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Sila- and germa-enolate anions. The reaction of acylgermanes with triethylgermyllithium

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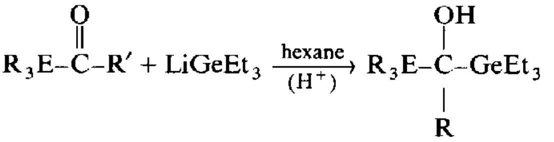
Abstract

Thermostable silaenolate anions $(Me_3Si)_2Si \approx C(OLi)R$, unusual compounds of the silaolefinic series were obtained by the reaction of tris(trimethylsilyl)acylsilanes with triethylgermyllithium in tetrahydrofuran.

Acylsilanes react with organolithium compounds and with Grignard reagents in the same way as normal ketones, forming tertiary alkoxides which are converted to carbinols after hydrolysis [1]. Heating of these carbinols in hexamethylphosphortriamide (HMPA) with KH leads to migration of the organosilicon group to the oxygen atom [2]. This rearrangement spontaneously occurs in alkoxides either with the allyl substituent [3] or with a substituent containing a group that is leaving readily [4]. In these two cases enol silyl ethers form. The fluoride ion breaks the silicon–carbonylic carbon bond Si–C(O) in acylsilanes, possibly with intermediate formation of acyl anions [5]. The fluoride ion-acylsilane adduct has been noted to undergo, at the same time, an unusual rearrangement involving migration of the substituent from the silicon to the carbonylic carbon [6].

In a hydrocarbon medium triethylgermyllithium Et_3GeLi (I) reacts with acylgermanes in a similar way as it does with organic ketones [7,8] to form tertiary carbinols after hydrolysis.



$$R_3E-\overset{\overset{\displaystyle O}{\|}}{C}-R' + LiGeEt_3 \xrightarrow[(H^+)]{hexane} R_3E-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-GeEt_3 \qquad (1)$$

$(R_3E = Et_3Ge, Et_3GeGeEt_2; Me_3SiGeEt_3; R' = CMe_3, Ph)$

These alcohols are oxidized very rapidly in air, unlike monogermylated ones.

In basic media (THF, HMPA) cleavage of the germanium–carbonylic carbon bond, Ge–C(O), is observed. This may be due to an SET mechanism followed by

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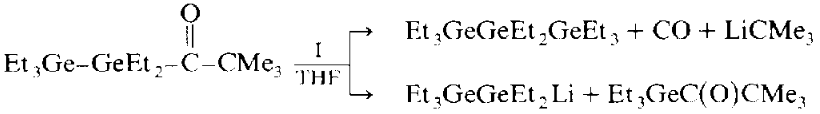
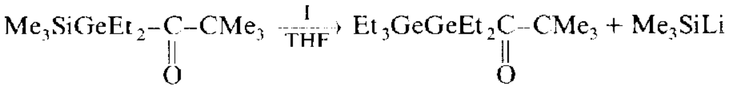
decomposition of the acylgermane anion-radical as shown by their reaction with benzoyltriethylgermane $PhC(O)GeEt_3$ [7]. For pentaethylpivaloyldigermane $Et_3GeGeEt_2C(O)Me_3$ (II) the nucleophilic attack seems to be most responsible for the bond cleavage, which is indicated by the absence of hexaethyldigermane $(Et_3Ge)_2$ and decaethyltetragermane $Et_{10}Ge_4$, the products from recombination of $Et_3Ge^{\bullet}$ and $Et_5Ge_2^{\bullet}$ radicals in the reaction mixture:



$$\mathrm{Et_3Ge{-}GeEt_2{-}\overset{\overset{O}{\|}}{C}{-}CMe_3} \xrightarrow[\text{THF}]{\text{I}} \begin{cases} \mathrm{Et_3GeGeEt_2GeEt_3 + CO + LiCMe_3} \\ \mathrm{Et_3GeGeEt_2Li + Et_3GeC(O)CMe_3} \end{cases} \qquad (2)$$

Two routes of reaction 2 are possible owing to nucleophilic attack at both carbon and germanium of the Ge–C(O) bond. In this reaction only some traces of Ge–Ge bond cleavage are revealed whereas in the reaction with acylgermanes III and IV Si–Ge bond cleavage is the prevailing process:

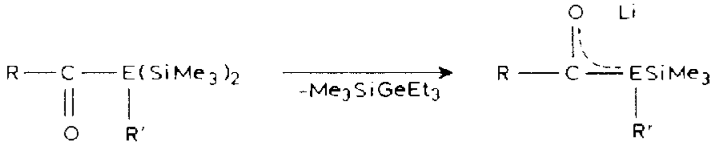


$$\mathrm{Me_3SiGeEt_2{-}\underset{\underset{O}{\|}}{C}{-}CMe_3} \xrightarrow[\text{THF}]{\text{I}} \mathrm{Et_3GeGeEt_2\underset{\underset{O}{\|}}{C}{-}CMe_3 + Me_3SiLi} \qquad (3)$$

(III)

In reaction 3 the attack at the germanium atom of the Si–Ge bond in the acylgermane (III) takes place. If the ethyl substituents attached to the germanium atom are replaced by trimethylsilyl substituents, lithiation of acylgermane becomes a dominant reaction, i.e. the attack is at the silicon atom. In this way, the germaenolate anion (Va′) was prepared for the first time; the same is true of the silaenolate anion (Va, Vc) in the reaction with acylpolysilane of similar structure.

It should be noted that the replacement of the trimethylsilyl substituent by a t-butyl group (IVc) does not affect the reaction direction:



(IVa-IVc) (Va, Vc) (4)

(R = CMe3 , R′ = SiMe3 , E = Si (a) , Ge (a′) ;
R = adamanthyl , R′ = SiMe3 , E = Si (b) ;
R = R′ = CMe3 , E = Si (c))

The presence of the enolate anions V has been proved by the reactions with alkyl halides, which result in the formation of the corresponding acyl-germanes and -silanes.

Example

To 2.19 g (0.0066 mol) of pivaloyltris(trimethylsilyl)silane, $Me_3CC(O)Si(SiMe_3)_3$ (IVa) a solution of 1.1 g (0.0066 mol) of I in 10 ml of THF at room temperature was added. The reaction mixture was coloured dark-red (UV-spectrum, λ_{max} 425.9

($\sim 10^2$) nm, the absorption maxima for acylsilane lithium enolates (Vb and Vc) (λ_{max} 428.8 and 428.0 nm, respectively, were observed).

The structure of the compounds Me_3Si-$Si(R')$=$C(OLi)R$ (V) was demonstrated by ^{29}Si NMR spectroscopy. In the spectra of these derivatives the data for the olefinic Si resonance region 68.09, 64.86 and 67.77 ppm for IVa, IVb and IVc, respectively, were consistent with those for Brook's thermostable silaolefins [1a]. The central Si atom double-bonding is confirmed by non-equivalence of the silicon atoms in trimethylsilyl groups (-10.69, -11.59 ppm) for Va, (-8.97, -10.86 ppm) Vb and (-16.04 ppm) Vc.

Treatment of Va with an excess of alkyl iodides (MeI, Me_2CHI) in THF leads to the products of Si-alkylation, the corresponding alkylsilanes, $(Me_3Si)_2Si(Alk)C(O)CMe_3$.

Bis(trimethylsilyl)pivaloisopropylsilane, $(Me_3Si)_2Si(Me_2CH)C(O)CMe_3$, was isolated by elution of the reaction mixture on a silica gel column with a hexane/ether mixture (10/1). Yield 50%, m.p. 38°C Found: C, 54.82; H, 10.90; Si, 28.62. $C_{14}H_{34}Si_3O$ calcd.: C, 55.56; H, 11.32; Si, 27.84%. Mass-spectrum: 287 $[M - Me]^+$, 259 $[M - Me_2CH]^+$, 246 $[M - Me_3Si]^+$, 217 $[M - C(O)CMe_3]^+$, 175 $[(MeSi)_2Si]^+$, 146 $[(Me_3Si)_2]^+$, 85 $[CMe_3C(O)]^+$, 73 $[Me_3Si]^+$, 57 $[CMe_3]^+$.

Si-alkylated derivatives of other enolates were obtained by use of an analogous technique.

The reactions of triethylgermyllithium with acylsilanes (IV) were carried out in evacuated sealed ampoules.

NMR spectra were run on an FX-90 Q spectrometer (90 MHz) (TMS).

The reaction products were identified by use of mass spectrometry on an MAT-212 spectrometer.

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References

1 A.G. Brook, M.A. Quigly, G.J.D. Peddle, N.V. Schwartz and C.M. Warner, J. Am. Chem. Soc., 82 (1960) 5102.

1a A.G. Brook, J. Organomet. Chem., 300 (1986) 21.

2 S.R. Wilson, M.S. Hague and R.N. Miisra, J. Org. Chem., 47 (1982) 747.

3 J. Enda and J. Kuwajima, J. Am. Chem. Soc., 107 (1985) 5495.

4 H.J. Reich, J.J. Rusek, R.E. Olson, J. Am. Chem. Soc., 101 (1979) 2225; H.J. Reich, R.C. Holton, S.L. Borkowsky, J. Org. Chem., 52 (1987) 312.

5 C.H. Heathcock and D. Schinzer, Tetrahedron Lett., 28 (1981) 1881.

6 P.B. Bulman Page, S. Rosental, R.V. Williams, Tetrahedron Lett., 28 (1987) 4455.

7 D.A. Bravo-Zhivotovskii, I.S. Biltueva, T.I. Vakulskaya, N.S. Vyazankin and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1987) 2872.

8 I.S. Biltueva, D.A. Bravo-Zhivotovskii, T.I. Vakulskaya, N.S. Vyazankin and M.G. Voronkov, Metalloorg. Khimiya, 1 (1988) 789.