CHEMISTRY LETTERS, pp. 1829-1830, 1985.

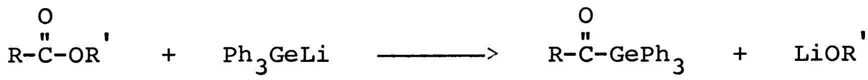
FACILE SYNTHESIS OF ACYLGERMANES

Syun-ichi KIYOOKA * and Akinori MIYAUCHI
Department of Chemistry, Kochi University,
Akebono-cho 2-5-1, Kochi 780

Acylgermanes are prepared from the corresponding esters with triphenylgermyllithium at room temperature in good yields.

Organogermaniums are gradually attracting the attention of synthetic organic chemists because of their inherent properties different from organosilicons and organotins.[1,2,3)] Acylgermanes have been recognized to be versatile synthetic intermediates[4)] and then its facile preparative method is being desired to be developed. Two typical synthetic routes have been used to prepare acylgermanes; from the hydrolysis of germyl-1,3-dithianes[5)] and from the addition of triphenylgermyllithium to acid chlorides.[6,7)] The latter way is more easier but it needs acid chlorides and lower temperature conditions; e.g., in the case of benzoyl chloride at -20 °C in 50% yield and at -78 °C in 80% yield. Recently, N,N-dialkylated carboxamides have been chosen as substrate of the reaction with triethylgermyllithium;[8,9)] pivaloyltriethylgermane was prepared at 20 °C in 30% yield with a by-product of 1,1-bis(triethylgermyl)-2,2-dimethylpropan-1-ol.

We now report the reaction of commercially available esters with triphenylgermyllithium.[10)]



$$R-\overset{O}{\overset{\|}{C}}-OR' + Ph_3GeLi \longrightarrow R-\overset{O}{\overset{\|}{C}}-GePh_3 + LiOR'$$

A typical experimental procedure is as follows: To a solution of triphenylgermyllithium in THF (10 ml) prepared from triphenylgermane (305 mg, 1 mmol) and butyllithium (0.62 ml [15% solution in hexane], 1 mmol) was added dropwise via syringe methyl phenylacetate (0.15 ml, 1 mmol) at room temperature under argon atmosphere. After stirring for 10 min, the reaction mixture was quenched with aq. NH_4Cl and the organic layer was extracted with ether. The ethereal layer was dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash column chromatography to give phenylacetyltriphenylgermane, which has Rf value 0.21 on thin layer chromatography (Merck silica gel 60) with 3% AcOEt in hexane (triphenylgermane has Rf value 0.61).

As shown in Table 1, this reaction is excellent for the synthesis of acylgermanes. By-products could not be found in the reaction except triphenylgermane. The alkoxy group (OR') is a nice leaving group in this nucleophilic substitution reaction and then the resulting lithium alkoxide (LiOR') may not be so basic as to disturb the reaction.

Table 1. Acylgermanes from the reaction of esters with triphenylgermyllithium[11)]

Ester	Product	Yield[a)] %	IR[b)] ν/cm^{-1}	^{13}C-NMR[c)] δ (ppm)(TMS)
CH_3COOEt	$CH_3COGePh_3$ 1 (mp 103-105 °C)	76	1655	237.5
CH_3CH_2COOEt	$CH_3CH_2COGePh_3$ 2 (mp 95-97 °C)	82	1655	238.4
Me_2CHCH_2COOMe	$Me_2CHCH_2COGePh_3$ 3 (mp 72-75 °C)	75	1655	238.5
$PhCH_2COOMe$	$PhCH_2COGePh_3$ 4 (mp 81-83 °C)	80	1655	234.7
PhMeCHCOOMe	$PhMeCHCOGePh_3$ 5 (mp 87-88 °C)	81	1655	236.2
PhCOOMe	$PhCOGePh_3$ 6 (mp 85-86 °C)	86	1625	227.3

a) Isolated yield. b) IR spectral data in $CHCl_3$ (frequency of carbonyl group).
c) ^{13}C-NMR spectral data in $CDCl_3$ (chemical shift of carbonyl carbon).

References

1) H. Oda, Y. Morizawa, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 25, 3217 (1984).

2) H. Sakurai and M. Kira, *Kagaku No Ryoiki*, 22, 898 (1968); K. Mochida and N. Matsushige, *J. Organomet. Chem.*, 229, 11 (1982).

3) W. Kitching, H. A. Olszowy, and K. Harvey, *J. Org. Chem.*, 47, 1893 (1982).

4) A. G. Brook and S. A. Fieldhouse, *J. Organomet. Chem.*, 10, 235 (1967).

5) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Am. Chem. Soc.*, 89, 431 (1967).

6) D. A. Nicholson and A. L. Allred, *Inorg. Chem.*, 4, 1714 (1965).

7) G. J. D. Peddle, *J. Organomet. Chem.*, 14, 139 (1968).

8) D. A. Bravo-Zhivotovskii, S. D. Pigarev, I. D. Kalikhman, O. A. Vyazankina, and N. S. Vyazankin, *J. Organomet. Chem.*, 248, 51 (1983).

9) D. A. Bravo-Zhivotovskii, S. D. Pigarev, I. D. Kalikhman, O. A. Vyazankina, and N. S. Vyazankin, *Zh. Obshch. Khim.*, 53, 1838 (1983); *Chem. Abstr.*, 100, 6721r (1984).

10) Under similar conditions the reaction with triethylgermyllithium takes a different course which is now investigating in detail.

11) All new compounds gave satisfactory combution analyses. ^{1}H-NMR ($CDCl_3$, δ, TMS): 1: 2.47 (s, 3H), 7.34-7.80 (m, 15H); 2: 0.99 (t, J= 8 Hz, 3H), 2.84 (q, J= 8 Hz, 2H), 7.35-7.80 (m, 15H); 3: 0.83 (d, J= 6 Hz, 6H), 2.20 (m, 1H), 2.70 (d, J= 5 Hz, 2H), 7.30-7.78 (m, 15H); 4: 4.05 (s, 2H), 7.18-7.70 (m, 20 H); 5: 1.33 (d, J= 7 Hz, 1H), 4.30 (q, J= 7 Hz, 1H), 7.13-7.70 (m, 20H); 6: 7.29-8.10 (m).

(Received September 9, 1985)