegel, Topics Curr. Chem., 106 (1982) 55.
3 R.A. Olofson, C.M. Dougherty, J. Am. Chem. Soc., 95 (1973) 582.
4 T. McDonald, B. Amirthalingam Narayanan, and D.E. O'Dell, J. Org. Chem., 46 (1981) 1506.
5 S. Mirsadeghi and B. Rickborn, J. Org. Chem., 51 (1986) 986.
6 B. Mauzé, A. Doucoure and L. Miginiac, J. Organomet. Chem., 215 (1981) 1.
7 B. Mauzé, J. Organomet. Chem., 170 (1979) 265.
8 P. Ongoka, B. Mauzé and L. Miginiac, Synthesis, (1985) 1069.