static restoring force. If we then believe that k_H/k_T = 1.7 is an extreme lower limit for the isotope effect in a symmetrical hydrogen transfer, we must conclude that the transition states for the first three entries in Table I are unsymmetrical and contain a substantial amount of isotope dependent symmetric stretch zero-point energy. The inclusion of a tunnel correction merely strengthens the argument. In contrast to this conclusion, the benzylic carbon–hydrogen bond and the HBr bond have about the same energies (*ca.* 87 kcal/mol),[10] so that the cases of R = aryl would appear to be those with the least zero-point stretching vibration. These two contrary conclusions can be reconciled if the β-bromine (by virtue of a neighboring group participation) stabilizes the radicals and weakens the CH bond. Thus the maximum in the isotope effect from the stretching vibrations alone will not come at R = aryl but should come farther down the table. We cannot conclude that the maximum in fact occurs at R = H, nor can we guess which side of the maximum this point lies. It is only certain that the CH bond in ethyl bromide is the strongest one of the group.

The isotope effects thus show that the neighboring bromine lowers the energy of substituted β-bromoethyl radicals, possibly by formation of a cyclic species analogous to the bromonium ion in carbonium ion chemistry. This result is in complete agreement with those based on stereochemical arguments[6,11] and also those based on rates of bromine atom attack on alkyl bromides,[12–14] despite questions about some of the early results.[15]

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(10) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(11) P. S. Skell and P. D. Readio, *J. Amer. Chem. Soc.*, **86**, 3334 (1964); P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

(12) W. A. Thaler, *ibid.*, **85**, 2607 (1963).

(13) P. S. Skell and K. J. Shea, *ibid.*, **94**, 6550 (1972).

(14) J. G. Traynham, E. E. Green, Y.-S. Lee, F. Schweinsberg, and C.-E. Low, *ibid.*, **94**, 6552 (1972).

(15) D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *ibid.*, **81**, 5937 (1959).

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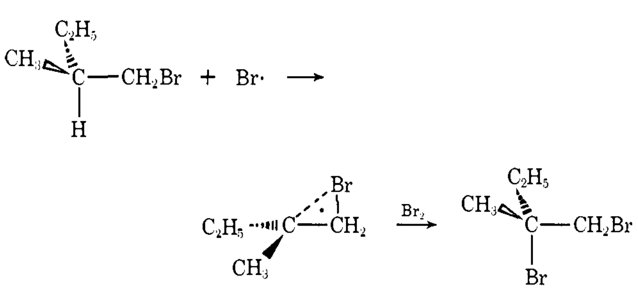
Stereospecific Radical-Chain Exchange of Hydrogens

Sir:

Among the infrequent instances in radical chemistry of retention of antipodal purity at the radical site are those in which a bromine or chlorine atom is located β to the radical site.[1] These observations have been explained with the postulate of an intermediate in which the halogen atom serves as a bridge. The postulate is illustrated for the photobromination of (+)-1-bromo-2-methylbutane.

Earlier, trapping of optically active bridged intermediates has been accomplished with bromine,[1a] *t*-BuOBr,[1b] and *t*-BuOCl.[2] We report here the successful trapping of a dissymmetric intermediate with DBr, resulting in addition of a deuterium to the radical center with >96% retention of the original skeletal configuration.



A solution of (+)-1-bromo-2-methylbutane (13.2 mmol, $[\alpha]^{27}\mathrm{D}$ +3.99° neat), bromine (4.0 mmol), and deuterium bromide (57 mmol) in trichlorofluoromethane (5 ml) was irradiated (GE A-H6 lamp, soft glass filter) at 0° in a sealed tube (dead space *ca.* 15 ml). Irradiation was discontinued when the bromine color was discharged, after 20 min. Analysis by glc showed a single product, 1,2-dibromo-2-methylbutane, as had been reported previously.[1a] Preparative glc separated "unreacted" 1-bromo-2-methylbutane, $[\alpha]^{21}\mathrm{D}$ +3.95° (neat). Mass spectrometric analysis (P and P − Br) showed the recovered monobromide to contain 51.8% d_1. The site of deuterium incorporation was established by dehydrohalogenation (DMSO-$(CH_3)_3COK$) which yielded 2-methyl-1-butene-d_0.[3,4]

Further dilution of reactants with trichlorofluoromethane does not significantly affect the results. Thus, photobromination of active amyl bromide, $[\alpha]^{21}\mathrm{D}$ +3.95°, with bromine (4 mmol), in the presence of DBr (36 mmol) in trichlorofluoromethane (30 ml), yields "unreacted" 1-bromo-2-methylbutane, $[\alpha]^{23}\mathrm{D}$ +3.83°, 54.2% d_1.

This experiment shows that in radical substitutions of deuterium for hydrogen in (+)-1-bromo-2-methylbutane (1) substitution occurs exclusively at C-2, (2) the sign of rotation is unchanged, and (3) the magnitude of the rotation is very little affected despite the high degree of conversion in a reversible reaction.

Whereas in the case of bromine substitution relating configuration and optical purity for starting material and product was difficult to accomplish, in this instance the correlation is almost trivial, since the substitution of H for D can have only a minor effect on the magnitude of rotation.[5]

Consequently, this experiment demonstrates the high degree of retention of configuration required by the bridging hypothesis (see Scheme I).[1]

A number of alternative explanations of the formation of optically active products in photohalogenations such as cage effects[6] or asymmetric induction[7] cannot explain the high degree of retention of antipodal purity which is observed for radical trapping by a *noncage reagent*, DBr.

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(1) (a) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, **85**, 2849 (1963); (b) P. S. Skell, *Chem. Soc., Spec. Publ.*, No. **19**, 131 (1964); (c) P. S. Skell and K. J. Shea, *Isr. J. Chem.*, **10**, 493 (1972); (d) P. S. Skell and K. J. Shea, "Free Radicals," Vol. 2, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., in press; (e) P. S. Skell and K. J. Shea, *J. Amer. Chem. Soc.*, **94**, 6550 (1972).

(2) D. C. Lewis, unpublished results, The Pennsylvania State University. Active 2-bromobutane was converted to active *erythro-* and inactive *threo*-2-bromo-3-chlorobutane.

(3) Exchange did not occur in the dehydrohalogenation system. When 1-bromo-2-methylbutane-d_0 was treated under the same conditions with DMSO-d_6 and $(CH_3)_3COK$, 2-methyl-1-butene-d_0 was obtained.

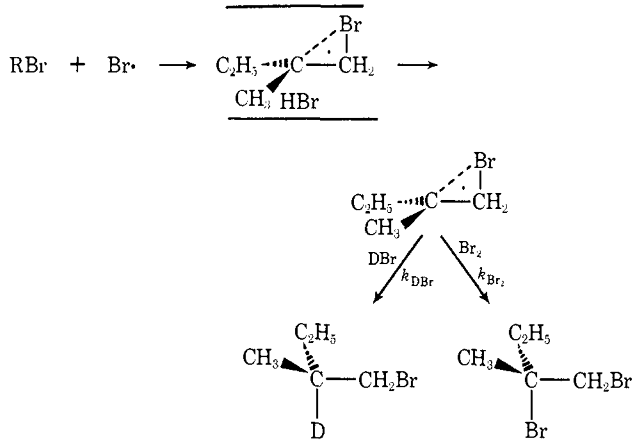
(4) A limit of <2% was placed on the deuterium analysis.

(5) The rotation estimated for 1-bromo-2-deuterio-2-methylbutane is 1% greater than for the protio compound: private communication from J. H. Brewster, Purdue University.

(6) W. O. Haag and E. I. Heiba, *Tetrahedron Lett.*, 3679 (1965).

(7) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972.

Scheme I



A second interesting aspect to this experiment is that it provides the hitherto elusive relative reactivities of bromine and hydrogen bromide.[8] The amounts of dibromide and deuteriobromide produced in the experiments are approximately equal. Since the initial concentration ratios of the trapping agents, Br_2 and DBr, are $^1/_9$ to $^1/_{14}$, and the Br_2 is exhausted during the reaction, a maximum value of $k_{Br_2}/k_{DBr} \approx 9\text{–}14$ is indicated.[9,10] Work in progress will refine this value. Other work in our laboratory has shown that k_{HBr} is approximately 50% greater than k_{DBr}.

Acknowledgment. The financial assistance of the Air Force Office of Scientific Research (Grant No. 1983) is acknowledged with gratitude.

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(8) W. A. Thaler, "Methods in Free Radical Chemistry," Vol. 2, E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969, p 137.

(9) Hydrogen bromide (*ca.* 4 mmol) is generated during the photobromination. Its accumulation is not expected to *significantly* alter the estimated relative rate ratio since deuterium bromide is in large excess.

(10) A decrease in bromine concentration during the reaction places a lower limit on the k_{Br_2}/k_{DBr} ratio.

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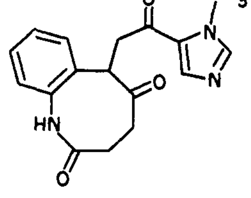
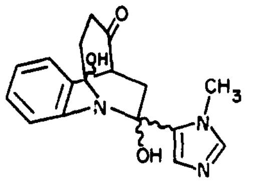
Synthesis and Revised Structure of Dehydroisolongistrobine

Sir:

In 1969 Arndt, Eggers, and Jordaan reported the isolation of several alkaloids from *Macrorungia longistrobus*.[1] Dehydroisolongistrobine was assigned the structure I by these workers even though no absorption above 3000 cm^{-1} was apparent in its infrared spectrum. Furthermore, structure II was proposed to account for the spectral properties of isolongistrobine, for which carbonyl absorption was reported to lie at 1660–1680 cm^{-1}. The ketonic carbonyl group of II would be expected to absorb at *ca.* 1710 cm^{-1}. The argument for the points of attachment of the succinic acid moiety in these structures rested primarily on rather unclear mass spectral labeling data.

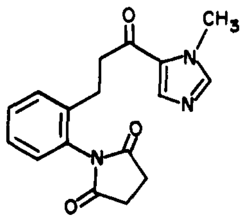


I

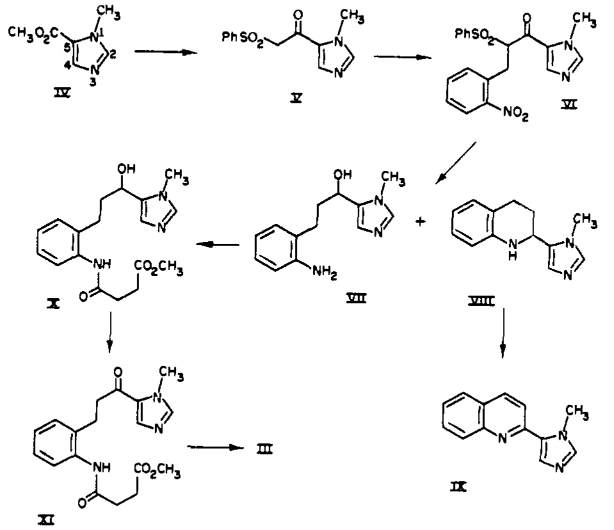


II

We concluded that structure III was in agreement with the data presented for dehydroisolongistrobine and undertook its synthesis. The imidazole ester IV, readily available *via* Jones' excellent procedure,[2] reacted with the Grignard reagent derived from methyl phenyl sulfone[3] in the procedure of Stetter and Hesse,[4] to give the β-keto sulfone V, mp 169–170.5° (EtOAc), in 88.8% yield.[5] Compound V, when treated in tetrahydrofuran at 60° under argon with an equivalent amount of potassium *tert*-butoxide in *tert*-butyl alcohol followed by addition of an equivalent amount of *o*-nitrobenzyl bromide in tetrahydrofuran and stirring at 60° overnight, provided the phenylsulfonyl nitro ketone VI, crystallized from absolute ethanol, mp 131–131.5°, in 77.4% yield.[6]



III



Compound VI, when reduced with aluminum amal-

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(1) R. R. Arndt, S. H. Eggers, and A. Jordaan, *Tetrahedron*, **25**, 2767 (1969).

(2) R. G. Jones, *J. Amer. Chem. Soc.*, 71, 644 (1949).

(3) "Organic Syntheses" Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 674.

(4) H. Stetter and R. Hesse, *Monatsh. Chem.*, 755 (1967).

(5) Physical data for V: ir (KBr) 1660 cm^{-1}; nmr (CDCl$_3$) δ 3.90 (3 H, s), 4.57 (2 H, s), 7.5–8.1 (7 H, m) ppm; uv (MeOH) λ_{max} 265 nm (ϵ 15,400) shifted to 246 nm (ϵ 12,100) in acid. *Anal.* Calcd for $C_{12}H_{12}N_2O_3S$: C, 54.54; H, 4.58; N, 10.60; S, 12.11. Found: C, 54.41; H, 4.65; N, 10.49; S, 12.08.

(6) Physical data for VI: ir (KBr) 1660 and 1530 cm^{-1}; nmr (CDCl$_3$ 100 MHz) δ 3.64 (1 H, d, J = 8 Hz), 3.65 (1 H, d, J = 6 Hz), 3.82 (3 H, s), 5.20 (1 H, d of d, J = 8, 6 Hz), 7.2–7.9 (11 H, m) ppm; uv (MeOH): λ_{max} 271 nm (ϵ 16,500) shifted to 251 nm (ϵ 15,400) in acid. *Anal.* Calcd for $C_{19}H_{17}N_3O_5S$: C, 57.14; H, 4.29; N, 10.52; S, 8.01. Found: C, 57.04; H, 4.38; N, 10.54; S, 8.08.