Experimental

Polymer 1.[1] 3-(4-Biphenyl)-3-chloro-2,1-benzoxathiol 1,1-dioxide (8 g, 22.4 mmol), nitrobenzene (11.2 mL), and $SbCl_5$ (0.14 mL) were placed under a flow of argon in a three-necked flask equipped with a mechanical stirrer and an air-cooled condenser, and the mixture was kept for 10 h at 100 °C. The resulting polymer was dissolved in DMF, precipitated with ethanol, filtered off, washed with ether, and dried for 10 h at 90 °C to give 7.0 g (97%) of polymer 1 as a white amorphous powder. Found (%): C, 70.60; H, 3.91; S, 9.54. $(C_{19}H_{12}SO_3)_n$. Calculated (%): C, 71.25; H, 3.75; S, 10.0.

Polymers 3—5 were prepared in a similar way.

Polymer 2. This polymer was prepared as a white powder from 4,4″-bis(3-chloro-3-sulfophthalide-1,1′:4′,1″-terphenyl (8 g, 12.5 mmol), 1,1′:4′,1″-terphenyl (2.9 g, 12.5 mmol), nitrobenzene (22.4 mL), and $SbCl_5$ (0.24 mL) under the same conditions as polymer 1. Yield 9.4 g (95%). Found (%): C, 75.4; H, 3.70; S, 7.70. $(C_{50}S_2O_6H_{28})_n$. Calculated (%): C, 76.10; H, 3.55; S, 8.12.

Polymer 6 was obtained in a similar way using *N*-methylcarbazole as a comonomer.

Viscosity was measured at 25 °C using the Ubbelohde viscometer. ESR spectra were recorded on an SE/X-2544 ESR spectrometer (Radiopan) in glass tubes of diameter ~4 mm at 20 °C. Electronic spectra were recorded on a Specord M-40 spectrophotometer in 2 mm-thick quartz cells. Freshly distilled aniline and cyclohexanone were used.

A weighed portion of the polymer (20 mg) was dissolved in 1 mL of aniline (or cyclohexanone) and mixed with 1 mL of cyclohexanone (or aniline). A part of the mixture was placed in an ESR tube, and some of the mixture was placed in a cell of the spectrophotometer.

References

1. M. G. Zolotukhin, Sh. S. Akhmetzyanov, A. N. Lachinov, N. M. Shishlov, S. N. Salazkin, Yu. A. Sangalov, and A. P. Kapina, *Dokl. Akad. Nauk SSSR*, 1990, **312**, 1134 [*Dokl. Chem.*, 1990, **312** (Engl. Transl.)].
2. Yu. K. Mikhailovskii, V. A. Azarko, and V. E. Agabekov, *Vestsi Akad. Nauk Belarusi* [*Bull. Beloruss. Acad. Sci.*], 1992, 27 (in Belorussian).
3. W. P. Neumann, W. Uzick, and A. K. Zarkadis, *J. Am. Chem. Soc.*, 1986, **108**, 3762.
4. D. Braun and P. Lehmann, *Macromol. Chem.*, 1976, **177**, 1387.
5. T. Z. Chu and S. Z. Weismann, *J. Chem. Phys.*, 1954, **22**, 21.
6. N. M. Shilov, Sh. S. Akhmetzyanov, M. G. Zolotukhin, I. V. Novoselov, and A. P. Kapina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1992, 1682 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1307 (Engl. Transl.)].
7. A. A. Kuznetsov, S. N. Novikov, and A. N. Pravednikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 297 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **38** (Engl. Transl.)].
8. N. M. Shishlov, Sh. S. Akhmetzyanov, M. G. Zolotukhin, I. V. Novoselov, G. I. Nikiforova, A. P. Kapina, and F. G. Valyamova, *Dokl. Akad. Nauk SSSR*, 1992, **322**, 304 [*Dokl. Chem.*, 1992, **322** (Engl. Transl.)].
9. V. D. Sholle and E. G. Rozantsev, *Usp. Khim.*, 1973, 2176 [*Russ. Chem. Rev.*, 1973, **42**, No. 12 (Engl. Transl.)].
10. D. W. Roberts and D. L. Williams, *Tetrahedron*, 1987, **43**, 1027.
11. N. O. Mchedlov-Petrosyan and I. N. Lyubchenko, *Zh. Obshch. Khim.*, 1987, **57**, 1371 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.)].
12. N. O. Mchedlov-Petrosyan, V. N. Kleshchevnikova, M. I. Rubtsov, L. L. Lukatskaya, R. Salinas Maiorga, and V. I. Kukhtik, *Dokl. Akad. Nauk SSSR*, 1989, **308**, 122 [*Dokl. Chem.*, 1989, **308** (Engl. Transl.)].

Received February 13, 1996;
in revised form October 16, 1996

A simple synthesis of non-solvated galliumtrialkyls

L. I. Zakharkin,* V. V. Gavrilenko, and N. P. Fatyushina

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085

A simple synthesis of non-solvated galliumtrialkyls is proposed based on the reaction of alkyl iodides with a mixture or an alloy of magnesium and gallium in the absence of a solvent or in aliphatic hydrocarbons.

Key words: galliumtrialkyls, alkyl iodides, magnesium, gallium, gallium arsenide.

Trimethylgallium and triethylgallium of high purity are used for the preparation of gallium arsenide semiconducting films by chemical vapor deposition of organometallic compounds.[1–3] The conventional methods by which they are synthesized, by the reaction of gallium trihalides with organolithium, organomagnesium, organo-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 392—393, February, 1997.

zinc, or organomercury compounds, require complicated additional purification of the target products from impurities of starting organometallic compounds.[3] The more convenient procedure for the preparation of Me_3Ga from $GaCl_3$ and Me_3Al also has disadvantages.[4] Solvated Me_3Ga has been obtained by electrolysis of dimethylmagnesium in THF with a gallium anode.[3] However, non-solvated Me_3Ga cannot be isolated from the $Me_3Ga \cdot THF$ formed in this case without decomposition.

A simple synthesis of galliumtrialkyls consists in the interaction of Ga—Mg alloys or Ga—Mg mixtures with alkyl halides in ethers, sulfides, or amines.[5,6] In this case, both solvated and non-solvated galliumtrialkyls are formed. However, the published results[5] concerning the synthesis of trimethylgallium etherates were not reproduced,[3] and attempts to carry out the reaction of alkyl halides with a mixture of magnesium and gallium in donor-type solvents failed.[7] Contrary to the results presented in the earlier work,[5] galliumtrialkyls were not isolated from the reaction of alkyl halides with Ga—Mg alloys or Ga—Mg mixtures in the absence of donor-type solvents.[7] Such contradictions in the literature data (*cf.* Refs. 3, 7 *vs.* Ref. 5) have remained unexplainable until now; especially since we obtained trimethylgallium etherate in high yield (independent of the study cited[5]) by the reaction of MeI with a Ga—Mg mixture in dibutyl ether.[6] We believe that these differences can be explained by the fact that the samples of Mg and Ga used in the studies by Russian researchers[5,6] differed in the composition of impurities from those employed in Refs. 3 and 7. We can assume that the samples of Mg or Ga that we used contained small amounts of impurities, which served as the promoters of the reaction.

In this work we found that unlike the previous data,[7] MeI, EtI, and Pr^nI react when heated with either Ga—Mg mixtures or alloys without any solvent or in an aliphatic hydrocarbon to give non-solvated galliumtrialkyls. The reaction occurs according to the following scheme:

$$6\,RI + 3\,Mg + 2\,Ga \longrightarrow 2\,R_3Ga + 3\,MgI_2$$

$$R = Me,\ Et,\ Pr^n$$

The reaction with EtI and Pr^n is carried out at atmospheric pressure, and the reaction with MeI is performed in an autoclave with stirring and at a temperature above 100 °C. The yields of galliumtrialkyls are in the range from 57 to 65%.

Experimental

The commercial magnesium powder of MPF-4 grade contained the following admixtures (%): Fe, $2 \cdot 10^{-2}$; Cu, $7 \cdot 10^{-3}$; Mn, $5 \cdot 10^{-2}$; Zn, $1 \cdot 10^{-4}$; Ga, $1 \cdot 10^{-2}$; Si, 0.1. The purity of gallium was 99.99%. The organic solvents and alkyl iodides were purified using standard procedures and distilled under an inert gas. The syntheses of galliumtrialkyls were carried out in an atmosphere of pure argon.

Trimethylgallium. Gallium (36 g), magnesium (21 g), and MeI (227 g) were placed into a rotating 0.5 L autoclave in an atmosphere of an inert gas. Steel balls with diameters of 5 to 10 mm were placed into the autoclave for better stirring. The autoclave was gradually heated to 100 °C with rotation; 2 h later the temperature was increased to 120—160 °C. The reaction was conducted for 12 h. When the autoclave was chilled, the reaction product was distilled off directly from the autoclave. Me_3Ga was obtained in a yield of 38.6 g (65%), b.p. 56 °C (*cf.* Ref. 8: b.p. 55.7 °C).

Triethylgallium. *A.* Gallium (15 g) and Mg (8 g) in the form of fine cuttings or filings were placed in a three-necked flask, and a crystal of I_2 was added. The mixture was heated *in vacuo* at 150 °C and chilled, and the flask was then filled with pure argon. Ethyl iodide (100.7 g) was added at 50—70 °C for 1 h, and the resulting mixture was heated at 90 °C for 4 h. Pure Et_3Ga (20.5 g) was distilled off from the reaction mixture, yield 61%, b.p. 34 °C (10 Torr), (*cf.* Ref. 8: b.p. 142.6 °C).

B. Gallium (15 g) and Mg (8 g) were placed in a three-necked flask, a crystal of I_2 was added, and the mixture was evacuated. Hexane (50 mL) was added to the reaction mixture, and EtI (100.7 g) was added dropwise while the hexane was boiling. When the reaction was completed, the solvent was distilled off from the flask, and triethylgallium (21.9 g) was isolated by distillation, b.p. 34 °C (10 Torr), yield 65%.

C. Cuttings (9.0 g) of a Ga—Mg alloy (Ga, 35%, Mg, 65%) were placed in a reaction flask, and a crystal of I_2 was added. The reaction mixture was heated *in vacuo* to 150 °C and chilled. Ethyl iodide (69 g) was then gradually added to the resulting mixture, and it was heated to 85 °C. Triethylgallium (4.49 g) was distilled off; b.p. 34 °C (10 Torr), yield (57%).

Tri-*n*-propylgallium. Gallium (15 g) and Mg (8 g) were placed in a three-necked flask, a crystal of I_2 was added, and the mixture was evacuated while it was heated to 150 °C and chilled. Propyl iodide (109.3 g) was then added over a 1h period, and the resulting mixture was heated for 6 h at 80 °C and for 1 h at 90 °C. $Pr^n{}_3Ga$ (23.3.9 g) was distilled off, b.p. 34 °C (1 Torr) (*cf.* Ref. 8: b.p. 184 °C). Yield 55%.

References

1. K. Yasuda and R. Okawara, *Organometal. Chem. Rev.*, 1967, **2**, 255.
2. Houben-Weyl, *Methoden der Organischen Chemie*, **XIII(4)**, Thieme, Stuttgart, 1970, 319.
3. A. C. Jones, D. J. Cole-Hamilton, A. K. Holliday, and M. J. Mahmad, *J. Chem. Soc., Dalton Trans.*, 1983, 1047.
4. L. I. Zakharkin and O. Yu. Okhlobystin, *Zh. Obshch. Khim.*, 1961, **31**, 3662 [*J. Gen. Chem. USSR*, 1961, **31** (Engl. Transl.)].
5. V. I. Bregadze, L. M. Golubinskaya, L. G. Tonoyan, B. I. Kozyrkin, and B. G. Gribov, *Dokl. Akad. Nauk SSSR*, 1973, **212**, 880 [*Dokl. Chem.*, 1973, **212** (Engl. Transl.)].
6. V. V. Gavrilenko, N. P. Fatyushina, V. A. L'vova, V. S. Kolesov, Yu. N. Karaksin, and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 126 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22** (Engl. Transl.)].
7. K. B. Starowieski and K. J. Klabunde, *Appl. Organomet. Chem.*, 1989, **3**, 219.
8. *Dictionary of Organometallic Compounds*, 2nd Ed., **2**, *Chemical Database*, Chapman and Hall, London, 1995.

Received September 30, 1996;
in revised form November 15, 1996