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SYNTHESIS, NMR STUDY, PARTIAL RESOLUTION AND REDOX-DEMERCURATION OF CHIRAL 2-BROMOMERCURI-4-DIMETHYLAMINOBUTANE *

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Summary

The preparation and ^1H, ^{13}C NMR spectra are reported for chiral 2-bromomercuri-4-dimethylaminobutane (**A**), a novel useful organomercurial model having both a mercury atom attached to a chiral carbon centre and a tertiary nitrogen in the γ-position. Racemic **A** has been resolved partially using dibenzoyl-*d* tartaric acid. Redox-demercuration with a palladium(0) complex was shown to give an optically active palladium metallocycle (**B**), the signs of optical rotation of **A** and **B** being the same.

The mechanistic study for substitution reactions of organomercurials needs stereochemical information derived from the investigation of model compounds in which a chiral carbon bears a mercury atom.

For some time we have been involved in the study of a new reaction, the redox-demercuration of organomercurials using zerovalent Pt, Pd and Ni complexes [ref. 1, for review, see ref. 2]. The stereochemical aspect was first investigated with the relatively easy accessible diastereomers of L-menthyl esters from α-mercuriphenylacetic acid [3]. More recently another new model, 8-(α-bromomercuriethyl)quinoline, was especially designed [4] whose enantiomer afforded expected optically active metallocycle when treated with $Pd(PPh_3)_4$ or $Pd_2(dba)_3$ (dba = dibenzylideneacetone). The stereochemistry of the reaction in that particular case was proved to be a net inversion at carbon which corresponded to a S_N2-like mechanism [5]. However, that system was rather peculiar because of the benzylic nature of the Hg–C bond and the compound exhibited a strong tendency to be cleaved homolytically [6]. Therefore, a more general type of model, without special features, was very desirable. We now report the synthesis and partial study of the simplest of possible organomercurials of the type in question (**4**). It contains one

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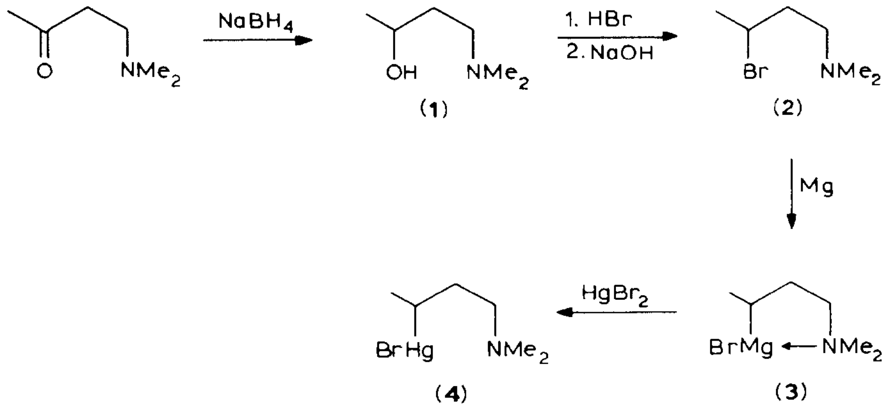
* Dedicated to Prof. Oleg A. Reutov on the occasion of his 65th birthday on September 5, 1985.

Scheme 1



SCHEME 1

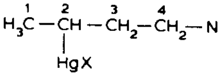
chiral carbon bearing mercury and one tertiary amine nitrogen which are connected by a two-carbon chain. These four atoms are attached to a palladium atom in a five-membered chelate ring. The fourth carbon is needed to ensure the chirality of the mercury-bearing carbon. This designed structure is, in general, 2-(anion)mercuri-4-di(organyl)aminobutane whose representative, **4**, has been prepared according to Scheme 1.

The best experimental procedure for the preparation of the aminobromide **2** is to reflux a precursor, amino alcohol **1**, with aqueous HBr; **2** was obtained as a colourless liquid in 76% yield, b.p. 48°C/10 Torr, $n_D^{24.5} = 1.4566$. Found: C, 39.66; H, 7.71; Br, 43.63. $C_6H_{14}BrN$ calcd.: C, 40.02; H, 7.83; Br, 44.37%. ^1H NMR (CCl_4, δ, ppm): 1.73 (3H, d, CH_3–C), 2.17 (6H, s, CH_3-N). On storage the colourless liquid **2** turns to a solid due to formation of a quaternary salt.

The preparation of Grignard reagents from γ-aminoalkyl halides recently received considerable attention with regard to the synthesis of biologically active substances [7] Organomagnesium **3**, prepared from **2** and activated magnesium in ether, was treated with $HgBr_2$ without isolation at room temperature to give **4**, which are white crystals, m.p. 40.5°C, in 47% yield. Found: C, 18.84; H, 3.70; Br, 21.02; Hg, 52.42.

TABLE 1

NMR $^{13}C\{^1H\}$ SPECTRUM OF 2-BROMOMERCURI-4-DIMETHYLAMINOBUTANE

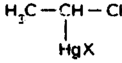


$$\overset{1}{H_3C}-\underset{\underset{HgX}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_2-N(\overset{5}{C}H_3)_2$$

Solvent	δ (ppm), ($J(^{13}C-^{199}Hg)$ (Hz))				
	C(1)	C(2)	C(3)	C(4)	C(5)
C_6D_6	22.11	44.01	35.95	57.59	44.82
	(54.4)	(1732.5)	(97.06)	(101.48)	
C_5D_5N	21.90	43.02	36.00	57.64	44.64
	(55.9)	(1775.2)	(95.6)	(103.0)	
$(CD_3)_2SO$	21.43	42.74	35.08	56.97	44.37
	(57.4)	(1782.5)	(100.0)	(106.1)	

TABLE 2

NMR $^{13}C\{^1H\}$ SPECTRUM OF 2-chloromercuri-4-dimethylaminobutane



$$\overset{1}{H_3C}-\underset{\displaystyle HgX}{\overset{2}{C}H}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{N(CH_3)_2}$$

Solvent	δ (ppm) ($J(^{13}C-^{199}Hg)$ (Hz))				
	C(1)	C(2)	C(3)	C(4)	C(5)
C_6D_6	21.40 (51.1)	40.23 [a]	35.57 (94.0)	57.52 (99.8)	44.53
C_5D_5N	21.97 (54.5)	39.95 (1797.7)	35.96 (95.25)	58.05 (102.8)	44.87 (10.1) [b]

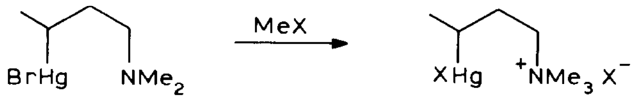
[a] ^{199}Hg satellites were not observed owing to the overlapping with other signals. [b] This is the only case where ^5J has been observed for this model.

$C_6H_{14}BrHgN$ calcd.: C, 18.93; H, 3.71; Br, 20.99; Hg 52.69%. ^1H NMR ($CDCl_3$, δ, ppm): 1.43 (3H, d, CH_3–C), 2.24 (6H, s, CH_3–N); $^3J(^1H-^{199}Hg)$ 288.3 Hz, $^3J(^1H-^1H)$ 7.3 Hz, which corresponds to the acyclic compound **4** without significant N–Hg coordination. The virtual absence of intramolecular coordination in **4** in solution has been confirmed by ^{13}C NMR spectra (Tables 1 and 2). Solvents used were benzene, pyridine and dimethylsulphoxide. Both chemical shifts and coupling constants (^1J) are slightly influenced, the change is not more than 3%. At the same time, ^3J increased by 4.6% when benzene was replaced by DMSO.

At present, information has been accumulated on conformationally rigid structures, which show that vicinal $^3J(^{13}C-^{199}Hg)$ follows Karplus-type dependence on the dihedral angle [8,9]. Partly, for alkylmercuric chlorides, magnitudes of about 75 and 240 Hz correspond to dihedral angles of 60° and 180°, respectively.

From the data presented in Tables 1 and 2 it can be concluded that **4** has a preferentially skewed conformation in solution. The difference between the bromide **4** and the corresponding chloride in NMR spectra is very small, not more than 1% in ^3J.

The organomercurial **4** gives readily with alkyl halides quaternary salts **5**, unlike sterically crowded 8-(α-bromomercuriethyl)quinoline [4], methyl iodide causes simultaneous exchange of the halogen atom at mercury.

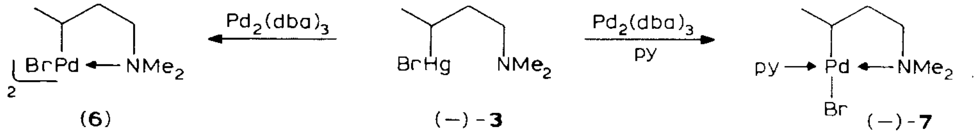


(**5a**, X = Br;
5b, X = I)

Salt **5a**, dec. 162°C. Found: C, 17.61; H, 3.58; Br, 33.63; Hg, 41.59. $C_7H_{17}Br_2NHg$ calcd.: C, 17.68; H, 3.60; Br, 33.60; Hg, 42.17%.

Common acidic reagents for the resolution of amines such as camphor-*d* sulphonic acid, tartaric-*d* acid or dibenzoyl-*d* tartaric acid form stable salts with aminomercurial **4**. Crystallization of the latter from ethanol resulted in partial resolution. The maximum rotation obtained for liberated **4** was $[\alpha]_{578}^{20}$ −3.02° and +2.65°.

Redox demercuration of **4** using $Pd_2(dba)_3 \cdot CHCl_3$ without added ligands gave the very unstable organopalladium dimer **6**. However, the addition of pyridine to the reaction mixture gave rise to a stable metallocycle **7** in 62% yield as colourless crystals, dec. 99°C. Found: C, 36.22; H, 5.30; Br, 21.57; N, 7.92; Pd, 29.28. $C_{11}H_{19}BrN_2Pd$ calcd.: C, 36.13; H, 5.24; Br, 21.85; N, 7.69; Pd, 29.09%. ^1H NMR ($CDCl_3$, δ, ppm): 0.46 (3H, d, CH_3–C), 0.96–1.53 (2H, m, α-CH_2), 2.43–2.64 (3H, m, β-CH_2 and CH), 2.85 (3H, s, CH_3–N), 2.91 (3H, s, CH_3–N), 7.05–8.93 (5H, m, Py).



(6) (−)-**3** (−)-**7**

Similar reaction of enantiomeric **4**, $[\alpha]^{20}_{578} - 1.55°$, gave optically active **7**, $[\alpha]^{20}_{578} - 16.37°$. Two points are noteworthy: (1) retention of a sign of rotation, and (2) increase of the $[\alpha]$ magnitude roughly by a factor of 10. The latter is doubtless connected with the conformational rigidity of chelated **7** unlike flexible, non-chelated **4**. Previously, we had an opportunity to note that organopalladiums have normally a much stronger tendency to be chelated than organomercurials with similar structures * [10]. The significance of the stereochemical results now observed for the mechanism of redox-demercuration will be discussed later.

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* The opinion claimed recently [11] that "... the M–N bond strength follows the order Pt–N < Pd–N < Hg–N, Tl–N" is erroneous.