by a straight line convoluted by a triangular slit function.[4] An error estimate of ±20 nm is based on uncertainties in threshold location, monochromator calibration, and convolution. For reasons similar to those outlined previously,[3-5] we think these thresholds correspond to good upper limit estimates of EA's.

Using McIver's DH° − EA values and our EA's, we calculate the RO–H bond energies for methanol, *tert*-butyl alcohol, and neopentyl alcohol as 101.2 ± 1.2, 102.2 ± 1.2, and 102.3 ± 1.5 kcal/mol, respectively. These numbers are within experimental error of the "best" gas kinetic values,[11] although they are systematically lower by about 2 kcal/mol.

Provided the anion is in its ground vibronic state, the photodetachment threshold represents an upper limit to the EA[3-5] and correspondingly an upper limit to DH°. However, vibrationally excited anions which photodetach with $\Delta v < 0$ would result in an apparent EA which was low. A number of factors suggest this is not happening in our experiments. First, the ions were formed by processes which are only slightly exothermic. In addition, hot bands have not previously been observed in ICR photodetachment experiments, presumably due to the long (≥1 sec) trapping times which allow radiative relaxation and thermalizing collisions to occur. Furthermore, although formed by different processes, each of the three anions studied has this same 2 kcal/mol discrepancy, and thus vibrational excitation would have to have been present to the same extent in each anion. Finally, Franck–Condon factors estimated from calculated geometries[13] suggest that diagonal transitions should be much stronger than nondiagonal transitions. Thus, even if the $v = 1$ state is appreciably populated, the $1 \rightarrow 0$ transition would be weak. Consistent with a $0 \rightarrow 0$ threshold we observe no shift for CD_3O^-.

Bond energies for aliphatic alcohols have been determined via pyrolyses of alkyl peroxides, nitrites, and nitrates,[7-11] with the usual assumption of zero barrier for radical recombination.[14] These results are internally consistent and have no obvious source of error. The systematic discrepancy (Figure 1) of 2 kcal/mol appears to be well outside of our experimental uncertainty and suggests that one of the more fundamental quantities used in the analyses may be in error.

In summary, we believe that the determination of DH° in complex molecules via these cycles is a viable alternative to other methods.[15] The apparent small discrepancy is more likely to be a result of errors in other basic data than a result of direct experimental error or unwarranted assumptions.

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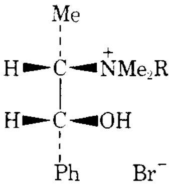
Enantioselective Oxirane Synthesis by Means of Dimethylsulfonium Methylide and Chiral Phase-Transfer Catalysts

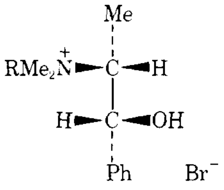
Sir:

We wish to report a novel type of asymmetric synthesis[1] of 2-phenyloxirane from benzaldehyde and the achiral Corey's ylide in the presence of an optically active, β-oxido quarternary ammonium zwitterion, V, as a catalyst.[2,3]

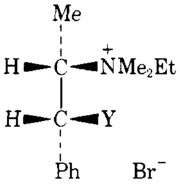
In a standard experiment benzaldehyde (283 mg, 2.68 mmol) dissolved in dichloromethane (1.5 ml) was added dropwise with stirring to a mixture of trimethylsulfonium iodide (612 mg, 3.00 mmol), 50% aqueous sodium hydroxide (1.8 g of NaOH in 1.8 ml of water) and (−)-*N*,*N*-dimethylephedrinium bromide (Ia)[4] (41.1 mg, 0.15 mmol) at 38° under nitrogen atmosphere. After 48 hr at this temperature[5] work-up and preparative TLC (silica gel, *n*-hexane: ether 10:1, R_f 0.5) gave a single product, 2-phenyloxirane (240 mg, 77%), $[\alpha]^{25}\mathrm{D}$ +4.36° (*c* 5.28, acetone),[6] 67% enantiomeric excess (*R* predominating).[6b] Use of the higher homologous R groups in I resulted in a slight increase of the chemical yield and a less effective asymmetric induction (the added quaternary ammonium salt,[7] chemical yield (%), $[\alpha]^{25}\mathrm{D}$ (*c*), enantiomeric excess (%)): Ib, 81, +4.15° (10.1), 52;[6a] Ic, 66, +4.87° (8.21), 61;[6a] Id, 83, +3.91° (3.86), 47.[6b] In the presence of the (−) quaternary ammonium salts of ψ-ephedrine[4,9] (II) the opposite direction of the asymmetric induction (*S* predominating) has been observed (ammonium salt, chemical yield (%), $[\alpha]^{25}\mathrm{D}$ (*c*), enantiomeric excess (%)): IIa, 71, −2.64° (3.63), 40;[6b] IIb, 65, −1.64° (3.29), 25.[6b] Thus the configuration of the carbon atom bearing the ammonium group is apparently responsible for the direction. The role of the hydroxyl group in I and II, however, cannot be overlooked, as the following experiments show. The catalysis of the chiral ammonium salts, III and IV,[10] gave 2-phenyloxirane in 67 and 72% yields, respectively, without any trace of optical rotation.



Ia, R = Me
b, R = Et
c, R = *n*-Pr
d, R = *n*-Bu

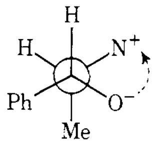


IIa, R = Me
b, R = Et

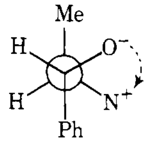


III, Y = H
IV, Y = OMe

These observations suggest that zwitterionic species such as V and VI in the organic phase should account for the induction, which originates from the dipole–dipole interaction of the chiral catalyst with otherwise achiral dimethylsulfonium methylide. The ylide attack thus occurs preferentially on one of the enantiotopic faces of benzaldehyde.[11-13]



V



VI

In order to confirm this proposal the solvent effect has been investigated. In a water-miscible solvent such as tetrahydrofuran or acetonitrile, the oxirane formation in the presence of Ia proceeded in 66 or 48% chemical yield with negligible asymmetric induction (9.1 or 0% enantiomeric excess, respectively). This is understood in terms that these solvents favor the protonation of dipole V converting it to an ammonium hydroxide of no enantioselectivity similarly as III and IV. In benzene, therefore, the catalysis did proceed with a high degree of induction (65% chemical yield, $[\alpha]^{24}\mathrm{D}$ +4.60 (c 8.92), 58% enantiomeric excess).[14]

Finally the change of the molar ratio of the catalyst to benzaldehyde gave remarkable response in the induction in the benzaldehyde–Ib reaction system (mole ratio, chemical yield (%), $[\alpha]^{31}\mathrm{D}$ (c), enantiomeric excess (%)): $^1/_{100}$, 61, +2.32° (2.16), 35;[6b] $^1/_5$, 45, +6.43° (1.64), 97.[6b] This finding shows that nearly complete asymmetric induction can be attained in the presence of as much as 0.2 equiv of the catalyst used. In the duplicated experiment 89% enantiomeric excess[6b] (51% chemical yield) was obtained.

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(4) The ammonium salt was prepared by quaternization of commercially available ephedrine (100% optically pure) with methyl bromide. The precipitated salt was washed with *n*-hexane and dried: mp 215°, $[\alpha]^{31}\mathrm{D}$ −22.5° (c 2.18, water).

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(6) The optical rotation of 2-phenyloxirane is dependent upon the concentration; the optical rotation of the same sample was found to be $[\alpha]^{25}\mathrm{D}$ +3.78° (c 3.40). The recorded maximum value is (a) $[\alpha]\mathrm{D}$ +7.94 (c 9.78, acetone) (C. R. Johnson and C. W. Schroeck, *J. Am. Chem. Soc.*, **95**, 7418 (1973)) (b) $[\alpha]\mathrm{D}$ +6.64 (c 4.9, acetone) (C. R. Johnson and C. W. Schroeck, *ibid.*, **93**, 5303 (1971)). Therefore the optical yield in this report was estimated on the basis of either the value (a) or (b) depending on the value of c.

(7) Each salt was prepared by the quaternization of *N*-methylephedrine[8] with alkyl bromide: Ib, mp 182–185° dec, $[\alpha]^{31}\mathrm{D}$ −13.9° (c 2.42, water); Ic mp 189–190° dec, $[\alpha]^{31}\mathrm{D}$ −12.2° (c 3.27, water); Id, no apparent melting point, $[\alpha]^{31}\mathrm{D}$ −8.3° (c 2.19, water).

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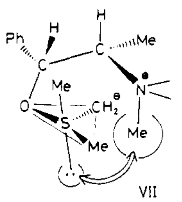
(9) (±)-ψ-Ephedrine was resolved upon treatment with tartaric acid to yield (−)-ψ-ephedrine $[\alpha]^{33}\mathrm{D}$ −43.7° (c 1.14, EtOH). Methylation of (−)-ψ-ephedrine was carried out according to the reported procedure,[8] giving (−)-*N*-methyl-ψ-ephedrine $[\alpha]^{33}\mathrm{D}$ −39.8° (c 1.22, EtOH). The tertiary amine was mixed with methyl bromide or ethyl bromide, and the resulting salts were collected, washed with *n*-hexane, and dried: IIa, mp 182–186° dec, $[\alpha]^{31}\mathrm{D}$ −34.8 (c 1.89, water); IIb, mp 160–164° dec, $[\alpha]^{31}\mathrm{D}$ −38.7° (c 0.59, water).

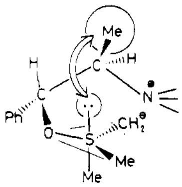
(10) III, no apparent melting point, $[\alpha]^{20}\mathrm{D}$ −1.99 (c 2.51, water); IV, mp 210°, $[\alpha]^{20}\mathrm{D}$ −88° (c 0.40, water).

(11) The rate enhancement effect of the β-hydroxyethyl unit in the quaternary ammonium salt has been observed in ester hydrolysis: (a) G. Meyer, *C.R. Acad. Sci., Ser. C*, **276**, 1599 (1973); (b) C. Lapinte and P. Viout, *Tetrahedron Lett.*, 4221 (1972); (c) *ibid.*, 1113 (1973); (d) V. Gani, C. Lapinte, and P. Viout, *ibid.*, 4435 (1973); (e) C. A. Bunton, L. Robinson, and M. F. Stam, *ibid.*, 121 (1971); see also (f) Y. Ohgo, Y. Natori, S. Takeuchi, and J. Yoshimura, *Chem. Lett.*, 1327 (1974).

(12) A possible explanation of the oxirane chirality is based on the intermediates VII and VIII containing pentavalent, trigonal bipyramidal sulfur resulting from I and II, respectively. The hypothesis is also supported by the fact that methylphenylsulfonium methylide derived from dimethylphenylsulfonium tetrafluoroborate under this condition gave a lower asymmetric induction: 87% yield, $[\alpha]^{22}\mathrm{D}$ +1.95° (c 5.64), 25% enantiomeric excess. In this case the chiral dipole V supposedly interacted with the chiral ylide disfavorably.



VII



VIII

Less severe non-bonded interaction in the preferred conformer of skew boat type.

(13) Under similar condition acetophenone afforded 2-methyl-2-phenyloxirane (76% yield, 15% conversion) of $[\alpha]^{18}\mathrm{D}$ −10.8° (c 0.98, acetone). The enantiomeric excess value was not estimated as the optical rotation of the pure sample had been unknown.

(14) *n*-Hexane as a solvent proved futile.

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Electron Spin Resonance Spectra and Structures of 9-Benzonorbornenyl and 9-Benzonorbornadienyl Radicals

Sir:

The radicals in the title and related compounds are of interest with respect to their structure,[1,2] stereoselectivity in radical-transfer reactions,[1b,3] and possible bishomoallylic and bishomobenzylic interactions. Recently Underwood and Friedman[4] reported the structure of 9-azabenzonorbornene and 9-azabenzonorbornadiene complexed to nickel acetylacetonate with the conclusion that the NH bond lies anti to the aromatic ring in both the substrates.[5] In the present investigation, interestingly the ESR data showed that the C_9–H_9 bond lies syn to the aromatic ring in 9-benzonorbornenyl (I) and 9-benzonorbornadienyl (II) radicals, which prompted us to make a preliminary report on these radicals.

The ESR spectrum of Figure 1 was observed during photolysis[6] of a cyclopropane solution of a mixture of 9-*anti*-bromobenzonorbornadiene,[7] triethylsilane, and di-*tert*-butyl peroxide[8] at −116°. The spectrum was analyzed as a doublet of 8.27 G split into two sets of 1:2:1 triplets of 1.68 and 0.28 G, respectively, split further into 1:4:6:4:1 quintets of 0.14 G.[9] Cristol and Noreen[3a] reported that the reduction of 9-*anti*-bromobenzonorbornadiene with tri-*n*-butyltin deuteride at 60° (azobisisobutyronitrile initiation) resulted in *syn*- and *anti*-9-deuteriobenzonorbornadiene without rearrangement of the skeleton. Thus the spectrum in Figure 1 was assigned to II. Figure 2 shows the ESR spectrum of I at −120° generated similarly from 9-*anti*-bromobenzonorbornene.[7] This spectrum consists of a doublet (12.7_8 G) of three sets of 1:2:1 triplets (1.93, 1.33, and 0.29 G).[9]

The largest doublets of I (12.7_8 G) and II (8.27 G) are due to α-protons (H_9). These radicals (I and II) together with the radicals III and IV are listed below in decreasing order of their α-proton hyperfine splitting constants (hfsc). Dobbs, Gilbert, and Norman[10] found a monotonic relationship between $J(^{13}CH)$ of R_2CH_2 and $a(H_\alpha)$ of $R_2\dot{C}H$. Values of $J(^{13}CH)$ between C_7 and H_7 of norbornane and norbornene and those between C_9 and H_9 of benzonorbornene and benzonorbornadiene were observed to be 132, 133, 133, and 135 Hz, respectively. These values, together with the $J(^{13}CH)$–$a(H_\alpha)$ relationship, predict that the α-proton