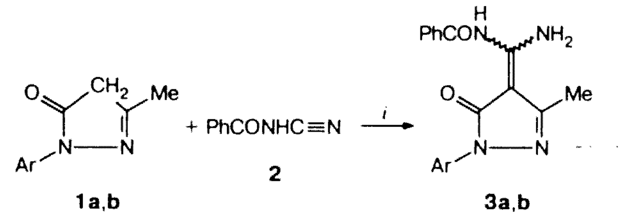

Ar = p-$NO_2C_6H_4$ (**a**), C_6F_5 (**b**)
Reagents and conditions: *i.* $Ni(OAc)_2$, DMF, Δ, 2 h.

for 2 h. The precipitate that formed during cooling was filtered off and recrystallized (DMF). Ketene aminal **3a** (0.24 g, 65%) was obtained (m.p. 336—338 °C).

MS (IE, 70 eV), *m/z*: 365 $[M]^+$. IR (KBr), ν/cm^{-1}: 3460, 3290 br, 3120—2800 (NH), 1698 sh, 1675, 1650, 1595. ^{1}H NMR (DMSO-d_6), δ: 2.40 (s, 3 H, Me), 7.60—8.10 (m, 5 H, Ph); 8.29 (br.s, 5 H, $C_6H_4NO_2$ + NH); 9.63 (br.s, 1 H, NH), 13.60 (br.s, 1 H, NH).

4-(*N*-Benzoyl)diaminomethylene-1-pentafluorophenyl-3-methylpyrazolin-5-one (3b) was obtained from pyrazolinone **1b** and cyanamide **2** similarly to the preparation of compound **3a**. After the mixture was refluxed, the solvent was distilled off, and water was added to the residue, which was filtered off and recrystallized from MeCN. The yield of **3b** was 54%, m.p. 254—256 °C. MS (IE, 70 eV), *m/z*: 410 $[M]^+$. ^{1}H NMR (DMSO-d_6), δ: 2.40 (s, 3 H, Me), 7.60—8.10 (m, 5 H, Ph), 8.32 (br.s, 1 H, NH), 9.65 (s, 1 H, NH), 13.65 (br.s, 1 H, NH).

The data of elemental analysis of compounds **3a,b** correspond to the calculated values.

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References

1. V. A. Dorokhov, M. F. Gordeev, Z. K. Dem'yanets, M. N. Bochkareva, and V. S. Bogdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1806 [*Bull. Acad. Sci. USSR, Div. Chem. Sci*, 1989, **38**, 1654 (Engl. Transl.)].
2. V. A. Dorokhov and M. F. Gordeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1211 [*Bull. Acad. Sci. USSR, Div. Chem. Sci*, 1989, **38**, 1104 (Engl. Transl.)].

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One-step synthesis of 4,5-dichloroanthrone from 1,8-dichloroanthraquinone

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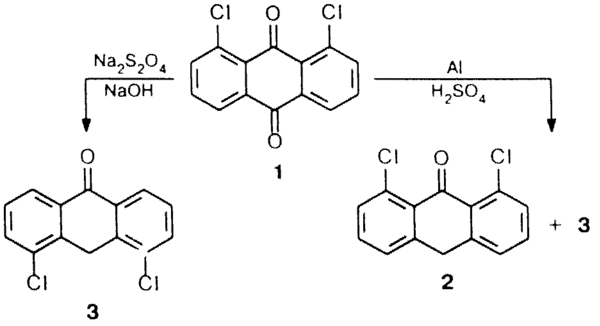
When 1,8-dichloroanthraquinone (**1**) reacts with reducing agents, the formation of both 1,8-dichloro- (**2**) and 4,5-dichloroanthrones (**3**) is possible. It is known[1] that reduction by powdered Al and conc. H_2SO_4 leads to anthrone **2**, while anthrone **3** can be obtained from 1,8-dichloroanthracene[2] in six stages or from 1,8-dichloro-9-methoxy-10-(dimethoxyphosphoryloxy)anthracene synthesized from quinone **1** and trimethyl phosphite in three stages.[3]

We found that anthrone **3** can by obtained with high regioselectivity by the reduction of quinone **1** by sodium dithionite in an alkaline medium. Small amounts of anthrone **3** are also formed when **1** is reduced in the Al—H_2SO_4 system. According to the data of ^{1}H NMR spectroscopy, the ratio of anthrones **2** and **3** formed is equal to ~ 4 : 1.



The results obtained indicate that the dependence of the direction of reduction of quinone **1** on the nature of the reducing agent is similar to that for 1-chloroanthraquinone.[4]

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4,5-Dichloroanthrone (3). A suspension of quinone **1** (0.56 g, 2 mmol) in dioxane (10 mL) and then $Na_2S_2O_4 \cdot 2H_2O$ (1,26 g, 6 mmol) were added to a solution of NaOH (0.48 g, 12 mmol) in water (50 mL) heated to 100 °C. The mixture was stirred for 20 min with boiling and then cooled. The residue was separated and recrystallized from benzene. Anthrone **3** was obtained (0.29 g, 59%), m.p. 196—201 °C (*cf.* Ref. 2: m.p. 198 °C). ^{1}H NMR ($CDCl_3$), δ: 4.17 (s, 2 H, CH_2), 7.42 (br.t, 2 H, H(2), H(7), J = 8.0 Hz), 7.67 (br.d, 2 H, H(3), H(6), J = 8.0 Hz), 8.25 (br.d, 2 H, H(1), H(8), J = 8.0 Hz). IR (KBr), ν/cm^{-1}: 1660 (C=O). MS, m/z: 262 $[M]^+$.

References

1. E. de B. Barnett and M. A. Matthews, *J. Chem. Soc.*, 1923, **123**, 2549.
2. E. de B. Barnett, J. Cook, and M. A. Matthews, *Rec. Chim. Pays-Bas.*, 1926, **45**, 68; Beilst., 7, II, 418.
3. J. S. Meek and L. L. Koh, *J. Org. Chem.*, 1968, **33**, 2942.
4. V. A. Loskutov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, No. 2 [*Russ. Chem. Bull.*, 1997, **46** (Engl. Transl.)].

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The first example of Ge—Ge and Sn—Sn bond cleavage by arylmagnesium halides

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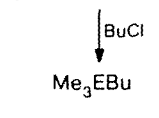
It is known[1,2] that E—E bonds (E = Ge, Sn) can be cleaved by the action of organolithium compounds, alkali metals, their alkoxides, hydroxides, and fluorides to form metal-centered anions R_3E^-. In this work, we report on the first example of E—E bond (E = Ge, Sn) cleavage by Grignard reagents under mild conditions. The reaction found suggests the intermediate formation of organogermanium (organotin) Grignard reagents of the R_3EMgX type (E = Ge, Sn) and can serve as a new method for generation of these poorly studied organometallic compounds.[1,2]

Hexamethyldistannane and hexamethyldigermane react readily with PhMgBr (THF, 20 °C) to form a mixture of equimolar amounts of the corresponding $PhEMe_3$ and Me_3EBu or Me_3EH (E = Ge, Sn) in high yields (according to the data of GC-MS and ^{1}H NMR spectroscopy) after treatment of the reaction mixture with n-BuCl (or H_2O).



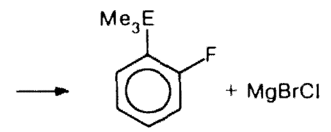
(1)

E = Ge, Sn; Ar = Ph; o-FC_6H_4

The formation of Me_3EBu (or Me_3EH) when n-BuCl (or H_2O) is added to the reaction mixture is significant evidence that organogermanium (organotin) Grignard reagents Me_3EMgBr are involved in the reactions of ArMgX with Me_6E_2 (E = Ge, Sn).

Under similar conditions (THF, 20 °C), the Si—Si bond in Me_6Si_2 does not cleave under the action of o-FC_6H_4MgBr.

Reaction (1) occurs fairly readily. Thus, even the very labile Grignard reagent from o-bromofluorobenzene (o-FC_6H_4MgBr) cleaves the E—E bonds in Me_6E_2 (E = Ge, Sn) in THF at 20 °C more rapidly than it decomposes to give MgBrF and dehydrobenzene.[3] According to the data of GC-MS, the reaction products (o-$FC_6H_4EMe_3$ and Me_3EBu) are formed in quantitative yields after treatment of the reaction mixture with n-BuCl. The intermediate participation of labile o-fluorophenylmagnesium bromide in the transformations described above was proved by trapping reactions. o-Bromofluorobenzene reacts readily with Me_3ECl (E = Si, Sn)



E = Si, Sn

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