

BIS(TRIBROMOMETHYL)MERCURY

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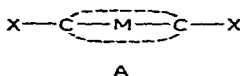
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SUMMARY

Bis(tribromomethyl)mercury can readily be prepared in high yield and pure form and shows promise as a convenient dibromocarbene generator under comparatively mild conditions.

INTRODUCTION

We have been exploring a number of synthetic approaches to novel unsaturated organometallic systems of the type A in which M is a Group II metal and in which the



central linear CMC system is bound by a total of eight bonding electrons distributed in two 2-centre σ -bonds and two 3-centre π -bonds (represented by dotted lines). One of the approaches which has so far proven unsuccessful involved attempted 1,3-debromination of bis(tribromomethyl)mercury whereby we hoped to obtain A in which M=Hg and X=Br. This report describes the synthesis and some of the properties of the previously unknown intermediate in the above scheme, bis(tribromomethyl)mercury (I) and of the related (tribromomethyl)mercuric bromide (II).

RESULTS AND DISCUSSION

Bis(trichloromethyl)mercury can be conveniently prepared by reaction of sodium trichloroacetate with mercuric chloride in boiling dry monoglyme¹ and we chose a modification of this method for the preparation of (I). However, alkali metal salts of tribromoacetic acid had not, to our knowledge, been previously isolated although the tribromoacetate anion was known to undergo facile decarboxylation in aqueous solution². Evaporation at room temperature *in vacuo* over H₂SO₄ and P₂O₅ of a concentrated solution of tribromoacetic acid which had been carefully neutralised with sodium bicarbonate gave a colourless anhydrous solid product which was contaminated with sodium hydroxide and carried a strong odour of bromoform. Pure sodium tribromoacetate was obtained by freeze-drying the aqueous solution.

Attempted synthesis of (I) from sodium tribromoacetate and mercuric chloride in 2:1 molar proportions respectively in boiling anhydrous monoglyme yielded mercuric bromide as the only water insoluble product. Even at room temperature

evolution of carbon dioxide was very rapid and the reaction mixture quickly discoloured. The optimum reaction temperature was found to be 5–10° and effectively pure, crystalline (I) could be precipitated in 85–90% yields from the reaction mixture simply by slow addition of water at 0°. The mercuric chloride could be replaced as starting material by mercuric acetate with equally good recoveries of (I).

With regard to the mechanism of formation of the mercury–carbon bond, our results are in accord with the displacement process proposed by Logan¹ for the trichloroacetate reaction. Thus, the facts that sodium tribromoacetate in monoglyme at room temperature undergoes decarboxylation at a negligible rate whereas addition of mercuric salts leads to immediate vigorous evolution of carbon dioxide and that the product of reaction with mercuric chloride contains tribromomethyl rather than dibromochloromethyl fragments clearly exclude the possibility of initial decarboxylative generation of CBr₂ followed by insertion into an Hg–X bond.

Attempts to prepare (tribromomethyl)mercuric bromide (II) by reaction of sodium tribromoacetate with mercuric bromide in 1:1 molar proportions yielded mixtures of comparable quantities of (I) and (II) (as indicated by thin layer chromatography and IR spectra). This is to be contrasted with the results of analogous reactions with trichloroacetate¹ whereby (trichloromethyl)mercuric chloride was the only product isolated from 1:1 reaction with mercuric chloride and (trichloromethyl)mercuric bromide was the only product isolated from reaction with mercuric bromide, even when trichloroacetate was in excess. It would appear that the attachment of the first trichloromethyl anion to the mercuric cation deactivates the remaining mercuric substituent towards further substitution more than does the introduction of the first tribromomethyl residue. The introduction of the second trihalomethyl fragment could proceed by one of a number of different mechanisms about which it would be unwise, at this stage, to speculate but it does seem likely that the difference between the effects of the first tribromomethyl and the first trichloromethyl residues is related to the greater electron withdrawing character of the latter.

It was found that (II) could readily be prepared from (I) by thermal decomposition in tetrachloroethylene at approximately 90°. In boiling tetrachloroethylene (120°) mercuric bromide and not (II) was the product isolated.

(I) behaves as a dibromocarbene generator under conditions much milder than those required to generate dichlorocarbene from bis(trichloromethyl)mercury¹. Analytically pure 7,7-dibromobicyclo [4.1.0] heptane was recovered in 54% yield based on (I)→(II) (actual yields probably much higher than this) from the reaction of (I) with cyclohexene in boiling benzene. Even in the case of the deactivated olefin, tetrachloroethylene, which was used as the reaction solvent, reaction with (I) at 90° produced 1,1-dibromo-2,2,3,3-tetrachlorocyclopropane and (II). Recovery of the dibromotetrachlorocyclopropane with the facilities available to us was only 10% [based on (I)→(II)] but judging from the cleanness of the reaction and the high yield of (II) we feel that actual yields were probably much higher than this. Seyferth *et al.*³ report a 26% recovery of this dibromotetrachlorocyclopropane using phenyl(tribromomethyl)mercury as the carbene generator.

EXPERIMENTAL

The mercuric salts, tribromoacetic acid, cyclohexene, tetrachloroethylene and

solvents used were commercially available AR grade chemicals. Monoglyme was purified by refluxing over lithium aluminium hydride followed by fractional distillation and was stored over molecular sieves under dry nitrogen. Benzene and tetrachloroethylene were dried by distillation from molecular sieves.

Melting points were observed on a Koffler block and are uncorrected.

Sodium tribromoacetate

Tribromoacetic acid (5.94 g) dissolved in water (20 ml) was neutralised by careful addition of solid AR grade sodium bicarbonate (1.68 g). The resulting clear solution was freeze-dried to a dry powder and finally desiccated *in vacuo* over P_4O_{10} . (Found: C, 7.7; Br, 75.1; $C_2Br_3NaO_4$ calcd.: C, 7.5; Br, 75.3%). IR (KBr disc): 1692 m, 1670 s (CO stretch), 765 s, 754 s, 597 s (C-Br stretch).

Bis(tribromomethyl)mercury

From mercuric chloride. Solid mercuric chloride and solid sodium tribromoacetate were mixed in the molar proportions 1:2.5–3.0 respectively in a vessel of the appropriate size protected from atmospheric moisture and immersed in a water-ice bath maintained at 5–10° by small additions of ice. Anhydrous monoglyme (3–4 ml per g sodium tribromoacetate) was added and the resulting effervescent suspension was stirred. Evolution of CO_2 effectively stopped after $\frac{1}{2}$ –1 h and the suspension was stirred at 5–10° for a further hour. Dropwise addition of water at 0° gave bis(tribromomethyl)mercury as a colourless crystalline precipitate which was collected, washed with water and dried over P_4O_{10} *in vacuo*. Yield, 85–90% based on mercuric chloride. (Found: C, 3.8; Br, 67.5; Hg, 28.7. C_2Br_6Hg calcd.: C, 3.4; Br, 68.1; Hg, 28.5%). Recrystallisation of this product from dichloromethane gave a colourless crystalline sample with only slightly improved elemental analysis. (Found: C, 3.6; Br, 67.7; Hg, 28.3%). M.p. 148° (with decomn.). IR (nujol or KBr disc): 701 w, 640 s (C-Br stretch), 622 s (C-Br stretch), 601 (sh), 586 (sh).

From mercuric acetate. Exactly the same procedure as above with mercuric chloride replaced by mercuric acetate yielded colourless crystalline bis(tribromomethyl)mercury (85–90% yield based on mercuric acetate). (Found: C, 3.8, Br, 67.6; Hg, 28.4%). IR spectra and m.p. identical to those of product from mercuric chloride.

7,7-dibromobicyclo [4.1.0] heptane from cyclohexane and (I)

Bis(tribromomethyl)mercury (2.47 g) and cyclohexane (5 ml) were heated in dry benzene (10 ml) under reflux in an atmosphere of dry nitrogen for one h. The resulting dark blue solution was allowed to stand at room temperature for 12 h and the dark blue solid (0.9 g) which separated was filtered off. Two recrystallisations of this solid from chloroform yielded tribromomethylmercuric bromide as slightly off-white plates. (Found: Br, 59.6; Hg, 36.9. CBr_4Hg calcd.: Br, 60.1; Hg, 37.7%). IR (KBr disc): 600 w, 629 (sh), 621 s (C-Br stretch). The blue reaction filtrate was evaporated under reduced pressure to a dense blue liquid residue which was extracted with 60–80° petroleum ether (70 ml). The clear colourless extract was evaporated under reduced pressure and micro-distillation of the residue gave 7,7-dibromobicyclo [4.1.0]heptane [0.48 g, 54% base on (I)→(II)] as a clear colourless liquid, b.p. 50–84° (bath)/1 mm, the IR spectrum of which was identical to that of an authentic

sample (see below). (Found: C, 33.7; H, 4.2; Br, 62.0. $C_7H_{10}Br_2$ calcd.: C, 33.1; H, 4.0; Br, 62.9%.) Authentic 7,7-dibromobicyclo[4.1.0]heptane was prepared by the method of Doering and Hoffman⁴, $n_D^{22} = 1.5578$, (ref. 4) = 1.5578.

(Tribromomethyl)mercuric bromide and 1,1-dibromo-2,2,3,3-tetrachlorocyclopropane from (I) and tetrachloroethylene

Bis(tribromomethyl)mercury (4.2 g) dissolved in tetrachloroethylene (35 ml) was heated under argon in an oil bath maintained at approximately 90°. After approx. $\frac{1}{2}$ h a colourless crystalline solid began to separate and after 1 h the reaction mixture was cooled in ice. The colourless crystalline product, (tribromomethyl)mercuric bromide, was separated from the pale yellow supernatant by filtration and was washed with tetrachloroethylene and dried *in vacuo*: yield, 2.81 g, 89%. Recrystallisation from chloroform yielded colourless plates, m.p. 155–6°. (Found: Br, 59.4; Hg, 37.5. CBr_4Hg calcd.: Br, 60.1; Hg, 37.7%.) IR (KBr disc or nujol): 700 w, 629 (sh), 621 s (C–Br stretch). The pale yellow reaction filtrate was evaporated in a stream of nitrogen to a semi-solid yellow residue sublimation of which at 40–60° (bath)/~1 mm pressure yielded crystals still slightly damp with tetrachloroethylene. The solid was quickly washed with ethanol and dried in a stream of nitrogen yielding 1,1-dibromo-2,2,3,3-tetrachlorocyclopropane (0.19 g, 10%). Further sublimation [40–60° (bath)/~1 mm] followed by washing with ethanol and drying in a nitrogen stream gave pale yellow crystals m.p. 112–112.5° (m.p. ref. 4, 114–115.5°). (Found: C, 10.7. $C_2Br_2Cl_4$ calcd.: C, 10.7%.)

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REFERENCES

- 1 T. J. LOGAN, *J. Org. Chem.*, 28 (1963) 1129.
- 2 P. JOHNSON AND E. A. MOELWYN-HUGHES, *Proc. Roy. Soc., Ser. A*, 175 (1940) 118.
- 3 D. SEYFERTH, R. J. MINASZ, A. J. H. TREIBER, J. M. BURLITCH AND S. R. DOWD, *J. Org. Chem.*, 28 (1963) 1163.
- 4 W. VON E. DOERING AND A. K. HOFFMAN, *J. Amer. Chem. Soc.*, 76 (1954) 6162.

J. Organometal. Chem., 15 (1968) 7–10