Letters to the Editor

A convenient method for the synthesis of chlorocymantrene and bromocymantrene

Yu. I. Lyakhovetsky, P. G. Mingalyov, T. Yu. Orlova, S. O. Yakushin, and Yu. S. Nekrasov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Chlorocymantrene (**1**) and bromocymantrene (**2**) generally are obtained from cymantrene (cyclopentadienylmanganese tricarbonyl, CMT) by means of two-step syntheses, with the isolation of intermediate cymantrenylmercury halogenides[1] or cymantreneboric acid[2]. Direct halogenation of CMT is not possible because it decomposes under the action of chlorine and bromine[3]. The other existing methods are also two- or multi-step processes, since they involve the preliminary preparation of halocyclopentadienylthallium[4], diazocyclopentadiene[5] or aminocymantrene[6].

On the other hand, there exists a method which allows the introduction of a halogen into molecules of organic and organometallic compounds *via* a metal-halogen interchange reaction between their lithio derivatives and polyhalogenated hydrocarbons[7,8]. The method has been employed for the introduction of a halogen into some complexes of tricarbonylchromium with aromatic ligands[9,10]. CMT is known to be rather easily metallated at the cyclopentadienyl ring with BuLi to form a monolithiated derivative[11]. We used this as a basis to develop a simple "one-pot" method for the synthesis of complexes **1** and **2** from commercially available CMT, involving the successive treatment of the latter with BuLi and the corresponding polyhalogenated hydrocarbon, both also being commercially available.

To a stirred solution of CMT (2 mmol) in 40 mL of anhydrous THF at −63.5 °C (in a $CHCl_3$/liquid N_2 bath) under an atmosphere of argon, purified from oxygen and moisture, a twofold excess of BuLi in hexane was added. After 1 h, CCl_4 (20 mmol) was added, and the resulting solution was allowed to warm to ~20 °C and kept at this temperature for 1.5 h. The reaction mixture was then treated with AcCl (4 mmol) to decompose the possible residues of BuLi, and evaporated *in vacuo*. The residue was dissolved in hexane, and complex **1** was isolated by means of column chromatography on silica gel with hexane as eluent (the separation was monitored visually, the main yellow band being collected). The yield of **1** was 84%. ^{1}H NMR (C_6D_6, δ, ppm): 3.65 (m, 2H), 4.14 (m, 2H). The spectrum also contained a singlet at 3.97 ppm corresponding to the impurity (<1%) of the starting CMT. Mass spectrum (EI, 70 eV), *m/z* (I_{rel} (%)): 240, 238 $[M]^+$ (7.0, 22); 212, 210 $[M-CO]^+$ (1.5, 4.1); 184, 182 $[M-2CO]^+$ (9.2, 29); 156, 154 $[M-3CO]^+$ (32, 100); 130, 128 $[C_3H_2ClMn]^+$ (1.9, 4.3); 92, 90 $[MnCl]^+$ (12, 28); 63 $[C_5H_3]^+$ (3.7); 55 $[Mn]^+$ (17). When the reaction mixture was quenched with water or AcOH instead of AcCl, product **1** was isolated in a yield of *ca.* 60%.

A similar procedure with the use of a 1.6-fold excess of BuLi and 5-fold excess of 1,2-dibromotetrafluoroethane (**3**) was employed to synthesize complex **2**, which was isolated in a 68% yield. In this case the ^{1}H NMR spectra indicated that product **2** contained ~4% of CMT, recrystallyzation from hexane failing to get rid of it.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2046—2047, November, 1994.

1066-5285/94/4311-1935 $12.50

By application of the related procedure, we have also obtained bromobenchrotrene from benchrotrene and compound **3** in a 57% yield. The product was identified by mass and ^{1}H NMR spectra.

References

1. V. A. Nefedov, *Zh. Obshch. Khim.*, 1969, **39**, 665 [*J. Gen. Chem. USSR*, 1969, **39** (Engl. Transl.)].
2. A. N. Nesmeyanov, V. A. Sazonova, and N. N. Sedova, *Dokl. Akad. Nauk SSSR*, 1970, **194**, 825 [*Dokl. Chem.*, 1970, **194** (Engl. Transl.)].
3. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and I. B. Zlotina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 898 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1968 (Engl. Transl.)].
4. B. G. Conway and M. D. Rausch, *Organometallics*, 1985, **4**, 688.
5. K. J. Reimer and A. Shaver, *J. Organometal. Chem.*, 1975, **93**, 239.
6. M. Cais and N. Narkis, *J. Organometal. Chem.*, 1965, **3**, 269.
7. B. J. Wakefield, in *Comprehensive Organometallic Chemistry*, Eds G. Wilkinson et al. Pergamon Press, Oxford a.o., 1982, **7**, 75.
8. R. L. Gay, T. F. Crimmins, and C. R. Hauser. *Chemistry and Industry*, 1966, 1635.
9. Yu. I. Lyakhovetsky, M. N. Nefedova, T. Yu. Orlova, and V. I. Losilkina, *Metalloorgan. Khimiya*, 1990, **3**, 135 [*Organometal. Chem. USSR*, 1990, **3**, 72 (Engl. Transl.)].
10. Y. Kondo, J. R. Green, and J. Ho, *J. Org. Chem.*, 1991, **56**, 7199
11. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and Yu. V. Makarov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 686 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1968, 672 (Engl. Transl.)].

Received October 10, 1994

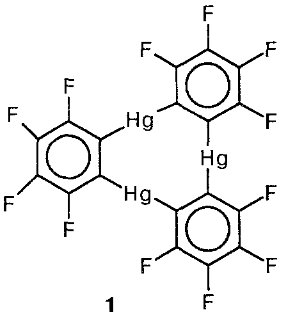
New highly efficient phase transfer catalyst for nitration with dilute nitric acid

A. P. Zaraisky,[a] O. I. Kachurin,[a] L. I. Velichko,[a] I. A. Tikhonova,[b] A. Yu. Volkonsky,[b] and V. B. Shur[b]★

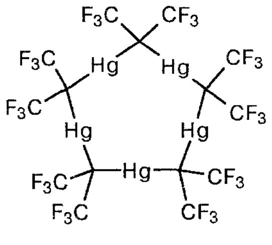
[a]L. M. Litvinenko Institute of Physical Organic Chemistry and Coal Chemistry, Ukrainian Academy of Sciences,
70 ul. R. Luxembourg, 340114 Donetsk, Ukraine
[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

One of the methods of preparation of nitroderivatives of phenols, arylamines and other highly active aromatic substrates is nitration with dilute nitric acid in the presence of initiating additives of nitrous acid[1].

Recently we reported that it is possible to increase the rate of the process[2,3] carrying out this reaction under phase transfer catalysis conditions. We found that[3] the cyclic trimeric perfluoro-o-phenylenemercury (o-$C_6F_4Hg)_3$ (**1**), which is able to form complexes with halide anions[4], is an efficient phase transfer catalyst for nitration of acenaphthene with 21.3 % HNO_3 in the presence of sodium nitrate and NaCl (organic phase: a mixture of benzene and nitrobenzene). The reaction proceeds at room temperature and after ~40 min leads to almost quantitative formation of nitroacenaphthenes. The role of the chloride anions in this reaction is essential. It consists in coordination with mercury atoms of the catalyst to form lipophilic complex anion, which is the phase transfer carrier of cationic electrophilic species responsible for the formation of nitroproducts.



1



2

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2047—2048, November, 1994.

1066-5285/94/4311-1936 $12.50