

It is now clear that, because of the small size difference between methyl and isopropyl⁹ (which was not known to Bose³), coupled, possibly, with a "3-alkyl ketone effect,"¹³ (-)-isocarvomenthone oxime (I) may exist to a considerable extent in conformation Ia and thus it is not unreasonable that its reduction with sodium and ethanol produces V.

Partial hydrogenation of VI produces (+)-*trans*-carvotanacetylamine, XI, benzoyl derivative¹⁴ m.p. 95–97°, $[\alpha]_D + 193^\circ$, whereas partial hydrogenation of VII produces (-)-*cis*-carvotanacetylamine, XII, benzoyl derivative¹⁴ m.p. 162°, $[\alpha]_D - 85.5^\circ$, whose configurations are therefore proved to be as shown in the formulations. Compound XI had previously been correlated with V by hydrogenation of the respective tartrate.¹⁴

Although the configuration we have proved for (-)-isocarvomenthylamine is different from that assigned by Bose, we feel that the name for this compound should be retained, the prefix "iso" indicating that the 4-isopropyl group is *cis* to the 1-methyl group and the absence of the prefix "neo" indicating that the 2-amino group is *trans* to the 1-methyl group. The as yet unknown isomer corresponding to configuration II in which the functional group at C₂ is *cis* to the methyl at C₁ would thus be called neoisocarvomenthylamine.

According to Brewster's calculations,¹⁵ neoisocarvomenthylamine (II) in the conformation shown should have $M_D - 55^\circ$ whereas isocarvomenthylamine should have $M_D - 55^\circ$ in conformation Va and $M_D 0^\circ$ in conformation Vb. The actual molecular rotation^{1b} of -23° for V supports the configurational assignment, assuming that both conformations Va and Vb contribute appreciably.¹⁶

In the full paper we shall deal with the rotations of the unsaturated amines VI, VII, XI, and XII, the correlation of the amines with the corresponding alcohols, and the steric course of reduction of the carvomenthone oximes with lithium aluminum hydride.

(13) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **84**, 2201 (1962); see, however, B. Rickborn, *ibid.*, **84**, 2414 (1962). Little is known about the 3-alkylketone effect of groups larger than methyl.

(14) J. Read and G. Swann, *J. Chem. Soc.*, 239 (1937).

(15) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5483 (1959); cf. E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 406–409.

(16) The argument is weakened because the observed rotation for the conformationally homogeneous carvomenthylamine, $M_D + 20^\circ$, is also less than the calculated, $M_D + 55^\circ$. Professor J. H. Brewster has indicated to the authors that better agreement might be expected using the hydrochlorides of the amines.

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The Absolute Configurations of the Carvomenthols

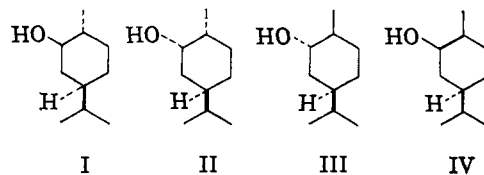
Sir:

We wish to cite an error in the stereochemical configurations assigned by Bose to the isomeric carvomenthols.¹ While the evidence for the configurations of carvomenthol (I) and neocarvomenthol (II) leaves

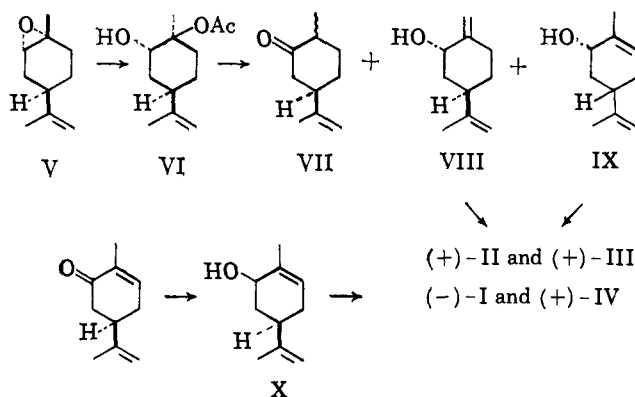
(1) A. K. Bose, *Experientia*, **8**, 458 (1952); the assignments of J. Simonsen and L. N. Owen, "The Terpenes," Vol. III, 2nd Ed., University Press, Cambridge, England, 1951, pp. 515–516, which were based on the work of R. G. Johnston and J. Read [*J. Chem. Soc.*, 1138 (1935)] are correct.

no doubt as to the stereochemistry of these isomers,² the configurations of isocarvomenthol (III) and neoisocarvomenthol (IV) have never been rigorously determined.

In connection with a study of the stereospecific ring opening of the (+)-limonene 1,2-oxides,³ (+)-*cis*-limonene 1,2-oxide (V, $[\alpha]^{25}_D + 36.00^\circ$)⁴ was treated with an acetic acid-sodium acetate solution to yield (+)-1-acetoxyn neodihydrocarveol (VI). Pyrolysis of this hydroxy acetate at 370° afforded a mixture of (+)-dihydrocarvoneisodihydrocarvone (VII, $\alpha^{25}_D + 21.80^\circ$), (+)-*trans*-isocarveol (VIII, $[\alpha]^{25}_D + 82.00^\circ$), and (-)-*trans*-carveol (IX, $[\alpha]^{25}_D - 181.80^\circ$) which were separated by fractional distillation.⁵



Hydrogenation of (-)-*trans*-carveol (IX) gave a carvomenthol fraction consisting of 63% neocarvomenthol (II) and 37% isocarvomenthol (III), while (+)-*trans*-isocarveol (VIII) gave 24.5% neocarvomenthol (II) and 75.5% isocarvomenthol (III). A sample of (-)-*cis*-carveol (X)⁶ gave a mixture of 49% carvomenthol (I) and 51% neoisocarvomenthol (IV).^{7,8}



These facts are incompatible with the configurations of isocarvomenthol (IV) and neoisocarvomenthol (III) assigned by Bose.¹ There is, however, an obvious

(2) (a) J. T. Gresham, M.S. thesis, Emory University, 1961; (b) H. P. Orloff, *Chem. Rev.*, **54**, 375 (1954), and references therein.

(3) (a) J. C. Leffingwell, Ph.D. dissertation, Emory University, August, 1963. The application of the Fürst-Plattner rule to substituted monocyclic cyclohexene epoxides will be discussed in detail in another paper. See also: (b) J. A. Angyal, *Chem. Ind. (London)*, 1230 (1954); *Quart. Rev. (London)*, **11**, 212 (1957); (c) H. Kuczynski and K. Piatkowski, *Roczniki Chem.*, **33**, 299 (1959); *ibid.*, **33**, 311 (1959); (d) J. Sicher, F. Sipos, and M. Tichy, *Coll. Czech. Chem. Comm.*, **26**, 847 (1961); (e) H. Kuczynski and A. Zabza, *Bull. acad. polon. sci., Ser. sci. chim.*, **9**, 551 (1961); *Roczniki Chem.*, **35**, 1921 (1961); *ibid.*, **37**, 773 (1963).

(4) Preparation of this heretofore unreported isomer was effected by the sequence: (+)-*trans*-limonene 1,2-oxide → (+)-1-hydroxyneodihydrocarveyl → (-)-1-mesyln neodihydrocarveyl acetate → (+)-*cis*-limonene 1,2 oxide.

(5) The purity of each component was in all cases >95% (via v.p.c.); C, H, O analyses, derivatives, and infrared spectra were consistent for these structures.

(6) Prepared according to R. H. Reitsem, *J. Am. Chem. Soc.*, **75**, 1996 (1953).

(7) The hydrogenation experiments were carried out with PtO₂ in ethyl acetate. Analyses were by v.p.c. over a 20% Carbowax on firebrick substrate using authentic samples of the four isomeric carvomenthols as internal standards.

(8) Identical results were obtained from the carvotanacetols, prepared as above from (+)-*cis*-carvomenthene oxide.

answer to this discrepancy. Assignment of the configurations of cyclohexylamines (and their corresponding alcohols) by analysis of the reactions of the amines with nitrous acid⁹ is unreliable when applied to cases in which the conformations are mobile¹⁰ (e.g., isocarvomethylamine-isocarvomethylol¹¹). Similarly, configurational assignments on the basis of esterification rates of cyclohexanols must be applied with care in mobile systems.¹²

Based on the evidence presented, and the interrelationships of the carvomethylols with the known structures of the carveols,¹³ dihydrocarveols, and sobrerols,¹⁴ the stereochemistry and absolute configurations¹³ of the isomeric carvomethylols may be assigned as follows: D-(−)-carvomethylol (I), D-(+)-neocarvomethylol (II), D-(+)-isocarvomethylol (III), and D-(+)-neoisocarvomethylol (IV).

The reversal of Bose's configurations for iso- and neoisocarvomethylol¹⁵ must of necessity change the configurational assignments which have been based on converting structures of unknown stereochemistry to either of these two carvomethylols.¹⁶ Since completion of the present work, other reports have appeared¹⁷ confirming that isocarvomethylol has configuration III.

Acknowledgment.—J. C. L. expresses appreciation for a National Defense Education Act Fellowship for the years 1960–1963.

(9) J. A. Mills, *J. Chem. Soc.*, 260 (1953); A. K. Bose, *Experientia*, **9**, 256 (1953).

(10) It has been recognized only recently that the isopropyl group is not as bulky as a *t*-butyl group and therefore does not necessarily fix the conformation of a cyclohexane ring as has so often been assumed. For example, A. H. Lewin and S. Winstein, *J. Am. Chem. Soc.*, **84**, 2464 (1962); N. L. Allinger, L. A. Freiberg, and S.-E. Hu, *ibid.*, **84**, 2836 (1962); N. Mori and F. Suda, *Bull. Chem. Soc. Japan*, **36**, 227 (1963).

(11) J. H. Brewster, (a) *J. Am. Chem. Soc.*, **81**, 5483 (1959); (b) *ibid.*, **81**, 5493 (1959).

(12) E. Eliel, *Experientia*, **9**, 91 (1953).

(13) The reversal of the *cis* and *trans* configurations for the carveols (and therefore of all the other related terpenes) as proposed by G. Farges and A. Kergomard [*Bull. soc. chim. France*, 51 (1963)] was rejected on the basis of the above arguments inasmuch as the absolute configurations of the (+)-*cis*- and (+)-*trans*-limonene 1,2-oxides have been established.² This confirmed the absolute configurations of the carveols previously postulated. The direct relationships of (+)-limonene with D-(+)-isopropylsuccinic acid has been shown¹; see also K. Freudenberg and W. Lwowski, *Ann.*, **587**, 213 (1954). The relationships of (+)-limonene → (+)-limonene 1,2-oxides⁴ and of (−)-limonene → (+)-carvone → (+)-*cis*- and (+)-*trans*-carveol have long been known.^{2b} Johnston and Read have previously found that (+)-*cis*-carveol → (+)-carvomethylol and (−)-neoisocarvomethylol and (+)-*trans*-carveol → (−)-neocarvomethylol and (−)-isocarvomethylol.

(14) H. Schmidt, *Ber.*, **83**, 193 (1950); *ibid.*, **88**, 453 (1955); *ibid.*, **88**, 459 (1955); *ibid.*, **86**, 1437 (1953).

(15) Brewster's method for calculating the molecular rotation of saturated cyclic compounds also supports such a reversal of configurational assignments.¹⁰

(16) a) Y. R. Naves and A. V. Grampoloff, *Bull. soc. chim. France*, 37 (1960); (b) Z. Chabudzynski, *Bull. acad. polon. sci., Ser. sci. chim.*, **10**, 157 (1962).

(17) A. Blumann, E. W. Della, C. A. Hendrick, J. Hodgkin, and P. R. Jefferies, *Australian J. Chem.*, **15**, 290 (1962); Z. Chabudzynski, Z. Rykowski, and H. Kuczynski, *Roczniki Chem.*, **37**, 1571 (1963).

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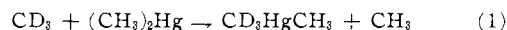
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The Reaction of Methyl Radicals with Dimethylmercury Sir:

In a recent publication¹ from this laboratory, acetone-*d*₆ was photolyzed in the presence of dimethyl-

(1) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **85**, 3086 (1963).

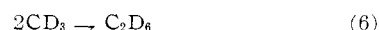
mercury in the gas phase. The following reaction was postulated



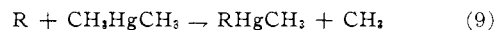
Evidence for the occurrence of this reaction in the gas phase was based mainly on the appearance of CH₃ as an important radical specie. In order to verify this interpretation, further experiments have been carried out with mixtures in which the deuteration has been reversed, as CH₃COCH₃-CD₃HgCD₃. In this way the rate of formation of CD₃, which may tentatively be ascribed to the reaction



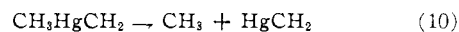
was studied and compared to the rate of formation of CH₃ which was ascribed to reaction 1 in the previous paper. The values obtained for $k_1'/k_8^{1/2}$ were found to be a factor of three lower than those ascribed previously to $k_1/k_8^{1/2}$. k_6 and k_8 are the rate constants for the combination reactions



Because this is an unusually large deuterium isotope effect for this type of process, serious doubts arose as to the correctness of the original interpretation. For this reason attempts were made to determine the actual rate of formation of CH₃HgCD₃ produced in these systems. In order to obtain reliable yields of this product, conversions had to be increased from 0.5% in the original work to about 5.0%. Blank runs carried out for long periods of time indicated that in the absence of light, the formation of CD₃HgCH₃ in CD₃COCD₃-CH₃HgCH₃ mixtures at 453°K. was negligible. However, CD₃HgCH₃ is a product when CD₃COCD₃ is photolyzed in the presence of CH₃HgCH₃. On the basis of the yield of this product as determined by mass spectrometry a value of $6.0 \times 10^{-3} \text{ l.}^{1/2} \text{ mole}^{-1/2} \text{ sec.}^{1/2}$ was calculated for the rate constant ratio $k_1/k_8^{1/2}$. Although the determination of this product does provide a more unambiguous proof for the occurrence of process 1, it should be noted that the rate constant ratio is considerably lower than the value of $30.0 \times 10^{-3} \text{ l.}^{1/2} \text{ mole}^{-1/2} \text{ sec.}^{-1/2}$ reported in the previous study. It is clear, therefore, that in the CD₃COCD₃-CH₃HgCH₃ system, CH₃ radicals are also produced by processes other than 1, such as



and/or



This is also substantiated in the earlier work in which the ratio (ethane + 1/2 methane)/CO is greater than unity at the highest temperature. Reaction 10 was not considered originally as a likely process because the quantum yield of the decomposition of dimethylmercury was reported to be independent of temperature from 26 to 198°.² Likewise, it was excluded on the basis of the pyrolytic studies of Gowenlock, *et al.*,³ which were carried out in a flow system. However, as pointed out by Srinivasan,⁴ the possibility exists that in a static system

(2) R. E. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **31**, 631 (1953).

(3) B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc. (London)*, **A218**, 269 (1953).

(4) R. Srinivasan, *J. Chem. Phys.*, **28**, 895 (1958).