Chemistry

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1961

SovietRxiv

Abstract

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A NEW METHOD FOR THE SYNTHESIS OF TRICHLOROMETHYL ORGANOMERCURY COMPOUNDS

Several methods are known for the synthesis of organomercury compounds based on the use of carbenes—short-lived compounds of divalent carbon.

Thus, for example, methylene, generated from diazomethane, inserts into the mercury—halide bond with the formation of halomethyl organomercury compounds ([1,2]). Diphenylcarbene, generated from diphenyldiazomethane, reacts analogously ([1]). In the synthesis of organomercury compounds by the reaction of hydrazones, aldehydes, and ketones with mercuric acetate ([3,4]), carbenes apparently also participate.

We have found ([5]) that dichlorocarbene, formed by the action of potassium tert-butoxide on chloroform, is also capable of inserting into the mercury—chlorine bond with the formation of trichloromethyl organomercury compounds*. The present article describes a method, developed on the basis of this reaction, for the synthesis of trichloromethyl organomercury compounds:

$$R\text{—}Hg\text{—}Cl + :CCl_2 \rightarrow R\text{—}Hg\text{—}CCl_3.$$

The reaction of dichlorocarbene was carried out with sublimate (R = Cl), phenylmercuric chloride, *n*-nitrophenylmercuric chloride, *n*-methoxyphenylmercuric chloride, *n*-dimethylaminophenylmercuric chloride, β-naphthylmercuric chloride, trans-β-chlorovinylmercuric chloride, and cis-β-chlorovinylmercuric chloride.

The yields and certain properties of the trichloromethyl organomercury compounds obtained are given in Table 1.

Table 1

Starting material	Product obtained	Yield, %	m.p., °C	Analysis: found	Analysis: calculated
$HgCl_2$	CCl_3HgCl	2	178–180	Hg 56.83	Hg 56.60
C_6H_5HgCl	$C_6H_5HgCCl_3$	52	114–116	–	–

Starting material	Product obtained	Yield, %	m.p., °C	Analysis: found	Analysis: calculated
n-$O_2NC_6H_4HgCl$	n-$O_2NC_6H_4HgCCl_3$	31	141–143	C 19.23; 19.22;H 1.16; 1.20Hg 45.74; 45.34	C 19.06H 0.91Hg 45.48
n-$CH_3OC_6H_4HgCl$	n-$CH_3OC_6H_4HgCCl_3$	85	123–123.5	C 22.87; 23.09;H 1.97; 2.02Hg 47.30; 47.03	C 22.55H 1.66Hg 47.08
n-$(CH_3)_2NC_6H_4HgCl$	n-$(CH_3)_2NC_6H_4HgCCl_3$	49	117.5–118	Hg 45.60	Hg 45.66
β-$C_{10}H_7HgCl$	β-$C_{10}H_7HgCCl_3$	57	147–149	C 30.42; 30.32;H 1.93; 1.88;Hg 45.13	C 29.61H 1.58Hg 44.97
trans-ClCH=CHHgCl	trans-ClCH=CHHg—CCl_3	53	79–80	Hg 53.06	Hg 52.72
cis-ClCH=CH—HgCl	cis-ClCH=CH—Hg—CCl_3	10	Oil	–	–

* See also the shortly subsequent brief communication by G. A. Razuvaev ([6]) on the synthesis of CCl_3HgCl and $C_6H_5HgCCl_3$ by the reaction of sublimate and phenylmercuric chloride with the sodium salt of trichloroacetic acid.

The presence of the CCl_3 group in the substances was proved by decomposition of the substance with hydrochloric acid and by the color reaction for the chloroform formed*.

cis- and trans-β-chlorovinyltrichloromethylmercury liberate acetylene on heating; in reaction with bromine both substances give CCl_3HgBr:

$$\mathrm{ClCH{=}CH{-}Hg{-}CCl_3} \xrightarrow{\mathrm{Br_2}} \mathrm{CCl_3HgBr} + [\mathrm{ClCH{=}CHBr}]^{**}.$$

On the action of chlorine on trans-β-chlorovinyltrichloromethylmercury, trichloromethylmercuric chloride is formed:

$$\text{trans-}\mathrm{ClCH{=}CH{-}Hg{-}CCl_3} \xrightarrow{\mathrm{Cl_2}} \mathrm{CCl_3HgCl} + [\mathrm{ClCH{=}CHCl}]^{**}.$$

Phenyltrichloromethylmercury is converted by the action of bromine into phenylmercuric bromide:

$$C_6H_5HgCCl_3 \xrightarrow{Br_2} C_6H_5HgBr + [CCl_3Br]^{**}.$$

All compounds of the type R–Hg–CCl_3, where R is an aromatic radical, decompose on heating in alcohol according to the scheme:

$$2R{-}Hg{-}CCl_3 \rightarrow 2R{-}Hg{-}Cl + [CCl_2{=}CCl_2]^{**}.$$

Dibromocarbene, formed by the action of potassium tert-butylate on bromoform, is also capable of insertion into the mercury–halogen bond. Thus, phenylmercuric bromide gives phenyltribromomethylmercury in 41% yield and m.p. 98-99° (with decomposition).

$$C_6H_5HgBr + :CBr_2 \rightarrow C_6H_5HgCBr_3.$$

The reaction of insertion of dihalocarbenes into metal–halogen bonds apparently has a fairly general character; it proved applicable to compounds of antimony, copper, cobalt, and some other metals.

Experimental Part

Preparation of trichloromethylmercuric chloride CCl_3HgCl. To a suspension of 15 g (0.055 mole) of sublimate in 90 ml of abs. benzene were added 8 ml (0.1 mole) of abs. chloroform and, with stirring and cooling with water, dry potassium tert-butylate prepared from 4 g (0.1 g-atom) of potassium. After the addition of butylate was complete, the reaction mixture was stirred for 30 min, poured into water, the benzene layer was separated and dried, and the benzene was evaporated. The residue was washed with petroleum ether. 0.4 g of trichloromethylmercuric chloride was obtained (2% of theory). M.p. 178-180° (from alcohol). Literature data: m.p. 173° (7).

$$\text{Found } \% : \text{Hg } 56.83$$
$$\text{Calculated } \% : \text{Hg } 56.60$$

Preparation of phenyltrichloromethylmercury $C_6H_5HgCCl_3$. To a suspension of 4.9 g (0.016 mole) of phenylmercuric chloride in 100 ml of abs. benzene were added 5 ml (0.062 mole) of abs. chloroform and gradually, with stirring and cooling with ice water, potassium tert-butylate prepared from 1.2 g (0.03 g-atom) of potassium. After 30 min of stirring, the blackened reaction mixture was poured into water, and the precipitate was filtered off and washed with benzene. On evaporation of the benzene, 1.7 g of $C_6H_5HgCCl_3$ was obtained. M.p. 114° (from alcohol). Literature data: m.p. 114-116° (8). The precipitate insoluble in benzene was extracted with hot acetone, after evaporation of which a mixture of phenylmercuric chloride and phenyltrichloromethylmercury (2.32 g) was isolated. From it, 1.55 g of $C_6H_5HgCCl_3$ with m.p. 112–114° was washed out with cold benzene. The residue was 0.55 g of unreacted phenylmercuric chloride with m.p. 256°. Literature data: m.p. 258° (9). The total yield of phenyltrichloromethylmercury was 3.25 g (52% of theory).

On heating phenyltrichloromethylmercury in alcohol, phenylmercuric chloride with m.p. 255–256° is formed in quantitative yield. Literature data: m.p. 258° (9). On the action of a solution of bromine in carbon tetrachloride on a benzene solution of phenyltrichloromethylmercury, C_6H_5HgBr with m.p. 270–271° was isolated in quantitative yield. Literature data: m.p. 275° (10).

* On heating chloroform with 10% NaOH and pyridine, a raspberry coloration appears.

** The substances indicated in square brackets were not identified.

Preparation of **p-nitrophenyltrichloromethylmercury** *p*-$O_2NC_6H_4HgCCl_3$. To a suspension of 5.2 g (0.012 mole) of *p*-nitrophenylmercuric chloride in 35 ml of absolute dioxane were added 2.5 ml (0.031 mole) of absolute chloroform and, gradually with stirring and cooling with ice water, 3.3 g (0.03 mole) of potassium *tert*-butoxide. After the addition of the butoxide was complete, the reaction mixture was stirred for 30 min at room temperature; the precipitate was filtered off, most of the dioxane was removed on a water-jet pump, and the organomercury compound was precipitated with water. Weight 1.8 g. The precipitate insoluble in dioxane was washed with water and dried. Weight 2.7 g. From the combined precipitates, 1.22 g (31% of theory) of *p*-nitrophenyltrichloromethylmercury, m.p. 141–143°, was extracted with ether.

Found, %: C 19.23; 19.22; H 1.16; 1.20; Hg 45.74; 45.34
Calculated, %: C 19.06; H 0.91; Hg 45.48

In the residue, 2.5 g of unreacted *p*-nitrophenylmercuric chloride remained.

Preparation of **p-methoxyphenyltrichloromethylmercury** *p*-$CH_3OC_6H_4HgCCl_3$. To a suspension of 4.2 g (0.012 mole) of *p*-anisylmercuric chloride in 35 ml of absolute dioxane were added 3 ml (0.037 mole) of absolute chloroform and, gradually with stirring and cooling with ice water, 2.8 g (0.025 mole) of potassium *tert*-butoxide. After 30 min of stirring, the precipitate was filtered off, the dioxane was removed on a water-jet pump, and the organomercury compound was precipitated with water. The precipitate was filtered off, washed with water, dried, dissolved in cold benzene, filtered again, and evaporated. This gave 3.9 g (85% of theory) of *p*-$CH_3OC_6H_4HgCCl_3$. After two recrystallizations, first from ether and then from alcohol, m.p. 123–123.5°.

Found, %: C 22.87; 23.09; H 1.97; 2.02; Hg 47.30; 47.02
Calculated, %: C 22.55; H 1.66; Hg 47.08

When *p*-anisyltrichloromethylmercury is heated in alcohol, *p*-anisylmercuric chloride is formed in quantitative yield, m.p. 235-236°. Literature data: m.p. 239° (11).

Preparation of **p-dimethylaminophenyltrichloromethylmercury** *p*-$(CH_3)_2NC_6H_4HgCCl_3$. To a suspension of 3.9 g (0.011 mole) of *p*-dimethylaminophenylmercuric chloride in 40 ml of absolute benzene were added 2 ml (0.025 mole) of absolute chloroform and, gradually with stirring and cooling with ice water, 2.5 g (0.022 mole) of potassium *tert*-butoxide. After the addition of the butoxide was complete, the darkened reaction mixture was stirred for 20 min; the precipitate was filtered off and washed with benzene. On evaporation of the benzene, 2.3 g (49% of theory) of *p*-$(CH_3)_2NC_6H_4HgCCl_3$ was obtained. After two recrystallizations from a mixture of alcohol and benzene, m.p. 117.5-118°.

Found, %: Hg 45.60
Calculated, %: Hg 45.66

The substance decomposes on storage.

Preparation of β-**naphthyltrichloromethylmercury** β-$C_{10}H_7HgCCl_3$. To a suspension of 4 g (0.011 mole) of β-naphthylmercuric chloride in 55 ml of absolute dioxane were added 2 ml (0.025 mole) of absolute chloroform and, gradually with stirring and cooling with cold water, 2.5 g (0.022 mole) of potassium *tert*-butoxide. After the addition of the butoxide was complete, the reaction mixture was stirred for 1 h; the precipitate was filtered off, most of the dioxane was distilled from the filtrate, and the substance was precipitated with water. The precipitate of the organomercury compound was filtered off, dried, and dissolved in benzene. After filtration and evaporation of the benzene, 2.35 g of β-$C_{10}H_7HgCCl_3$, m.p. 148-149°, was obtained. The precipitate insoluble in dioxane was washed with water, dried, and extracted with acetone. On evaporation of the acetone, a mixture of β-naphthylmercuric chloride and β-naphthyltrichloromethylmercury was obtained, from which 0.45 g of β-$C_{10}H_7HgCCl_3$, m.p. 147-149°, was washed out with cold benzene. The total yield of β-$C_{10}H_7HgCCl_3$ was 2.8 g (57% of theory).

Found, %: C 30.42; 30.32; H 1.93; 1.88; Hg 45.13
Calculated, %: C 29.61; H 1.58; Hg 44.97

From the reaction, 0.5 g of unreacted β-naphthylmercuric chloride, m.p. 268°, was recovered. Literature data: m.p. 270° (9).

Preparation of trans-β-chlorovinyltrichloromethylmercury $ClCH=CH—HgCCl_3$. To a solution of 13.5 g (0.045 mole) of trans-β-chlorovinylmercuric chloride in 90 ml of absolute benzene were added 8 ml (0.1 mole) of absolute chloroform, and then, gradually with stirring and ice cooling, potassium tert-butylate prepared from 4 g (0.1 g-atom) of potassium was added. The reaction mixture darkens strongly. After the addition of the butylate had been completed, the reaction mixture was poured into water, filtered from the black precipitate, the benzene layer was separated and dried, and the benzene was evaporated. 9.1 g (53% of theory) of trans-$ClCH = CHHgCCl_3$, m.p. 79-80° (from alcohol), was obtained.

Found % Hg 53.06
Calculated % Hg 52.72

On thermal decomposition the compound liberates acetylene, demonstrated by the formation of a red precipitate of copper acetylide.

To a benzene solution of trans-β-chlorovinyltrichloromethylmercury was added a solution of bromine in carbon tetrachloride. A precipitate of trichloromethylmercuric bromide immediately separates, m.p. 160–162°. Literature data: m.p. 165° (7). To a solution of the bromide obtained in benzene, pyridine was added; the mixture was evaporated to 1 ml, and then water was added. The complex of trichloromethylmercuric bromide with pyridine was extracted with ether. After evaporation of the ether, a yellow powder was obtained, m.p. 85.5-86.5° (from benzene). Literature data: m.p. 87° (7). To a benzene solution of trans-β-chlorovinyltrichloromethylmercury was added a solution of chlorine in carbon tetrachloride. The precipitated trichloromethylmercuric chloride was filtered off, washed with a small amount of hot water, dried, and recrystallized from benzene. It darkens at 176° and melts at 180°. Literature data: m.p. 173° (7).

Preparation of cis-β-chlorovinyltrichloromethylmercury
$ClCH = CH—HgCCl_3$. To a solution of 3.75 g (0.013 mole) of cis-β-chlorovinylmercuric chloride in 40 ml of absolute benzene were added 3 ml (0.037 mole) of absolute chloroform, and then, gradually with stirring and cooling with ice water, 2.85 g (0.025 mole) of potassium tert-butylate was added. After 30 min of stirring, the precipitate was filtered off, washed with benzene, and the benzene solution was evaporated. Part of the substance had decomposed. From the blackened residue the substance was extracted with benzene, and the benzene was rapidly evaporated. The oily residue was triturated with petroleum ether. The powder insoluble in petroleum ether, m.p. 75–77° (0.82 g), does not give a color reaction for chloroform and is unreacted cis-β-chlorovinylmercuric chloride. Literature data: m.p. 78-79° (12). After evaporation of the petroleum ether, 0.5 g of cis-$ClCH = CH—HgCCl_3$ was isolated in the form of a sharply smelling oil (10.5% of theory). Upon addition to the benzene solution of the substance obtained of a solution of bromine in carbon tetrachloride, a precipitate of trichloromethylmercuric bromide separates, m.p. 160–163°. Literature data: m.p. 165° (7).

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Received
31 III 1961

LITERATURE CITED

1. L. Hellerman, D. Newman, *J. Am. Chem. Soc.*, **54**, 2859 (1932).
2. R. Kh. Freidlina, A. N. Nesmeyanov, F. A. Tokareva, *ZhOKh*, **7**, 262 (1937); *Ber.*, **69**, 2019 (1936).
3. A. N. Nesmeyanov, O. A. Reutov, A. S. Loseva, *DAN*, **111**, 835 (1956).
4. A. N. Nesmeyanov, O. A. Reutov, A. S. Loseva, M. Ya. Khorlina, *Izv. AN SSSR, OKhN*, 1958, 1315.
5. O. A. Reutov, A. N. Lovtsova, *Izv. AN SSSR, OKhN*, 1960, 1716.
6. G. A. Razuvaev, N. S. Vasileiskaya, L. A. Nikitina, *Tr. po khim. i khim. tekhnol.*, **1**, No. 3, 638 (1960).
7. A. N. Nesmeyanov, R. Kh. Freidlina, F. K. Velichko, *Izv. AN SSSR, OKhN*, 1958, 40.
8. A. N. Nesmeyanov, R. Kh. Freidlina, F. K. Velichko, *DAN*, **114**, 557 (1957).
9. A. N. Nesmeyanov, *ZhRKhO*, **61**, 1393 (1929).
10. S. Hilpert, G. Grüttner, *Ber.*, **46**, 1686 (1913).
11. A. Michaelis, J. Rabinerson, *Ber.*, **23**, 2342 (1890).
12. A. N. Nesmeyanov, A. E. Borisov, V. D. Vilchevskaya, *Izv. AN SSSR, OKhN*, 1949, 578.

Note: Figure translations are in progress. See original paper for figures.