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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Vadim V. Bardin (1993) Perfluoroalkylation of CIGeEt₃ with Perfluoroalkyl Bromides and Iodides and $P(NEt_2)_3$, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:10, 1409-1413, DOI: <u>10.1080/00397919308011230</u>

To link to this article: http://dx.doi.org/10.1080/00397919308011230

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PERFLUOROALKYLATION OF CIGeEt3 WITH PERFLUOROALKYL

BROMIDES AND IODIDES AND P(NEt2)3

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Abstract: RFGeEts were prepared by reaction of CF3Br, CF3I or $n-C_4F_9Br$ with P(NEt₂)s whereas CF₂Br-CF₂Br underwent by debromination and *tert*-C₄F9I gave only FGeEt3. Interaction of CCl₄, ClGeEts and P(NEt₂)s led to formation of CCl₃GeEt3.

Recently, trichloromethylation of halosilanes with CCl₄ - $P(NEt_2)_3$ ¹, their perfluoro and polyfluorohaloalkylation with R_{FX} - $P(NEt_2)_3$ (X = Cl, Br, I) ²⁻⁵ have been described. Nevertheless, there are no data about the application of this reaction for the preparation of the corresponding germanes. This paper presents results of the synthesis of perfluoroalkyltriethylgermanes and trichloromethyltriethylgermane using tris(diethylamino)phosphine and some limitation of this reaction.

Treatment of the solution of bromotrifluoromethane and chlorotriethylgermane in CH₂Cl₂ with tris(diethylamino)phosphine at -60 °C and heating of the reaction mixture up to 20-22 °C leads to formation of trifluoromethyltriethylgermane and the corresponding phosphonium salt. Trifluoromethylation of CIGeEt₃ with iodotrifluoromethane and $P(NEt_2)_3$ proceeds in a similar manner.

This approach is convenient for the synthesis of fluorinated tetraalkylgermanes which contain a long unbranched perfluoroalkyl group. For instance, the interaction of *n*-bromononafluorobutane with ClGeEt₃ and P(NEt₂)₃ leads to the formation of nonafluoro-*n*-butyltriethylgermane.

 $P(NEt_2)_3$ $n-C_4F_9Br + CIGeEt_3 \longrightarrow n-C_4F_9GeEt_3$ $-P(NEt_2)_3CIBr \qquad 78 \%$

On the other hand, the interaction of CIGeEt₃ with $P(NEt_2)_3$ and nonafluoro-*tert*-butyl iodide gives only fluorotriethylgermane in high yield and no RFGeEt₃ was detected in the reaction mixture. Attempted synthesis of 2-bromotetrafluoroethyltriethylgermane from CF₂Br-CF₂Br failed due to the fast debromination of this substance by tris(diethylamino)phosphine.

It should be noted that CCl4 easily alkylates ClGeEt3 under the action of P(NEt2)3.

CCl4 + ClGeEt3

-P(NEt2)3Cl2 68 %

Table

Perfluoroalk	viation	of	CIGeEt ₂
1 CITICO CUTA	Juanon	01	

RfX	CIGeEt₃	P(NEt ₂) ₃	Product	Yield
mmol	mmol	mmol		%
CF3Br				
121	51	48	CF3GeEt3	52
CF3I				
87	51	57	CF3GeEt3	66
n-C₄F9Br				
84	51	61	n-C₄F9GeEt3	78
t-C4F9I				
31	25	25	FGeEt₃	87
1,2-C2Br2F4				
53	51	55	CF2=CF2	85

Experimental

The ¹H and ¹⁹F NMR spectra were recorded on a Bruker WP 200 SY spectrometer at 200 MHz (¹H) and 188.3 MHz (¹⁸F) (TMS and CFCI₃ as internal references). The IR spectra were recorded on a Specord M 80 instrument.

Perfluoroalkylation of chlorotriethylgermane. A solution of chlorotriethylgermane and haloperfluoroalkane in CH_2Cl_2 (30 mL) was cooled up to -(40-50) °C with stirring in a dry argon atmo-

sphere (CF₃Br and CF₃I were condensed at -60 °C). Then a solution of P(NEt₂)₃ in an equal volume of CH₂Cl₂ was added dropwise within 15-20 min. The reaction mixture was stirred for 1-1.5 h and heated up to RT within 2-3 h. The resulted solution was extracted with pentane (3 x 50 mL), the extract washed with ice water, dried with MgSO₄ and the solvent distilled off at reduced pressure. Vacuum distillation of the residue gave the product (Table).

The reaction of CF₂Br-CF₂Br was carried out in a similar way but evolution of tetrafluoroethene (identified by IR) proceed during an addition of P(NEt₂)₃ and no fluoro-containing substance was found in the reaction mixture after heating up to RT. *Trifluoromethyltriethylgermane:* Bp 147 °C [lit. ⁶ 59-60 °C (40 mm)]; ¹H NMR (CCl₄), δ : 0.95-1.15 (GeEt₃); ¹⁹F NMR (CCl₄), δ : -55.7 (s) [lit. ⁷ 22.7 ppm from ext. CF₃COOH].

Nonafluoro-n-butyltriethylgermane: Bp 75-76 °C (20 mm); ¹H NMR (CCl4), δ: 0.96-1.11 (GeEt₃); ¹⁹F NMR (CCl4), δ: -81.9 (CF₃), -120.1 (CF₂), -120.9 (CF₂), -126.6 (CF₂); IR (neat liquid): 2968, 2920, 2887, 1466, 1429, 1386, 1349, 1236, 1197, 1152, 1129, 1096, 1062, 1017, 1000, 853, 807, 779, 743, 718, 705, 680, 615, 584 cm⁻¹. Found: C 32.1, H 4.04, F 45.0. C10H15F3Ge. Requires: C 31.7, H 3.96, F 45.2.

Trichloromethylation of chlorotriethylgermane. A solution of CCl_4 (20 mmol) and $ClGeEt_3$ (20 mmol) in 20 mL of pentane was cooled with ice water in a dry argon atmosphere. Then a solution of $P(NEt_2)_3$ (21 mmol) in 5 mL of pentane was added dropwise. Immediately a white precipitate was formed. The reaction mixture

PERFLUOROALKYLATION OF CIGeEt₃

was stirred for 1.5 h and filtered. *Trichloromethyltriethylgermane* was isolated by vacuum distillation in 68 % yield. Bp 92-95 °C (6 mm); ¹H NMR (CCl₄), δ: 1.10-1.14 (GeEt₃); IR (neat liquid): 2968, 2947, 2917, 2880, 1460, 1386, 1255, 1240, 1031, 1012, 980, 765, 666, 587, 540 cm⁻¹. Found: C 30.5, H 5.77, Cl 38.1. C₇H₁₅Cl₃Ge. Requires: C 30.2, H 5.39, Cl 38.3.

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(Received in The Netherlands 15 December 1992)