13.7. Allene **9b** was shown to be stable to typical reducing conditions (see below).

Reduction of 3-Chloro-3-methyl-1-phenyl-1-butyne (10). Reduction with triphenyltin hydride for 3 hr at 65.0° gave 77% triphenyltin chloride. The nmr spectrum of the filtrate indicated 3-methyl-1-phenyl-1-butyne (**10a**) and starting chloride **10** but no 3-methyl-1-phenyl-1,2-butadiene (**10b**) under conditions where >10% would have been observable. Neither chloride **10** nor allene **10b** were stable to glpc analysis. The nmr spectrum from a TBTH reaction run for 3 hr did reveal allene with **10a**:**10b** >14. Control experiments (see below) showed however that allene **10b** slowly disappeared under typical reduction conditions. A tentative estimate of the initial **10a**:**10b** ratio is therefore >10.

Allene Stability Control Experiments. In a typical experiment, a mixture of 3-chloro-3-methyl-1-butyne (**3**, 0.01 mol), TBTH (0.01 mol), the allene in question (0.0025 mol), and an inert internal standard such as benzene was prepared and divided among several tubes which were sealed and heated at 65.0°. Tubes were removed periodically and analyzed by glpc. For the allenes examined in this manner (**7b, 8b,** and **9b**) there was no change in their concentration compared to the internal standard over a 2-hr period during which time 30–40% reduction of **3** had occurred.

With allene **10b**, glpc analysis could not be used but the nmr spectrum of an analogous reaction mixture was recorded periodically over a 4-hr period. The percentage **10b** remaining after 0, 30, 60, 90, and 240 min was 100, 89, 85, 81, and 65%.

A mixture of 3-methyl-1-butyne (**3a**, 0.009 mol), 3-methyl-1,2-butadiene (**3b**, 0.009 mol), TBTH (0.007 mol), and AIBN (0.0003 mol) was heated at 65.0° in a sealed tube for 3 hr. Glpc analysis revealed no significant change in the concentration of either **3a** or **3b**

Bromohydrin Formation in Dimethyl Sulfoxide[1]

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Abstract: A number of olefins have been converted to their respective bromohydrins by the use of N-bromosuccinimide (NBS) and moist dimethyl sulfoxide (DMSO). The mechanism of this stereospecific transformation has been elucidated and general trends have been observed. These include (1) Markovnikov orientation of addition in the absence of steric restrictions; (2) failure of the reaction with highly hindered olefins and olefins bearing electron-withdrawing substituents on the double bond; and (3) systems susceptible to carbonium ion rearrangements yield, where comparison is possible, less rearranged product than has been observed under other conditions.

The use of unsymmetrical addends as a probe to delineate the mechanism (or mechanisms) of olefin addition reactions has received wide attention.[2] In particular, much consideration has been accorded the questions relating to the symmetry of the first formed ion in such reactions.[3–6]

Recent reports[5,7] indicate that unsymmetrical olefins, on reaction with a source of positive bromine (*e.g.*, styrene, Figure 1, R′ = H), produce intermediates best described as Ia (unsymmetrical bridging) rather than Ib (symmetrical bridging) or Ic (no bridging).

However, it has been reported[8] that stereospecificity of addition to *cis*-stilbene (Figure 1, R′ = C_6H_5) (presumably *via* Ia–Ic) decreases with increased solvent polarity, implicating a species capable of rotation before reaction Ic.

Results and Discussion

We have examined the addition of the elements of HOBr across the carbon–carbon double bond of a number of olefins (Table I) in aqueous dimethyl sulfoxide (DMSO) (μ = 4.3)[9] utilizing N-bromosuccinimide (NBS), which is readily soluble in this medium, as a source of positive bromine.[10] Although the exact nature of the brominating agent remains undetermined[11–14] it is, nevertheless, clear from our labeling experiments in which there is specific incorporation of

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[1] A preliminary communication of part of this work has appeared: D. R. Dalton and D. G. Jones, *Tetrahedron Lett.*, 2875 (1967).

[2] (a) See, *e.g.*, P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966, and references therein; (b) J. G. Traynham, *J. Chem. Educ.*, 40, 392 (1963); (c) A. Hassner and C. Heathcock, *Tetrahedron Lett.*, 1125 (1964).

[3] (a) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2245 (1963); (b) *ibid.*, **85**, 2248 (1963); (c) *ibid.*, **85**, 3645 (1963).

[4] J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963).

[5] K. Yates and W. V. Wright, *Tetrahedron Lett.*, 1927 (1965).

[6] H. C. Brown and K. T. Liu, *J. Amer. Chem. Soc.*, **89**, 466 (1967).

[7] P. B. D. de la Mare and S. Galandauer, *J. Chem. Soc.*, 36 (1958).

[8] R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, 27, 4523 (1962).

[9] H. L. Schlafer and W. Schaffernicht, *Angew. Chem.*, 72, 618 (1960).

[10] L. Horner and E. H. Winkelmann in "Newer Methods of Preparative Organic Chemistry," W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1964, p 151 ff.

[11] For a similar problem in the case of aqueous solution, see E. Berliner, *J. Chem. Educ.*, 43, 124 (1966).

[12] We consider that, initially, the anion A^- is the succinimide anion. It is not impossible, however, that the transfer of Br^+ to the olefin is not accomplished by NBS directly. The observed induction period (see Experimental Section) might be construed as evidence that either H_2OBr^+ and/or $DMSOBr^+$ is the first species formed and/or that Br_2 is formed by the oxidation of DMSO.[13,14] Should this be the case, the anion A^- would be Br^-. We are currently examining the effect of added ion.

[13] The oxidation of DMSO by NBS with the concomitant formation of bromine is in competition with bromonium formation. Indeed, our results do not exclude formation of Br_2 first, followed by this species being utilized as the source of positive bromine. Preliminary indications dictate that bromine might be used under the proper conditions, in place of NBS.[14] Secondly, the bromide ion thus generated would be expected to compete for bromonium ion (or bromocarbonium ion) producing significant quantities of dibromide. The fact that dibromide, although sought, could not be detected, or could be detected in only trace amounts, in any but the indicated reactions, strongly suggests that (1) the reaction of bromonium (or bromocarbonium) ion, in the absence of unusual steric or electronic effects, with DMSO is very fast and that little bromide is formed before the reaction is over and/or (2) that except as noted, bromide does not effectively compete with DMSO in DMSO. We are currently attempting to generate evidence which will enable a decision to be made between these possibilities as well as that which involves displacement of DMSO from the bromodimethylsulfoxonium intermediate by bromide.

[14] C.-T. Chen and M.-Y. Wong, *Bull. Inst. Chem., Acad. Sinica*, 13, 61 (1967); *Chem. Abstr.*, 12581 (1968). We thank Professor D. Swern for bringing this reference to our attention.

Table I

Olefin	Bromohydrin	Yield,[a] %
trans-$C_6H_5CH{=}CHC_6H_5$ (**1**)	*erythro*-$C_6H_5CH(OH)CH(Br)C_6H_5$	80
cis-$C_6H_5CH{=}CHC_6H_5$ (**2**)	*threo*-$C_6H_5CH(OH)CH(Br)C_6H_5$	82
trans-$(CH_3)_3CCH{=}CHCH_3$ (**3**)	*erythro*-$(CH_3)_3CCH(Br)CH(OH)CH_3$	90
cis-$(CH_3)_3CCH{=}CHCH_3$ (**4**)	*threo*-$(CH_3)_3CCH(Br)CH(OH)CH_3$	90
$(CH_3)_3CCH{=}CH_2$ (**5**)	$(CH_3)_3CCH(Br)CH_2OH$	87
$(CH_3)_3CC(CH_3){=}CH_2$ (**6**)	$(CH_3)_3CC(CH_3)(OH)CH_2Br$	60[b]
$C_6H_5CH{=}CH_2$ (**7**)	$C_6H_5CH(OH)CH_2Br$	76
trans-$C_6H_5CH{=}CHCH_3$ (**8**)	*erythro*-$C_6H_5CH(OH)CH(Br)CH_3$	92
$C_6H_5CH{=}C(CH_3)_2$ (**9**)	(i) $C_6H_5CH(OH)C(CH_3)_2Br$	
	(ii) $C_6H_5CH(Br)C(CH_3)_2OH$	95[c]
p-$NO_2C_6H_4CH{=}CH_2$ (**10**)	*p*-$NO_2C_6H_4CH(OH)CH_2Br$	58[d]
Norbornene (**11**)	(i) Nortricyclene bromide	
	(ii) *syn*-7-Bromobicyclo[2.2.1]heptan-2-*exo*-ol	
	(iii) 3-Bromobicyclo[2.2.1]heptan-2-ol	83[e]
$C_6H_5CH{=}CHNO_2$ (**12**)	No reaction	
$C_6H_5CH{=}CHCO_2H$ (**13**)	No reaction	
$[(CH_3)_3C]_2C{=}CH_2$ (**14**)	No reaction	

[a] Average purified yield of two or more runs. [b] Accompanied by 24% dibromide. [c] The ratio i:ii is 43:57. [d] Accompanied by 21% dibromide. [e] The ratio i:ii:iii is 1:3:3.

oxygen from $DMS^{18}O$ only[1] (*vide infra*) that either DMSO is involved with the reaction of a species resembling Ia or Ib rather than Ic (since stereospecificity is observed, Table I, compounds **1**–**4** and **8**), or that reaction occurs before rotation.

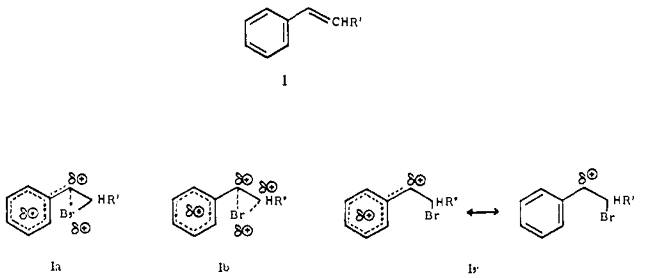

Figure 1.

We envisaged, *a priori*, three possible methods by which the bromohydrin could be stereospecifically generated from a bromonium or bromocarbonium ion in moist DMSO. The pathways, Figure 2,[12] involve (a) reaction of the bromonium ion or bromocarbonium ion with water present in the reaction medium, (b) solvation of the ion by DMSO without reaction until quenching in water, and (c) reaction of the ion with DMSO, followed by hydrolysis of the bromodimethylsulfoxonium ion so generated either by the water in the solution or during the aqueous quenching step.

In the event, epoxide formed from *trans*-stilbene, *via* the bromohydrin (i) formed in $DMS^{16}O$ containing $H_2{}^{18}O$ and the reaction quenched in $H_2{}^{16}O$ (path a); (ii) formed in $DMS^{16}O$ containing $H_2{}^{16}O$ and the reaction quenched in $H_2{}^{18}O$ (path b); and (iii) formed in $DMS^{18}O$ containing $H_2{}^{16}O$ and quenched in $H_2{}^{16}O$ (path c), demonstrated that at least 95% of the product arose from pathway c since ^{18}O was incorporated *only* in iii.

In almost all of the successful reactions reported (Table I, compounds **1**–**11**), even those involving nonsymmetric olefins (Table I, compounds **3**–**10**), a single bromohydrin product was observed (Table I, compounds **3**–**8** and **10**). Of these, only one 3,3-dimethyl-1-butene (Table I, compound **5**) resulted from the addition of DMSO to bromonium or bromocarbonium ion at the least substituted carbon atom.

The reason for this might be thought to lie in the previously observed[15] steric inhibition to addition at the highly hindered secondary carbon atom.

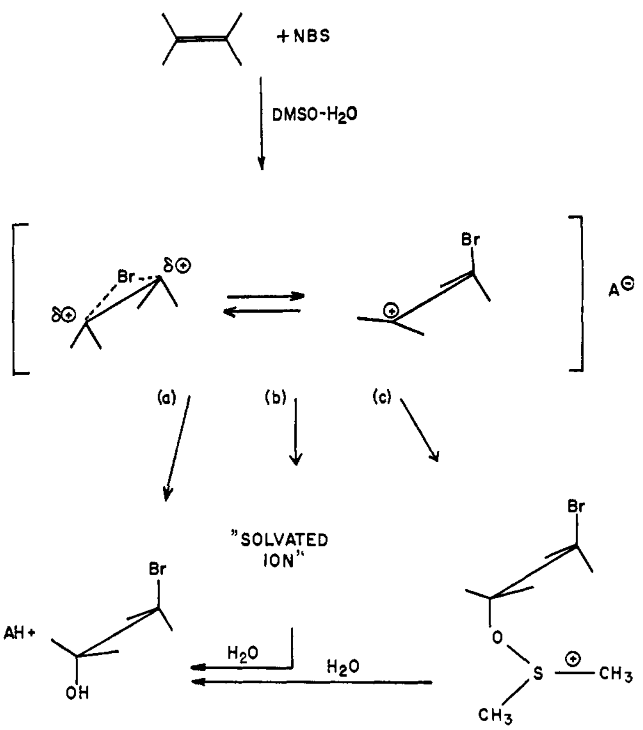

Figure 2.

In this respect, however, it is to be noted that the more highly hindered olefin, 2,3,3-trimethyl-1-butene (Table I, compound **6**), provides the bromohydrin expected on the basis of carbonium ion stability. That the reaction of this latter is not, nevertheless, particularly facile is demonstrated by the isolation of a considerable quantity of dibromide.[13,14]

Thus it appears clear that the *t*-butyl group in 3,3-dimethyl-1-butene (**5a**, Figure 3) is not particularly

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(15) W. H. Putterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, 79, 3469 (1957).

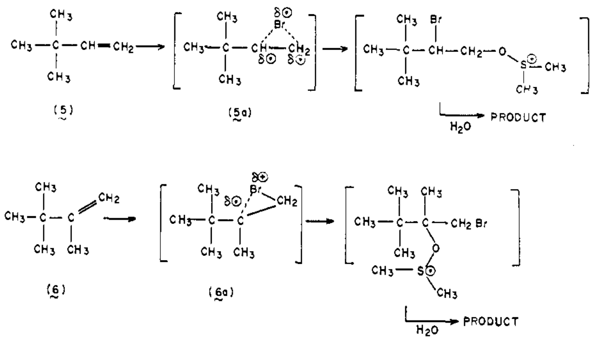

Figure 3.

effective in stabilizing the positive charge on the secondary carbon and, therefore, steric factors predominate. On the other hand, the additional methyl group provided in 2,3,3-trimethyl-1-butene (**6a**, Figure 3) does provide electronic stabilization, and product distribution reflects this.

In two cases (Table I, compounds **9** and **11**) more than one bromohydrin product was observed.

In the first of these, β,β-dimethylstyrene (Table I, compound **9**), both possible bromohydrins were obtained (in a 47:53 ratio). We suggest that an almost symmetrical bromonium ion obtains here, or in the event that no bridging is occuring, that the bromocarbonium ions are of approximately equal stability.[16]

In the second case, norbornene (Table I, compound **11**), the products obtained were identical with those previously found[17] for the reaction of the same olefin with NBS in *t*-butyl alcohol–water–sulfuric acid. However, the *ratio* of products formed was quite different. With DMSO–NBS, the ratio of nortricyclene bromide–*syn*-7-bromobicyclo[2.2.1]heptan-2-*exo*-ol–3-bromobicyclo[2.2.1]heptan-2-ol was 1:3:3 whereas in the former solvent system the ratio of the same compounds was 2:3:1. We therefore suggest that in DMSO the attack on the intermediate ion by DMSO is occurring at a rate which is competitive with bond migration.

Compounds that did not undergo reaction are those bearing electron-withdrawing substituents directly on the double bond (Table I, compounds **12** and **13**), suggesting that a high electron density in the double bond is necessary for reaction, and one (Table I, compound **14**) in which severe steric hindrance might preclude initial formation of the bromonium ion.

Conclusion

The results reported tend to support the contention that in unsymmetrical olefins capable of bromonium ion formation, unsymmetrical bridging obtains even in solvents of high dipole moment or that reaction of DMSO with the bromonium ion occurs before rotation.

Experimental Section

Reactions in aqueous DMSO and aqueous DMS^{18}O were run as previously described.[1,18] Olefins were purchased from Chemical Samples Co., Columbus, Ohio, and were used as received unless otherwise noted. Pmr spectra were obtained on a Varian A-60A spectrometer for all compounds reported and are in accord with assigned structures. Infrared spectra were obtained on a Beckman IR5-A spectrometer[19] and are in accord with assigned structures. Melting points were obtained on a Fisher-Johns block and are uncorrected. Analyses were performed by Micro-Analysis, Inc., Wilmington, Del. Gas–liquid partition chromatography (glpc) was performed with an Aerograph A90P3 chromatograph. A 10-ft SE-30 column on Chromosorb W, thermal conductivity detector, and helium as a carrier gas were used unless otherwise specified. Alumina and silica gel plates and columns of Woelm Activity Grade II supports were used unless otherwise specified. Mass spectra were obtained as previously reported.[1]

General Experimental Procedure. The olefin (1 equiv) in DMSO (Fisher reagent) under an atmosphere of nitrogen was treated with water (2 equiv) and cooled to *ca.* 10°. With stirring, NBS (2 equiv) (Arapahoe Chemical Co., Boulder, Colo., used as received) was added as one portion. After a short induction period of 2–3 min a yellow color developed and the solution became quite warm. (In the absence of external cooling the temperature may rise as high as 70°. While this is to be avoided in the case of volatile olefins, it does not appear to alter the course of the reaction.)

The color of the solution deepened as the reaction progressed in the absence or presence of cooling. Stirring for an additional 10–15 min was followed by quenching of the reaction mixture in water or dilute $NaHCO_3$ solution (with the concomitant discharge of color) and extraction of the product(s) into ether.

erythro-**2-Bromo-1,2-diphenylethanol (1).** The crude bromohydrin obtained from *trans*-stilbene was recrystallized from petroleum ether (bp 30–60°), mp 84° (lit.[20] mp 84.5–85.5°). Spectral and physical properties were identical with those of an authentic sample independently prepared.[20] The presence of *threo* isomer could not be detected (tlc, pmr).[21]

threo-**2-Bromo-1,2-diphenylethanol (2).** The crude bromohydrin obtained from *cis*-stilbene was crystallized from petroleum ether (bp 30–60°) by chilling at −70°. Recrystallization was effected in the same manner, mp 51° (lit.[20] mp 51–52°). Spectral and physical properties were identical with those of an authentic sample independently prepared.[20] The presence of *erythro* isomer could not be detected (tlc, pmr).[21]

erythro-**3-Bromo-2,2-dimethylpentan-4-ol (3).** The crude bromohydrin obtained from *trans*-4,4-dimethyl-2-pentene was crystallized from petroleum ether (bp 30–60°), mp 31°, bp 70° (2 mm).

Anal. Calcd for $C_7H_{15}OBr$: C, 43.08; H, 7.69; Br, 41.02. Found: C, 43.16; H, 7.70; Br, 41.31.

The pmr spectrum (CCl_4, TMS = 0) showed a singlet (9 H) at $\delta = 1.10$ ppm, a doublet ($J = 6.8$ Hz) (3 H) centered at $\delta = 1.28$ ppm, a singlet (1 H) at $\delta = 2.21$ ppm, a multiplet (1 H) centered at $\delta = 3.82$ ppm, and a doublet ($J = 3.0$ Hz) (1 H) centered at $\delta = 4.17$ ppm. The presence of *threo* isomer could not be detected (tlc, pmr).[21]

Oxidation of the purified alcohol with Jones reagent[22] in acetone at 0–5° afforded a quantitative yield of 3-bromo-2,2-dimethylpentan-4-one, bp 64° (1.5 mm), $n^{25}\text{D}$ 1.4640 (lit.[23] bp 83–87° (20 mm), $n^{25}\text{D}$ 1.4602).

threo-**3-Bromo-2,2-dimethylpentan-4-ol (4).** The crude bromohydrin obtained from *cis*-4,4-dimethyl-2-pentene was crystallized from petroleum ether (bp 30–60°), mp 38°, bp 52° (1.2 mm).

Anal. Calcd for $C_7H_{15}OBr$: C, 43.08; H, 7.69; Br, 41.02. Found: C, 43.23; H, 7.60; Br, 40.95.

The pmr spectrum (CCl_4, TMS = 0) showed a singlet (9 H) at $\delta = 1.09$ ppm and a doublet ($J = 6.8$ Hz) (3 H) centered at $\delta = 1.21$ ppm, the high-field signal of which was further split ($J = 1.2$ Hz) by long-range coupling. In addition, there was a singlet (1 H) at $\delta = 1.73$ ppm and an unsymmetrical doublet (2 H) ($J = 6.8$ Hz) centered at $\delta = 3.88$ ppm, the low-field signal of which was split ($J = 1.2$ Hz) by long-range coupling. The presence of *erythro* isomer could not be detected (tlc, pmr).[21]

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[16] We consider it specious, at present, to attempt to evaluate critically the possibility of (a) the presence of both bridged and nonbridged species and (b) the possibility of one species being more hindered to attack by DMSO.

[17] L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **29**, 1625 (1964).

[18] D. R. Dalton, J. B. Hendrickson, and D. G. Jones, *Chem. Commun.*, 591 (1966).

[19] The spectrometer was purchased from funds provided by a grant (CA08841) from the National Cancer Institute, National Institutes of Health. We gratefully acknowledge this financial assistance.

[20] H. O. House, *J. Amer. Chem. Soc.*, 77, 3070 (1955).

[21] By comparison with mixtures of known composition, less than 3% of the diastereomer could have been detected had it been present.

[22] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2555 (1953).

[23] C. G. Overberger and M. B. Berenbaum, *J. Amer. Chem. Soc.*, **74**, 3293 (1952).

Oxidation as described above yielded the same ketonic material.

2-Bromo-3,3-dimethylbutan-1-ol (5). The crude bromohydrin obtained from 3,3-dimethyl-1-butene was crystallized from petroleum ether (bp 30–60°), mp 38°.

Anal. Calcd for $C_6H_{13}OBr$: C, 39.78; H, 7.18; Br, 44.20. Found: C, 39.89; H, 6.59; Br, 43.68.

The pmr spectrum (CCl_4, TMS = 0) showed a singlet (9 H) at $\delta = 1.12$ ppm, a singlet (1 H) at $\delta = 1.90$ ppm, and a complex multiplet (3 H) centered at $\delta = 3.89$ ppm.

Oxidation as above afforded 2-bromo-3,3-dimethylbutyraldehyde (95%), mp 33° (lit.[24] mp 33–34°). Spectral and physical properties of this aldehyde were identical with those of a sample prepared independently.[24]

1-Bromo-2,3,3-trimethylbutan-2-ol (6). The crude product obtained from 2,3,3-trimethyl-1-butene was transferred to preparative tlc plates (silica gel) and eluted with petroleum ether (bp 30–60°). The leading band (R_f *ca.* 0.80) was eluted from the solid support with chloroform and identified (ir, pmr, tlc, glpc) as 1,2-dibromo-2,3,3-trimethylbutane by comparison with an authentic sample.[25]

The trailing band (R_f *ca.* 0.40) was eluted from the solid support with chloroform and distilled, bp 50–52° (2 mm), n^{25}D 1.4680.

Anal. Calcd for $C_7H_{15}OBr$: C, 43.08; H, 7.69; Br, 41.02. Found: C, 43.29; H, 7.49; Br, 41.11.

The pmr spectrum (CCl_4, TMS = 0) showed a singlet (9 H) at $\delta = 1.01$ ppm, an unsymmetrical doublet (long-range coupling, $J = 1.0$ Hz) (3 H) at $\delta = 1.28$ ppm, and a pair of doublets (2 H) centered at $\delta = 3.66$ ppm resulting from the diastereotropic and hence anisochronous hydrogens on the carbon bearing the bromine ($J_{\text{gem}} = 10$ Hz) with only the low-field doublet split (long-range coupling, $J = 1.0$ Hz).

In accord with its formulation as a tertiary alcohol, the bromohydrin was recovered from oxidation attempt (as above).

2-Bromo-1-phenylethanol (7). The crude bromohydrin obtained from styrene was distilled *in vacuo* in the presence of hydroquinone. The product,[18] bp 110–111° (4.2 mm) [lit.[26] bp 120–123° (5 mm)], was unstable to light and air.

Oxidation as previously described produced α-bromoacetophenone, mp 50° (lit.[27] mp 49–51°), in 86% yield.

***erythro*-2-Bromo-1-phenylpropanol (8).** The crude product obtained from *trans*-1-phenyl-1-propene was directly chromatographed on a silica gel column (the ratio of silica gel to crude product was *ca.* 25:1). The bromohydrin eluted with $CHCl_3$ was distilled, bp 108–110° (7.5 mm) [lit.[28] bp 102–104° (5 mm)]. It was identical (ir, pmr, glpc, and tlc) with a sample prepared by a published procedure.[28] The pmr spectrum ($CDCl_3$, TMS = 0) showed a doublet (3 H) centered at $\delta = 1.52$ ppm ($J = 6.2$ Hz), a broad singlet (1 H), $\delta = 2.58$, a multiplet (1 H) centered at $\delta = 4.39$ ppm, and a doublet (1 H) ($J = 4$ Hz) centered at $\delta = 4.95$ ppm. In addition, there was a singlet (5 H) at $\delta = 7.34$ ppm.

2-Bromo-2-methyl-1-phenylpropan-1-ol (9i) and 1-Bromo-2-methyl-1-phenylpropan-2-ol (9ii). The crude product obtained from 2-methyl-1-phenyl-1-propene was oxidized directly with Jones reagent[22] as above. The neutral products resulting (94% of the weight oxidized) were chromatographed on silica gel (the ratio of silica gel to crude product was *ca.* 25:1) and the products eluted with $CHCl_3$–hexane (1:1). α-Bromoisobutyrophenone (41%), bp 120–122° (2.5 mm), n^{25}D 1.5556 (lit.[29] bp 135–137° (17 mm), $n^{14.4}$D 1.5592).

Anal. Calcd for $C_{10}H_{11}OBr$: C, 52.86; H, 4.85; Br, 35.24. Found: C, 53.30; H, 4.71; Br, 35.19.

1-Bromo-1-phenyl-2-methylpropan-2-ol (54%) crystallized from petroleum ether (bp 30–60°), mp 60–60.5°.

The pmr spectrum ($CDCl_3$, TMS = 0) showed a singlet (3 H) at $\delta = 1.27$ ppm, a singlet (3 H) at $\delta = 1.32$ ppm, a singlet (1 H) at $\delta = 2.52$ ppm, a singlet (1 H) at $\delta = 5.02$ ppm, and a complex multiplet (5 H) centered at $\delta = 7.45$ ppm.

Anal. Calcd for $C_{10}H_{13}OBr$: C, 52.40; H, 5.68; Br, 34.93. Found: C, 52.63; H, 5.71; Br, 34.91.

2-Bromo-1-(*p*-nitrophenyl)ethanol (10). The crude product obtained from *p*-nitrostyrene[30] on trituration with benzene–petroleum ether (bp 30–60°) (1:1) yielded bromohydrin, mp 86–87° (lit.[31] mp 86–87°). The residue, in petroleum ether (bp 30–60°), on chilling in Dry Ice at −70° deposited 2-bromo-1-(*p*-nitrophenyl)ethyl bromide, mp 72°, identical with a sample prepared by the bromination of *p*-nitrostyrene in ether at 0–10°.

Nortricyclene Bromide (11i), *syn*-7-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (11ii), and 3-Bromobicyclo[2.2.1]heptan-2-ol (11iii). The mixture of crude products obtained from norbornene (purchased from Aldrich Chemical Co., Milwaukee, Wis., and used as received) was worked up as previously described[17] and direct comparison of samples was possible through repetition of the reported synthesis.[17] Our results were in complete accord with those published previously with the exception of the ratios noted.

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