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STEREOCHEMISTRY OF THE AMINOMERCURATION OF 2-BUTENES

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Summary

NMR and chemical analysis indicates that dimethylaminomercuration of 2-butenes proceeds, by *trans* addition with complete stereospecificity (NMR > 97%; chemical estimation > 99%).

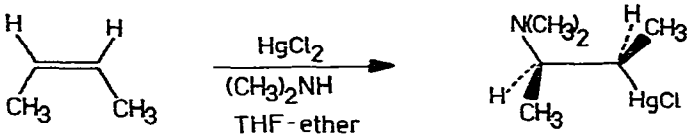
Introduction

Oxymercuration has been studied extensively for many years and the mechanism of the reaction is now reasonably clear [1]. Recent work indicates the initial formation of a mercurinium ion [2] and then attack by an external nucleophile. The expected *trans* addition of mercury and the nucleophile is usually found [3—5]. However, with strained olefins such as norbornene, [3, 4] and *trans*-cyclooctene, [6] oxymercuration gives *cis* addition.

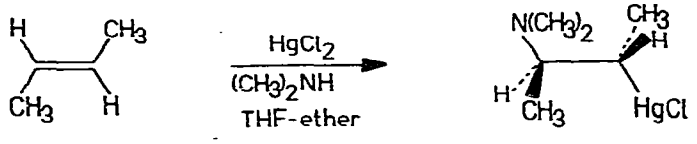
Nucleophiles other than water and alcohols have also been added to olefins, and recently considerable interest has been attracted to mercury(II)-promoted amination [7, 8]. NMR studies of the products obtained from mercury-promoted cyclization of some 5-aminoolefins suggest that the aminomercuration in these cases is a *trans* process [9]. Since intramolecular mercury-promoted additions have been shown to be *trans* processes even in systems where *cis* addition is normally observed [10] further studies on the stereochemistry of aminomercuration seemed desirable. In connection with other amination studies [11, 12], we therefore decided to determine the steric course of dimethylaminomercuration of *cis*- and *trans*-2-butene. This reaction has been found to proceed in a *trans* manner with ⩾ 99% stereospecificity in the case of *cis*-2-butene and ⩾ 97% with *trans*-2-butene.

Results and discussion

Aminomercuration of *cis*-2-butene with dimethylamine gave the mercury



(Ia) m.p. 104°



(Ib) m.p. 70-71°

compound Ia (m.p. 104°) while *trans*-2-butene gave the isomeric compound Ib (m.p. 70-71°)*. The vicinal coupling constant, J_{23}, was 9.0 Hz for the high melting isomer Ia** and 4.6 Hz for the low melting Ib. Since the methyl groups in the position β to mercury have rather different shifts for the two isomers (Table 1), each isomer could be shown by NMR to contain < 3% of the other.

Comparison with NMR data from other metal alkyls indicates that the high melting isomer has the *threo* configuration Ia and the low melting isomer has the *erythro* configuration Ib [13]. However, configurational assignments from NMR data are not completely unambiguous. In fact, J_{23} is 1.6 Hz for the *threo* compound obtained from oxymercuration of *cis*-1,2-di-tert-butylethene [14] and the

TABLE 1

NMR DATA[a] (PPM) FOR *threo* Ia AND *erythro* Ib MERCURATION PRODUCTS

β 3 2 α CH_3—CH(N$(CH_3)_2$)—CH(HgCl)—CH_3	*threo* isomer Ia from *cis*-2-butene	*erythro* isomer Ib from *trans*-2-butene
H-2	2.7	3.14
H-3	2.7	2.39
N-$(CH_3)_2$	2.23	2.29
α-CH_3	1.43	1.41
β-CH_3	0.92	1.16

[a] Chemical shifts are relative to TMS.

* Dr. G. Hess has informed us that similar results have been obtained by his group at the Wright State University.

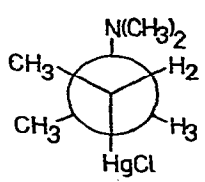
** The coupling constants were determined by comparing the shape of the complex signals from the methyl groups with calculated spectra based on different values of both J_{23} and $\Delta\nu$ (shift difference between H-2 and H-3). The estimated error is ± 0.5 Hz. A detailed study will be published separately.

two isomeric compounds obtained from hydroxymercuration of *cis*- and *trans*-2-butene give almost the same values for J_{23} (4.1 and 4.4 Hz, respectively) [15].

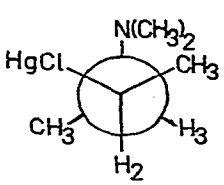
The effect of mercury on the chemical shift of neighbouring methoxy groups has recently been investigated for a series of methoxymercuration products from rigid cycloolefins, e.g. cyclobutenes. In compounds in which the methoxy group and mercury atom are *cis*, the signal from the methoxy group appears at a lower field than in the corresponding *trans*-compounds [3c, 16]. This effect should also be useful for studying preferred conformations of less rigid compounds. In fact, both configuration and preferred conformation for the aminomercuration products Ia and Ib can be determined by NMR analysis.

The NMR signal from the protons of the dimethylamino group of the compounds Ia and Ib appears at lower field (δ 2.23 and 2.29 ppm) than the corresponding signal from the free amine (2.13 ppm). The mercury atom and the dimethylamino group must therefore be mainly in a *gauche* conformation in both isomers Ia and Ib, which must have conformations B′ or C′ and B″ or C″ respectively. These conformations might be expected since Hg^{II} has a high affinity for animo groups [9]. The proton coupling constant J_{23} is 9.0 Hz for the compound Ia*. Application of the Karplus equation [17] shows that the protons H-2 and H-3 are predominantly *anti*. The preferred conformation of the compound Ia must therefore be C′ and this compound is consequently the *threo* isomer. This conclusion is strongly supported by the shifts of the β-methyl group and the β-proton, H-3, in compound Ia. The signal from the β-methyl group appears at 0.92 ppm, essentially at the same position as that of the corresponding methyl group in dimethylbutylamine (0.88 ppm). The β-methyl group and the mercury must therefore be *anti*. By contrast, the shift of H-3 (2.7 ppm) indicates that this proton is strongly deshielded by mercury, which must be in a position *gauche* to H-3. These results are compatible only with the conformation C′ for compound Ia.

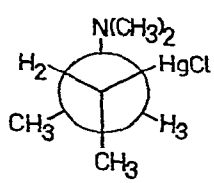
threo



A′

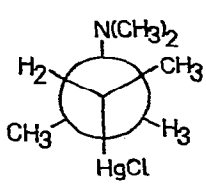


B′

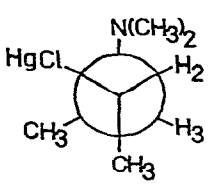


C′

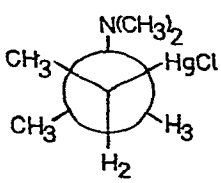
erythro



A″



B″

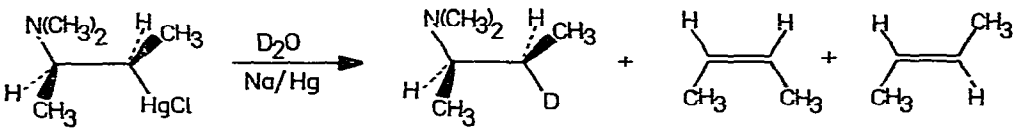


C″

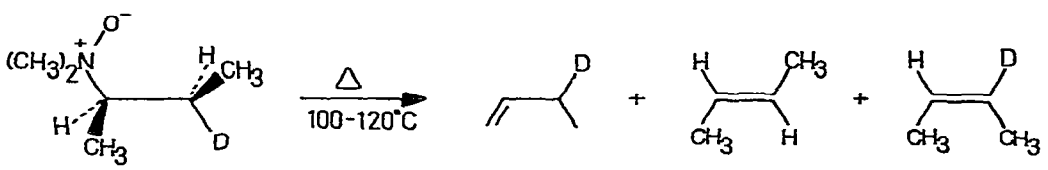
* See 2nd footnote on p. 178.

The chemical shift for the protons of the dimethylamino group and the magnitude of the coupling constant, J_{23}, indicates that the *erythro* isomer Ib has one of the conformations B″ or C″. However, the signal from the β-methyl group at 1.16 ppm is considerably displaced from that of dimethylbutylamine. The β-methyl group should thus be *gauche* to the mercury atom. Further, the shift of H-3 (2.39 ppm) indicates that this proton is *anti* to the mercury atom. The preferred conformation of the compound Ib must therefore be B″.

In order to give conclusive support to these NMR assignments we have also determined the configuration of the compound Ia by a chemical method similar to that used earlier for the palladium-promoted amination of the 2-butenes [12]. The compound Ia was treated with Na/Hg in D_2O to replace mercury by deuterium with retention of configuration (cf. ref. 18).



(Ia) (II) (III) (IV)



(V) (VI) (VII) (VIII)

The deuterated amine II obtained in this way was oxidized by H_2O_2 to the amine oxide V which on moderate heating underwent a *cis*- Cope elimination [12, 19, 20] to give a mixture of 1-butene (VI, > 99% d_1), *trans*-2-butene (VII, 4% d_1) and *cis*-2-butene (VIII, > 99% d_1) (Table 2).

Due to the isotope effect in the Cope elimination ($K_H/K_D \simeq 2.8$ [12]), the deuterium content and the isomer distribution were different from those expected from statistical considerations. Scheme 1 shows that an amination—reduction sequence proceeding with 99% stereospecificity would yield essentially the butene composition and deuterium content actually observed (Table 2).

TABLE 2

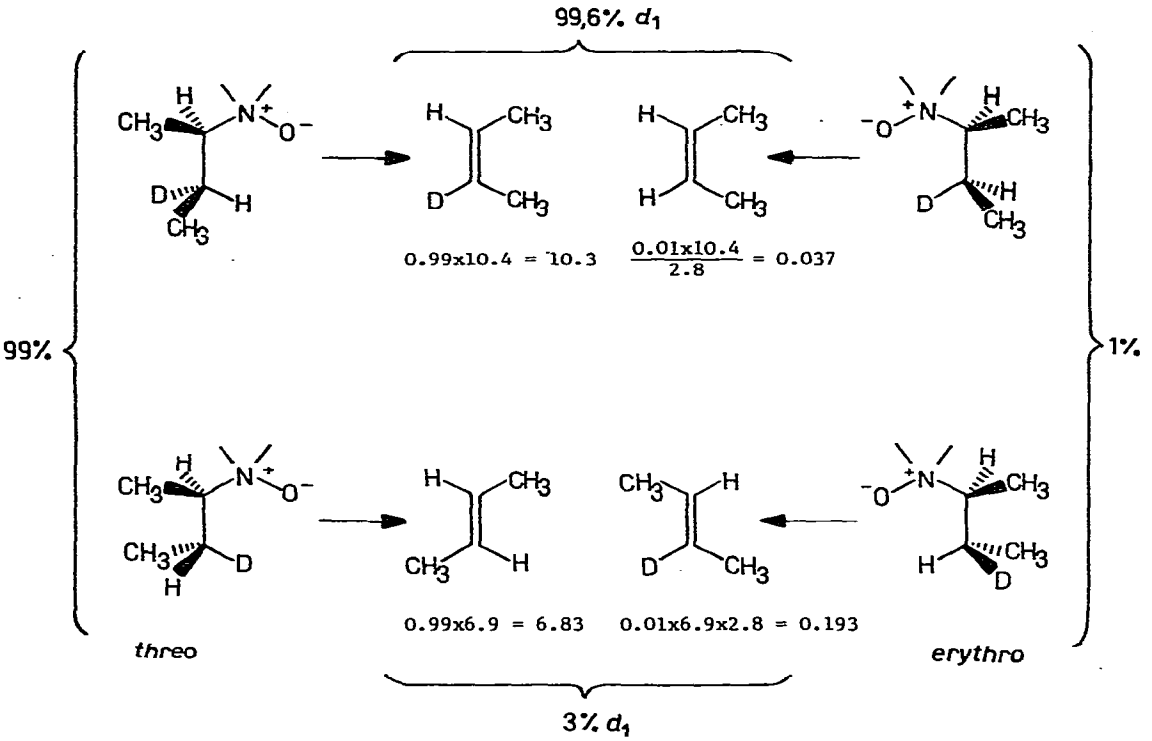
COMPOSITION OF THE PRODUCTS FROM THE AMINATION—ELIMINATION SEQUENCE APPLIED TO *cis*-2-BUTENE

Olefin	Relative yield	Butene-d_1 [a] (%)	Butene-d_0 [a] (%)	Relative yield from undeuterated amine oxide [b]
1-Butene	82.6	99.7	0.3	67.3
trans-2-Butene	6.9	4.0	96.0	21.0
cis-2-Butene	10.4	99.5	0.5	11.7

[a] The experimental error is about ± 0.5% (mean value of three determinations). [b] Ref. 19.

SCHEME 1.

DECOMPOSITION OF THE AMINE OXIDE OBTAINED FROM *cis*-2-BUTENE



When a similar reduction—elimination procedure was applied to the *erythro* compound Ib all the product butenes contained a large amount of deuterium: 1-butene (99% d_1), *trans*-2-butene (74% d_1) and *cis*-2-butene (61% d_1). The most likely explanation for this result is that epimerization took place during the reduction step, although redox decomposition* would probably give a similar result. Compound Ib was rather unstable compared with Ia. Analysis after about one week at room temperature indicated extensive decomposition with loss of olefin from the compound Ib while the isomer Ia gave a correct analysis. A correct analysis of Ib was obtained one hour after recrystallization (see Experimental).

The reduction of the mercury compound Ia to the amine II is accompanied by elimination yielding the olefins III and IV. The importance of this elimination—deaminomercuration—which proceeds *trans* with high stereospecificty, varies considerably with pH and is also dependent upon the solvent (Table 3). In 2*M* NaOH elimination was the dominating reaction and in order to get a reasonable yield of reduction product it was necessary to buffer the solution with $NaDCO_3$.

In spite of the high affinity of mercury for amine, *trans* elimination**

* The mechanism of the redox decomposition of oxymercurated 2-butene to 2-butanone has been studied [21].

** In acidic solution deaminomercuration [22] and deoxymercuration [23, 1a] proceed *trans* with high stereospecificity. Mercury bromide elimination also appears to be *trans* [24].

TABLE 3

EFFECT OF SOLVENT ON THE REDUCTION/ELIMINATION REACTIONS OF Ia

Reduction medium	Yield of amine (%)	Relative yield of *cis*-2-butene (%)
2*M* NaOH in H_2O	0.9	91.4
H_2O	5.4	91.5
$NaHCO_3$ in H_2O	19.8	91.5
C_2H_5OH(75%)/H_2O(25%)	11.5	95.7

occurs even in basic solutions. A reasonable explanation is that nucleophilic attack occurs on mercury, followed by an essentially concerted elimination of dimethylamine from the anion formed.

The effects of metal atoms on the chemical shifts of neighbouring groups are not entirely straightforward. However, from the results obtained for the dimethylaminomercuration products Ia and Ib, it appears that the deshielding effect of mercury shown by *cis*-methoxyl groups [3c, 16] may also be shown by other groups such as methyl, dimethylamine and hydrogen. Though experimental data are still insufficient, conformational analysis based on such a deshielding effect can be useful, provided that either one conformer dominates or the rotation barriers are sufficiently high to allow observation of the different conformers by NMR.

Experimental

IR, NMR, and mass spectra were recorded on Perkin—Elmer 421, Varian A60, and LKB 9000 spectrometers, respectively. Gas chromatographic separation of the butenes was carried out with a 15′ × 1/8″ column packed with 15% dimethylsulpholane on Gaschrom RZ 60/80 mesh. *cis*- and *trans*-2-Butene were commercial samples (BDH).

threo-2-Chloromercuri-3-dimethylaminobutane (Ia)

Dimethylamine (50 ml) in THF (250 ml) was added over one hour at room temperature to a solution of $HgCl_2$ (27.1 g, 0.1 mol) and *cis*-2-butene (30 g) in a mixture of THF (220 ml) and ether (50 ml). The clear solution was left in darkness for 3 days. Evaporation of the solvent gave a white solid which was extracted with chloroform. The chloroform phase was washed with water, evaporated to a small volume (5 ml), mixed with light petroleum (25 ml) and cooled to -10° to give white crystals. Yield 7.92 g (27.3%), m.p. 104° after recrystallization from light petroleum chloroform (5/1). NMR ($CDCl_3$): J_{12} = 7.0 Hz, J_{23} = 9.0 Hz*, J_{34} = 6.3 Hz, J(Hg—H_4) = 24 Hz, J(Hg—H_1) = 301 Hz (Shifts are given in Table 1.) IR (KBr): ν_{max} 2970, 2938, 2865, 2815, 2780, 1454 and 1160 cm^{-1}. (Found: C, 21.56; H, 4.13; Hg, 59.75; N, 4.27. $C_6H_{14}ClHgN$ calcd.: C, 21.43; H, 4.20; Hg, 59.66; N, 4.17%).

erythro-2-Chloromercuri-3-dimethylaminobutane (Ib)

This compound was prepared by the same procedure as the *threo* compound.

* See 2nd footnote on p. 178.

The reaction was allowed to continue for 4 days. Yield 1.33 g (4.0%), m.p. 70-71°. NMR ($CDCl_3$): J_{23} 4.6 Hz. (Shifts are given in Table 1.) IR (KBr): ν_{max} 2990, 2960, 2861, 2810, 2765, 1452 and 1291 cm^{-1}. (Found: C, 21.7; H, 4.1; N, 4.1 $C_6H_{14}ClHgN$ calcd.: C, 21.43; H, 4.20; Hg, 59.66; N, 4.17%).

Sodium amalgam reduction of threo-2-chloromercuri-3-dimethylaminobutane (Ia)

A solution of Na_2CO_3 (5.6 g, 0.06 *M*) in D_2O (30 ml) was carefully neutralized with 2 *M* DCl (30 ml) at 0°. 60 g of freshly prepared 2% sodium amalgam was added, followed by *threo*-2-chloromercuri-3-dimethylaminobutane (4.30 g) and the mixture was stirred for 24 h. The amine formed was extracted with ether. Yield 20% (GLC). The amine was purified by extraction from the ether phase with 1 *M* HCl. The water phase was washed with ether, evaporated to a small volume and made alkaline. The resulting residue was distilled to give 210 mg of pure 2-deutero-3-dimethyl-aminobutane, b.p. 92-93° (Lit. [19] 93-93.5°).

Sodium amalgam reduction of erythro-2-chloromercuri-3-dimethyl-amino-butane (Ib)

The mercury compound Ib (0.471 g) and freshly prepared sodium amalgam (7.5 g) were shaken in 8 ml of 1 *M* $NaDCO_3$ (prepared as described above) in D_2O for 24 h. The yield of amine was shown by GLC to be 11%. The product was purified by co-distillation with methanol and water, giving a methanol water (1/1) solution (0.50 ml) of the amine (16 mg). This solution was used for preparation of the amine oxide.

2-Deutero-N,N-dimethyl-3-butylamine-N-oxide

The *N*-oxides were prepared according to the procedure described by Cope et al. [19]. A solution of the amine in methanol or methanol/water was treated with 33% H_2O_2 for 24 h. The excess H_2O_2 was destroyed with platinum-black.

Elimination of hydroxylamine from threo- and erythro-2-deutero-N,N-dimethyl-3-butylamine-N-oxide

Following the procedure of Cope [19] the amine oxide (0.15 g) was heated to 150° (4°/min) under low pressure (10 mm Hg) nitrogen (flow 15 ml/min) in a 10 ml pear-shaped flask connected to a trap kept at -20°. This trap was connected via a drying tube (Drierite) to a trap held at -193°, where the butenes were collected. The relative yields and deuterium contents of the butenes are listed in Table 1.

Mass spectra

The butenes were separated by GLC and passed directly into the mass spectrometer at 12-14 eV in order to decrease the *M*-1 peaks. Blanks of each isomer were run under the same conditions. The *M*-1 peaks were less than 5% of the *M* peaks in all cases and were corrected for. The experimental error (three determinations) was ± 0.5%.

Acknowledgements

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