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Photochemical Decarbonylation of (α-Arylacyl)triphenylgermane

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Synopsis. (α-Arylacyl)triphenylgermanes were prepared from the corresponding esters with triphenylgermyllithium at room temperature in good yields. Photochemical decarbonylation of (α-arylacyl)triphenylgermanes took place under UV irradiation to quantitatively give (α-arylalkyl)-triphenylgermanes without by-products.

Organogermaniums are gradually attracting the attention of synthetic organic chemists because of their inherent properties, which are different from organosilicons and organotins.[1] Acylgermanes, among them, are expectantly situated to be relatively unique reagents by considering the acylsilane chemistry.[2] We recently wrote a preliminary report regarding the preparation of acylgermanes from the corresponding esters with triphenylgermyllithium,[3] the process is easier than the other routes.[4]

Upon studying the utility of acylgermanes to organic synthesis, we became aware of the instability of acylgermanes dissolved in solvents toward sunlight. Although the photochemistry of acylsilanes has been well-investigated,[5] little is known concerning that of acylgermanes. The germyl radical via a Norrish type-I cleavage has been observed in the laser photolysis (266 nm) of acylgermanes.[6] When (α-arylacyl)triphenylgermanes were irradiated, decarbonylation was found to take place. We therefore report here the synthesis of (α-arylacyl)triphenylgermanes and the subsequent photochemical decarbonylation to give (α-arylalkyl)-triphenylgermanes.

Results and Discussion

The reaction of *N*,*N*-dimethylpivalamide with triethylgermyllithium, from bis(triethylgermyl)mercury and metallic lithium, in hexane at 20 °C has been reported to give pivaloyltriethylgermane in 30% yield with a by-product of 1,1-bis(triethylgermyl)-2,2-dimethyl-1-propanol (24%).[1c] We examined the reaction of esters with triphenylgermyllithium, which is known to have sufficient nucleophilicity.[7] Triphenylgermyllithium can be produced by the addition of equimolar quantities of butyllithium into a tetrahydrofuran (THF) solution of triphenylgermane.[8] To a flesly produced THF solution of triphenylgermyllithium were added equimolar quantities of esters at ambient temperature. After stirring for 5—10 min, the reaction mixture was quenched with a saturated aqueous ammonium chloride solution to give acylgermanes in satisfactory yields (60—80%). The yield was independent of the bulkyness of R (methyl, ethyl, and *t*-butyl groups).

$$\mathrm{RCOOR'} + \mathrm{Ph_3GeLi} \rightleftharpoons \mathrm{RCOGePh_3} + \mathrm{LiOR'}$$

However, small amounts of triphenylgermane were always recovered without any other by-products. Thus, the reaction is not prone to proceed quantitatively. The incompleteness of the reaction can presumably be attributed to an equilibrium attainted under the basic conditions; but here, by the use of 10% excess of esters, the yield was not improved. Further, the reaction of esters having α-active hydrogen (e.g., (+)-methyl (*S*)-2-phenylpropionate) gave almost racemic acylgermanes under such conditions. The results of a synthesis of (α-arylacyl)triphenylgermanes are presented in Table 1.

The acyl carbon-germanium bond of acyltriphenylgermanes was found to be smoothly fissioned with light with a wavelength >300 nm. Actually, benzoyltriphenylgermane and propionyltriphenylgermane in THF was rapidly degradated in a Pyrex flask upon irradiation by a sunlamp (1 h) or a high-pressure mercury lamp (20 min). Though the reaction is apparently complex (many spots on their thin-layer chroma-

Table 1. Synthesis of Benzylic Acylgermanes from the Corresponding Esters

Compd	Yield[a]	Mp	IR (C=O)	^{1}H NMR δ/ppm	Found (Calcd)/%	
	%	°C	cm^{-1}	(J/Hz)	C	H
1a	70	81—83	1655	4.05(s, 2H), 7.18—7.70 (m, 20H)	73.88 (73.82)	5.25 (5.24)
1b	74	74—76	1660	2.23(s, 3H), 3.86(s, 2H), 6.81—6.73(m, 4H), 7.30(m, 15H)	74.42 (74.20)	5.51 (5.53)
1c	66	136—138	2220,[b] 1675	3.95(s, 2H), 7.40(m, 19H)	72.43 (72.38)	4.69 (4.72)
1d	71	115—117	1660	1.33(d, J=7, 1H), 4.30 (q,J=7, 1H), 7.13—7.70 (m, 20H)	74.18 (74.20)	5.55 (5.53)
1e	65	133—139	1665	4.36(ABq, J=11 and 23, 2H), 4.85(s, 1H), 6.80—7.75(m, 25H)	75.00 (74.90)	5.30 (5.33)

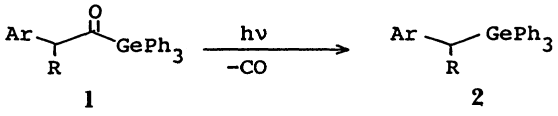
a) Isolated yield. b) Absorption of C≡N group.

Table 2. Synthesis of Benzyltriphenylgermanes by Photochemical Decarbonylation

Compd	Yield[a)]	Mp	^{1}H NMR δ/ppm	Found (Calcd)/%	
	%	°C	(J/Hz)	C	H
2a	95	84—87[b)]	2.96(s, 2H), 7.12(m, 20H)	76.09 (76.01)	5.64 (5.61)
2b	97	78—80	2.17(s, 3H), 2.87(s, 2H), 6.75(m, 4H), 7.22(m, 15H)	76.46 (76.34)	5.86 (5.91)
2c	88	135	2.95(s, 2H), 7.26(m, 19H)	74.27 (74.35)	5.02 (5.04)
2d	92	119—120	1.60(d, J=7.5,3H), 3.26 (q, J=7.5, 1H), 6.8—7.15 (m, 5H), 7.31(br s, 15H)	76.44 (76.34)	5.96 (5.91)
2e	90	125—127	4.49(ABq, J=12 and 31, 2H), 5.15(s, 1H), 6.90—7.60 (m, 25H)	76.70 (76.69)	5.59 (5.63)

a) Isolated yield. b) 86.5 °C in the literature; H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 5509 (1955).

tography after irradiation), the corresponding carboxylic acids were obtainted by a treatment of crude materials with 10% hydrochloric acid in low yields with hexaphenyldigermane.



	Ar	R
a	Ph	H
b	p-$CH_3C_6H_4$	H
c	p-CNC_6H_4	H
d	Ph	CH_3
e	Ph	$PhCH_2O$

In contrast, α-arylacylgermanes upon irradiation resulted in a different mode of fission. The stability of benzyl radical is well-known in various kinds of photochemistry[9)] and the photochemical fission of germanium-carbon bonds with shorter wavelengths has been observed regarding the benzyl radical,[10)] as well as that of silicon-carbon bonds via a benzyl radical-silyl radical pair in a primary photochemical process.[11)] When a THF solution containing α-arylacylgermanes in a Pyrex flask filled with argon was irradiated at ambient temperature with a 400-W high-pressure mercury lamp for 30 min, the reaction quantitatively gave α-arylalkylgermanes. (α-Arylacyl)triphenylgermanes absorbed light in their $n\rightarrow\pi^*$ excited states,[12)] and might have fissured to give an acyl radical-germyl radical pair; then, decarbonylation might have taken place at the acyl radical, because of the inherent stability of the α-arylalkyl radical. The photoreaction of α-arylacylgermanes in the presence of olefin (e.g., methyl acrylate) did not give any addition products; thus, the recombination between the resulting α-arylalkyl and triphenylgermyl radicals might have been an intramolecular process in a solvent cage.

Experimental

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled from sodium/bezophenone immediately prior to use. All melting points were uncorrected. IR spectra were determined with a JASCO A-302 infrared spectrophotometer. UV spectra were measured with a JASCO UNIDEC 670 spectrophotometer. ^{1}H NMR spectra were obtained with a Hitachi R-90H spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Merck silica gel 60 (230—400 mesh) was used for flash column chromatography and Merck aluminium sheets (silica gel 60) was used for thin layer chromatography. Ethyl 2-benzyloxyphenylacetate was prepared by the treatment of ethyl 2-hydroxyphenylacetate with benzyl bromide/sodium hydride in N,N-dimethylformamide.

General Procedure for the Reaction of Esters with Triphenylgermyllithium. Preparation of (Phenylacetyl)triphenylgermane (1a): To a solution of triphenylgermane (304.6 mg, 1 mmol) in THF (10 cm^3) was added butyllithium (15% solution in hexane, 0.62 cm^3, 1 mmol) at 0—−5 °C. The solution was stirred at room temperature for 1 h. Methyl phenylacetate (150.2 mg, 1 mmol) was added via syring to the solution. After stirring for 10 min, the reaction mixture was quenched with a saturated aqueous ammonium chloride solution and the organic layer was extracted with diethyl ether. The ethereal layer was dried over magnesium sulfate. After evaporation of the solvent, a crude solid was obtained and then purified by flash column chromatography (9 g of silica gel with 3% ethyl acetate in hexane) to give (phenylacetyl)triphenylgermane **1a** (296 mg) in 70% yield.

General Procedure for the Photochemical Decarbonylation of (α-Arylacyl)triphenylgermanes. Preparation of Benzyltriphenylgermane (2a): The solution of **1a** (84.6 mg, 0.2 mmol) in THF (10 cm^3) was irradiated with a 400-W high-pressure mercury lamp with stirring under argon for 30 min. The solvent was removed with a rotary evaporator to give a solid which was purified by flash column chromatography (6 g of silica gel with hexane) to give benzyltriphenylgermane (75 mg) in 95% yield.

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12) The UV spectra of compounds **1a**—**1c** were measured in 99% ethanol; **1a**: λ_{max}363 (ε 185), **1b**: λ_{max} 365 (ε 208), **1c**: λ_{max} 360 (ε 313) and λ_{max} 374 nm (ε 293).