

A dense liquid (34.3 g) was obtained. Found (%): Al, 5.57. $C_{30}H_{63}Al$. Calculated (%): Al, 5.98. After this product (22.6 g) in heptane was oxidized by air oxygen, decanol (18.6 g) was obtained, b.p. 108–109 °C (7 Torr), n_D^{20} 1.4352 (cf. Ref. 5: b.p. 107–108 °C (7 Torr), n_D^{20} 1.43719).

References

1. A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem. Soc.*, 1947, **69**, 1199.

2. K. Ziegler, H.-G. Gellert, H. Martin, K. Nagel, and J. Schneider, *Anal.*, 1954, **589**, 91; 115.
3. F. M. Brower, N. E. Matzek, P. F. Reigel, H. W. Rinn, Ch. B. Roberts, D. L. Schmidt, J. A. Snover, and K. Terada, *J. Am. Chem. Soc.*, 1976, **98**, 2450.
4. H. Clasen, *Angew. Chem.*, 1961, **73**, 322.
5. *Dictionary of Organic Compounds*, Eds. I. Heilborn and H. M. Bunbury, London, 1946.

Received May 14, 1997

Palladium-catalyzed reactions of organoboron compounds with acyl chlorides

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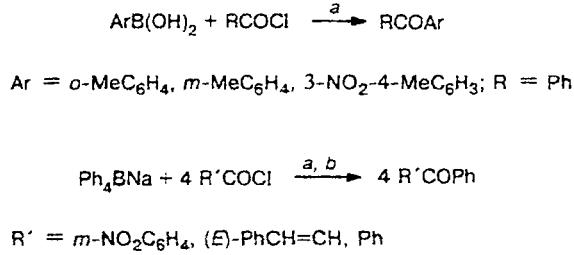
We have shown previously^{1–3} that the reaction of organoboron compounds (OBC) with organic halides, which is an important method for the formation of a new C–C bond,⁴ occurs readily in an aqueous organic solvent or in water when catalyzed by "ligand-free" palladium⁵ in the presence of a base. However, the interactions of OBC with acyl chlorides under similar conditions remain almost unstudied. It has only been reported⁶ that the $Pd(Ph_3P)_4$ -catalyzed reaction of Ph_4BNa with $RCOCl$ involves only one phenyl group of borate and results in the corresponding ketones $RCOPh$.

In this work, we have established for the first time that chloroanhydrides of carboxylic acids react with arylboric acids in the presence of "ligand-free" palladium to form the corresponding diaryl ketones in high yields (Scheme 1). It also was found that ketones are formed under similar conditions from chloroanhydrides of carboxylic acids and Ph_4BNa , and all four phenyl groups of OBC participate in the reaction.

The $PdCl_2$ -catalyzed reaction of benzoyl chloride with $ArB(OH)_2$ or Ph_4BNa in the presence of Na_2CO_3 in aqueous acetone is completed in 1 h at room temperature. Easily hydrolyzed acyl chlorides (*m*-nitrobenzoyl chloride and cinnamoyl chloride) react smoothly with OBC catalyzed by $Pd(OAc)_2$ in anhydrous acetone in the presence of Na_2CO_3 .

***m*-Methylbenzophenone.** *m*-Tolylboric acid (0.697 g, 0.5 mmol) was dissolved in a mixture of acetone (2 mL) and an aqueous 1.63 M solution of Na_2CO_3 (1 mL) in an atmo-

Scheme 1



Reagents and conditions: a. 1 mol.% $PdCl_2$, Na_2CO_3 , acetone, water, 20 °C; b. 1 mol.% $Pd(OAc)_2$, Na_2CO_3 , acetone, 20 °C.

sphere of argon, and $PhCOCl$ (0.06 mL, 0.5 mmol) and an aqueous 0.1 M solution of $PdCl_2$ (0.05 mL, 0.005 mmol) were added. After stirring at 20 °C for 15 min, Pd black precipitated from the reaction mixture. Then an aqueous 0.1 M solution of $PdCl_2$ (0.05 mL, 0.005 mmol) was added, and the mixture was stirred for 30 min. The reaction mixture was diluted with water (10 mL), saturated with $NaCl$, and extracted with ether (5×5 mL). The ether extract was dried by $MgSO_4$. After evaporation of the ether, *m*-methylbenzophenone (0.0804 g, 82%) was obtained, m.p. 220–222 °C (cf. Ref. 7: m.p. 221–222 °C).

3-Nitro-4-methylbenzophenone (yield 96%), *o*-methylbenzophenone (80%), and benzophenone (96%) were obtained similarly from $Ar(OH)_2$ or Ph_4BNa and $PhCOCl$.

m-Nitrobenzophenone. $\text{Pd}(\text{OAc})_2$ (0.0022 g, 0.01 mmol, 1 mol.% Pd) was added in an atmosphere of argon to a mixture of Ph_3BNa (0.0922 g, 0.25 mmol), Na_2CO_3 (0.159 g, 1.5 mmol), and $m\text{-NO}_2\text{C}_6\text{H}_4\text{COCl}$ (0.1858 g, 1 mmol) in dry acetone (9 mL), and the mixture was stirred at 20 °C for 2.5 h. Then acetone was evaporated on a rotary evaporator, and the residue was diluted with water (10 mL), extracted with chloroform (3×5 mL), and dried with MgSO_4 . After chloroform was removed on a rotary evaporator, *m*-nitrobenzophenone (0.149 g, 66%) was obtained, m.p. 96–97 °C (cf. Ref. 8: m.p. 95 °C).

Chalcone was obtained similarly from Ph_3BNa and cinnamoyl chloride (yield 96%).

Thus, the catalytic reactions found occur under very mild conditions and can be used as a new efficient method for the synthesis of nonsymmetric ketones.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09037).

References

1. N. A. Bumagin, V. V. Bykov, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2394 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2206 (Engl. Transl.)].
2. N. A. Bumagin, V. V. Bykov, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR*, 1990, **315**, 1133 [*Dokl. Chem.*, 1990 (Engl. Transl.)].
3. V. V. Bykov, A. A. Kir'yanov, N. A. Bumagin, and I. P. Beletskaya, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1582 [*Russ. Chem. Bull.*, 1996, **45**, 1508 (Engl. Transl.)].
4. A. Suzuki, *Pure Appl. Chem.*, 1985, **57**, 1749.
5. N. A. Bumagin, I. G. Burnagina, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR*, 1984, **274**, 1103 [*Dokl. Chem.*, 1984 (Engl. Transl.)].
6. C. S. Cho, K. Itoh, and S. Uemura, *J. Organomet. Chem.*, 1993, **443**, 253.
7. H. C. Brown and H. L. Young, *J. Org. Chem.*, 1957, **22**, 719.
8. *Dictionary of Organic Compounds*, Eds. G. Heilbron and H. M. Bumbery, London, 1946, **3**, 101.

Received January 10, 1997;
in revised form May 22, 1997

1-(1-Trimethylsilylcyclopropyl)germatrane as the first representative of cyclopropylgermatranes

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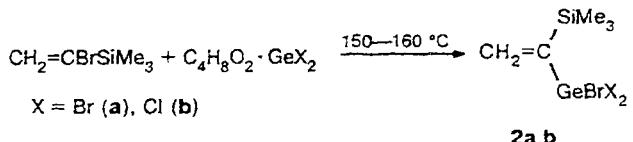
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Virtually all germatranes exhibit physiological activities that largely depend on the substituents present in their molecules.¹ Therefore, it seemed of interest to prepare a germatranes molecule containing a cyclopropane fragment, whose presence accounts for the activity of some compounds, in particular, pyrethroids.²

In this study, we synthesized the first representative of cyclopropylgermatranes, *viz.*, 1-(1-trimethylsilylcyclopropyl)germatrane (1). As the first step, we prepared 1-tribromogermyl-1-trimethylsilylethylene³ (2a) (yield 75%) and 1-bromodichlorogermyl-1-trimethylsilylethylene (2b) (yield 82%) by the reactions of 1-bromo-

vinyltrimethylsilane with the dioxane complexes of dichloro- and dibromogermylene, respectively.⁴



Subsequently 1-(trimethylsilyl)vinyltrihalogenanes 2 were converted into 1-trimethylsilyl-1-trimethoxygermylethylene (3) by treating them with methanol.