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LETTERS

A novel access to organogermanium compounds

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Abstract

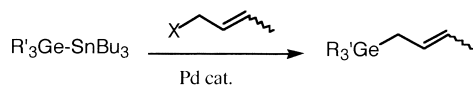
A simple and efficient procedure has been developed for the synthesis of organogermanium compounds by one-pot reaction of halogenogermanes, organic halides and magnesium under microwave irradiation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: organogermanium and compounds; sonication.

As shown by the numerous papers specifically dedicated to the study of sonochemical reactions, the interest of synthetic chemists is becoming increasingly focused on the use of sonochemical methods in organic synthesis.^{1–7}

Furthermore, the chemistry of the carbon–germanium bond has been studied in detail in the past and this bond was typically prepared by the reaction of germanium halides with organomagnesium (or organolithium) compounds.^{8,9} The yield of the desired product is highly dependent on the accessibility of the organomagnesium reactant.¹⁰

Some reports have recently been published concerning new methodologies for the formation of the carbon–germanium bond, for example the reactions of allylic halides with germysilane or germystannane under palladium catalysis.¹¹ This has shown a new focus for germanium chemistry.¹² We report a simplified and improved one-step synthesis of organogermane compounds by Barbier reaction between germanium halides, magnesium turnings and organic halides in the presence of 1,2-dibromoethane under ultrasonic conditions.¹³


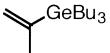

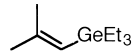

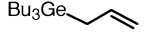

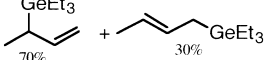

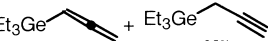

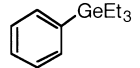
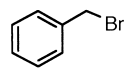
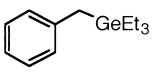
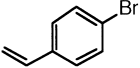
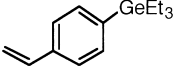


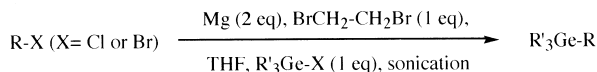
A wide range of germane compounds were subjected to this procedure to produce the corresponding products in quite high yields. Gram-scale reactions with 3–5 g of germanium

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halide¹⁴ were also carried out and found to give analogously good yields of the corresponding products (e.g. entry 7). The results are presented in Table 1.

Table 1

Entry	R-X	R'	R-GeR' ₃	N°	Yield
1		Bu		1a	83
2		Et		2a	82
3		Bu		3a	95
4		Et		4a + 4b	74
5		Et		5a + 5b	90
6		Et		6a	90
7		Et		7a	80
8		Et		8a	74



As we can see, this methodology can accommodate a variety of organic functional halides, the yields are nearly quantitative but need certain optimisation conditions for the substituted allylic halides (e.g. entry 4). It should be noted that: (a) the quality of the reactants is not critical (solvent or halides) and they do not need careful purification before use; and (b) the use of dibromoethane is not necessary but usually increases the yield.

In conclusion, the present procedure provides an efficient one-pot synthesis of functional organogermanium compounds from expensive germanium halides. The notable advantages of this procedure are: (a) operational simplicity; (b) fast reaction; and (c) high yield. We believe this will provide a better and more practical alternative to the existing methods for the synthesis of germanium compounds.

Acknowledgements

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- For proper use of cleaning bath, see: Mason, T. J. *Practical Sonochemistry*; Ellis Horwood: London, 1991.
- Typical procedure: preparation of 8a*: A Schlenk tube containing 25 mL of THF, 0.60 g (25 mmol, 2 equiv. mol) of magnesium turnings, 0.54 mL (6.22 mmol, 1 equiv. mol) of 1,2-dibromoethane, 3 g (12.5 mmol, 1 equiv. mol) of triethylbromogermane and 2.28 g (12.5 mmol, 1 equiv.) of 4-bromostyrene is plunged into a commercial ultrasonic cleaning bath (Branson B1200 E1, working frequency: 47 KHz) and sonicated for 2 h. The mixture is washed with 20 mL of a saturated solution of sodium chloride and extracted with diethylether (2×20 mL). The organic layers are dried over magnesium sulfate, the solvents are removed under reduced pressure and the compound **8a** is purified by column chromatography (petroleum ether:diethylether, 95:5). IR: 3060, 2980, 2900, 1635, 1400, 1090, 990, 830; ¹H NMR δ ppm (CDCl₃, 200 MHz): 0.9–0.12 (15H, m), 2.24 (1H, dd, J = 11 Hz, J = 2 Hz), 5.79 (1H, dd, J = 11 Hz, J = 2 Hz), 6.73 (1H, dd, J = 17.5 Hz, J = 11 Hz), 7.39 (2H, d, J = 8.5 Hz), 7.43 (2H, d, J = 8.5 Hz); ¹³C NMR δ ppm (50 MHz): 4.4 (3C), 9.0 (3C), 113.8, 125.9, 134.6, 137.3, 137.7, 140.1; MS (70 eV) *m/z* (⁷⁴Ge): 264 (M, 17), 235 (100), 207 (50), 177, 151 (14); anal. calcd for C₁₄H₂₂Ge: C, 63.69; H, 8.43; found: C, 63.56; H, 8.40. HMRS calcd: 264.0931; found: 259.0934.