

## REACTIONS OF ORGANIC ANIONS

### XLIV\*. CATALYTIC SYNTHESIS OF PHENYL(TRIHALOMETHYL)-MERCURY COMPOUNDS IN AQUEOUS MEDIUM

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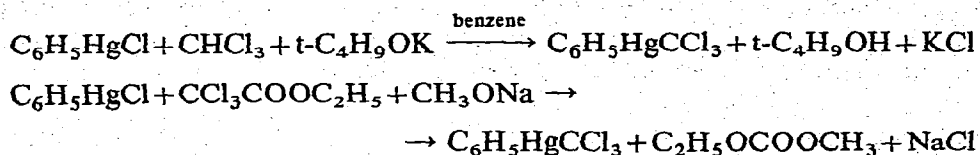
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#### SUMMARY

A useful new method of preparation of phenyl(trihalomethyl)mercury compounds has been elaborated. It consists of the reaction of haloforms (chloroform, bromoform, and mixed trihalomethanes) with phenylmercury chloride in the presence of aqueous NaOH/KF solution with a quaternary ammonium compound, triethylbenzylammonium chloride, as a catalyst.

Trihalomethyl derivatives of phenylmercury,  $C_6H_5HgCX_3$ , are very useful and versatile reagents for generation of dihalocarbenes<sup>1,2</sup>. The great value of these reagents consists in direct formation of dihalocarbenes from organomercurials without intermediate formation of trihalomethyl anions which are always formed as intermediates in all other methods of generation of dihalocarbenes<sup>3</sup>. Thus, the use of phenyl(trihalomethyl)mercury compounds as dihalocarbene sources makes it possible to prepare dihalocyclopropane derivatives from alkali-sensitive olefins and from olefins containing electron withdrawing groups. The latter compounds form mainly trihalomethyl derivatives with  $[CX_3^- \rightarrow :CX_2]$  reagents<sup>4</sup>. However, wide application of phenyl(trihalomethyl)mercurials for generation of dihalocarbenes is rather limited because they are not easily available. Synthesis of the phenyl(trihalomethyl)mercury compounds is generally performed by action of trihalomethyl anions on phenylmercury chloride. Haloforms and dry potassium tert-butoxide<sup>5</sup>, sodium trichloroacetate<sup>6</sup> or ethyl trichloroacetate and sodium methoxide<sup>7</sup> in anhydrous solvents are mainly used for generation of  $CX_3^-$  in this synthesis.

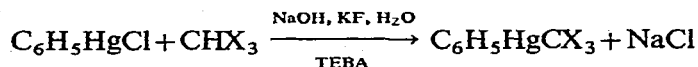


Since 1969 we have been working on a new method of generation of trihalo-

\* For Part XLIII see ref. 12.

methyl anions and dihalocarbenes in a two-phase system involving reaction of haloforms with concentrated aqueous sodium hydroxide solution in the presence of quaternary ammonium compound as a catalyst<sup>8</sup>. This method seems to be the most convenient one for the preparation of various dihalocyclopropane derivatives<sup>8,9</sup> and some other reactions with dihalocarbenes<sup>10</sup>. The catalytic method is particularly effective for generation and reactions of trihalomethyl anions, thus making the trihalomethyl derivatives of esters, nitriles and sulfones easily available<sup>11</sup>. However, so far every attempted synthesis of phenyl(trihalomethyl)mercury using this method failed, probably because of decomposition of phenylmercury chloride and/or the reaction products in the presence of highly concentrated sodium hydroxide solution. On the other hand, the decrease of concentration in aqueous phase is very unfavorable for the catalytic reaction because it results in inhibition of carbanion formation and the reaction does not proceed.

One could expect that the concentration of sodium hydroxide solution can be decreased without increasing the activity of water when this solution will be saturated with some inorganic salts that form well-solvated ions. In fact, when about 20% of potassium fluoride was dissolved in 20% NaOH solution, the resulting solution was of almost equal activity to a 50% NaOH solution as a source of base. At the same time, the use of this solution diminishes dramatically the participation of undesired side reactions in the process. Thus reaction of phenylmercury chloride with an excess of chloroform (used also as a solvent) in the presence of an aqueous solution composed of NaOH and KF and triethylbenzylammonium chloride (TEBA) as a catalyst leads to the formation of required phenyl(trichloromethyl)mercury in high yield (72%). Similar results were obtained with other haloforms: CHBrCl<sub>2</sub> (C<sub>6</sub>H<sub>5</sub>HgCBrCl<sub>2</sub>, 64%) and CHBr<sub>3</sub> (C<sub>6</sub>H<sub>5</sub>HgCBr<sub>3</sub>, 54%).



In the case of bromoform, the concentration of NaOH in aqueous phase has to be lower, not exceeding 10–15%, otherwise decomposition occurred and the yield of phenyl(tribromomethyl)mercury decreased significantly.

The phenyl(trihalomethyl)mercurials obtained in this way behave identically to those described by Seyferth<sup>2,5</sup>. Boiling with olefins in benzene solution leads to the decomposition to phenylmercury halide and corresponding dihalocarbenes. The carbene liberated adds to the olefins with the formation of dihalocyclopropane derivatives.

Thus the catalytic two-phase system, after some modifications, is also very convenient for the synthesis of phenyl(trihalomethyl)mercury compounds. The yields of pure compounds are generally higher than in the reaction with dry potassium tert-butoxide<sup>5</sup> or ethyl trichloroacetate<sup>7</sup>, the procedure is extremely simple and does not require any precautions against moisture or air.

## EXPERIMENTAL

### *Phenyl(trichloromethyl)mercury*

To a suspension of phenylmercury chloride (15.7 g, 0.05 mol) in chloroform (70 ml) and TEBA (0.4 g), a solution of NaOH (20 g) and KF · 2 H<sub>2</sub>O (60 g) in water

(80 ml) was added dropwise with vigorous stirring at 20–25°. The reaction was carried out for 2 h, then the mixture was diluted with water, the organic layer was separated, the aqueous phase was extracted with chloroform, the combined extracts were washed with water and dried. Evaporation of the solvent *in vacuo* yielded crude product which was purified by washing with methanol, and dried. Yield of phenyl(trichloromethyl)mercury: 14.3 g (72%), m.p. 115–116°, lit. 117–118°.

*Phenyl(bromodichloromethyl)mercury*

Procedure essentially as above. From phenylmercury chloride (3.13 g, 0.01 mol), bromodichloromethane (8.2 g, 0.05 mol), TEBA (0.1 g), methylene chloride as a solvent (10 ml) and a solution of NaOH (4 g) and KF · 2 H<sub>2</sub>O (15 g) in water (16 ml), 2.8 g of phenyl(bromodichloromethyl)mercury was obtained. Yield: 64%, m.p. 108–109°, lit. 110–111°.

*Phenyl(tribromomethyl)mercury*

From phenylmercury chloride (6.3 g, 0.02 mol), bromoform (20 ml), TEBA (0.2 g) and a solution of NaOH (5 g) and KF · 2 H<sub>2</sub>O (40 g) in water (45 ml), phenyl(tribromomethyl)mercury was obtained. The reaction was carried out at 10–15°, and the product was isolated by precipitation from bromoform/methanol solution with water. Yield: 54%, m.p. 118° (decomp.) (lit. 119–120° decomp.).

REFERENCES

- 1 D. Seyferth, J. M. Burlitch, R. J. Minas, J. Y.-P. Mui, H. D. Simmons Jr., A. J. H. Treiber and S. R. Dowd, *J. Amer. Chem. Soc.*, 87 (1965) 4259.
- 2 D. Seyferth, M. E. Gordon, J. Y.-P. Mui and M. Burlitch, *J. Amer. Chem. Soc.*, 89 (1967) 759; D. Seyferth, S. P. Hopper and T. F. Jula, *J. Organometal. Chem.*, 17 (1969) 193; D. Seyferth and C. K. Haas, *J. Organometal. Chem.*, 30 (1971) C38.
- 3 W. Kirmse, *Carbene Chemistry*, Academic Press, 1964.
- 4 W. A. Bruson and W. Niederhauser, *J. Amer. Chem. Soc.*, 67 (1945) 601; D. Seyferth, J. Y.-P. Mui and M. E. Gordon, *J. Amer. Chem. Soc.*, 87 (1965) 681; A. D. Petrov and V. M. Volovic, *Zh. Obshch. Khim.*, 27 (1957) 45; F. Nerdel, W. Brodowski, J. Buddrus, M. Flige and P. Weyerstahl, *Chem. Ber.*, 101 (1967) 1407.
- 5 O. A. Reutov and A. N. Lovtsova, *Dokl. Akad. Nauk SSSR*, 139 (1961) 622; D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, 4 (1965) 127.
- 6 T. J. Logan, *Org. Syn.*, 46 (1966) 98.
- 7 E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, 28 (1963) 851.
- 8 M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.*, (1969) 4659.
- 9 M. Makosza and M. Fedoryński, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 19 (1971) 105; E. V. Dehmlow and J. Schönefeld, *Justus Liebigs Ann. Chem.*, 744 (1971) 42; E. V. Dehmlow, *Tetrahedron*, 28 (1972) 175.
- 10 I. Tabushi, Z. Yoshida and N. Takahashi, *J. Amer. Chem. Soc.*, 92 (1970) 6670; 93 (1971) 1820; E. V. Dehmlow, *Tetrahedron*, 27 (1971) 4071; M. Makosza and M. Fedoryński, *Rocz. Chem.*, 46 (1972) 311; W. P. Weber and G. W. Gohel, *Tetrahedron Lett.*, (1972) 1637; T. Greibrokk, *Tetrahedron Lett.*, (1972) 1663.
- 11 M. Makosza and I. Gajos, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 20 (1972) 33; M. Makosza and M. Fedoryński, *Rocz. Chem.*, 46 (1972) 533; E. V. Dehmlow, *Justus Liebigs Ann. Chem.*, 758 (1972) 148.
- 12 A. Jończyk, M. Fedoryński and M. Makosza, *Tetrahedron Lett.*, (1972) 2395.