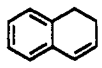
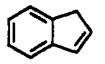
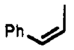
Table I. Asymmetric Epoxidation of Aromatic Alkenes[a]

entry	alkene	time,[b] h	yield,[c] %	ee,[d] %	abs[e] config
1		1	90	52	*S* (−)
2		1	97	56	1*R*,2*S* (+)
3		1	98	41	1*R*,2*S* (−)
4		4	91 (7, *E*)	76 (34, *E*)	1*R*,2*S* (−) (1*S*,2*S*)
5		8	40[f]	4	1*R*,2*R* (+)

[a] Reactions were run at 20 °C typically with 0.5 mmol of alkene, 2.5 mL of Clorox bleach, 2mL of CH_2Cl_2, 0.0025 mmol of **6**, 0.075 mmol of 4-*tert*-butylpyridine, 0.075 mmol of $n\text{-}C_{14}H_{29}(CH_3)_2(PhCH_2)NCl - 2H_2O$. [b] Time for complete consumption of alkene, except entry 5. [c] Isolated yield of epoxide after filtration through silica gel. [d] Determined by Chrompak cyclodextrin chiral capillary GC column and by ^1H NMR spectroscopy in the presence of Eu(hfc)$_3$. [e] Assigned by comparison of polarimetry measurements with literature (ref 2e, 12). [f] Percent conversion after 8 h.

by X-ray crystallography and is as shown in Scheme I. Removal of the ketal protecting group provided resolved aldehyde **2** in quantitative yield[8] and an 85% recovery of unisomerized (*R*,*R*)-hydrobenzoin. Condensation of benzaldehyde **2** with pyrrole according to Lindsey's procedure for the synthesis of hindered tetraphenylporphyrins[9] followed by oxidation afforded a 29% yield of the chiral tetraphenylporphyrin **1**, which exhibited D_4 symmetry in the ^1H NMR spectrum. Manganese was introduced by heating **1** with $MnCl_2 \cdot 4H_2O$ in DMF for 6 h, followed by treatment with HCl to provide a manganese–porphyrin complex **6**.[10]

Epoxidation reactions of several aromatic alkenes in the presence of commercial bleach, methylene chloride, a phase-transfer catalyst, and an axial amine ligand in the presence of 0.5 mol % of **6** were studied and the results are shown in Table I.[11] The enantioselectivities were determined either by resolution on a chiral gas chromatography column or by obtaining the ^1H NMR spectra in the presence of a chiral lanthanide shift reagent. The absolute configurations were assigned by polarimetry. In the cases where the alkene was terminal or cis-disubstituted the epoxidation was complete within 4 h, and following filtration of the crude reaction mixture through a plug of silica gel gave very high chemical yields of isolated epoxide with good enantioselectivity. Epoxidation of a trans alkene was markedly slower, not going to completion even after 8 h and gave much lower enantioselectivity. The epoxidation of styrene in the presence of 0.05 mol % of **6** was complete within 3 h with the identical chemical yield and enantioselectivity as the reaction using 0.5 mol % catalyst. The metalloporphyrin complex recovered from the reactions exhibited idential spectral characteristics as the original complex **6** and gave identical results when used in subsequent asymmetric epoxidation reactions.

The catalytic epoxidation results obtained with a manganese complex of the D_4-symmetrical porphyrin **1** are encouraging in that inexpensive commercial bleach can be used as the stoichiometric oxidant, very high (200–2000) rapid turnovers are possible, complete conversion of alkenes to epoxides are seen with most substrates, and the catalyst can be recycled.

Acknowledgment. We would like to thank the American Cancer Society (Grant CN-6) for funding this research and Mr. P. Cirillo of Boston University for very helpful discussions.

Supplementary Material Available: Experimental procedures, spectral data, and selected ^1H NMR and ^{13}C NMR spectra for compounds **4**, **5**, (+)-**2**, **1**, and **6** (13 pages). Ordering information is given on any current masthead page.

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(4) Dehn, W. M.; Jackson, K. E. *J. Am. Chem. Soc.* **1933**, *55*, 4284.

(5) Rieche, A.; Gross, H.; Höft, E. *Chem. Ber.* **1960**, *93*, 88.

(6) Mash, E. A.; Torok, D. S. *J. Org. Chem.* **1989**, *54*, 250.

(7) (a) Jacobsen, E. N.; Marko', I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968. (b) McKee, B. H.; Gilheany, D. G.; Sharpless, K. B. *Org. Synth.*, submitted for publication; procedure no. 2572.

(8) Mash, E. A.; Nelson, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 8256.

(9) (a) Wagner, R. W.; Lawrence, D. S.; Lindsey, J. S. *Tetrahedron Lett.* **1987**, *28*, 3069. (b) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828.

(10) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(11) Collman, J. P.; Brauman, J. I.; Hampton, P. D.; Tanaka, H.; Bohle, D. S.; Hembre, R. T. *J. Am. Chem. Soc.* **1990**, *112*, 7980.

(12) (a) Imuta, M.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 4540. (b) Boyd, D. R.; Sharma, N. D.; Smith, A. E. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2767.

Resonance Stabilization of Heteroallylic Radicals

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Summary: Estimates of the H–A BDEs in H—A—C═X, where A may be C, N, or O and X may be C, N, O, or S, support theoretical calculations suggesting that resonance energies in heteroallylic radicals decrease as the electronegativities of the terminal atoms increase.

In earlier papers we have found some remarkable differences in the homolytic bond dissociation energies (BDEs) of the H–A bonds in allylic heteroatom systems of the type H—A—C═X.[1-3] Thus, in the ketones, acetone and acetophenone, where C═X is a carbonyl group (H—C—C═O system), the H-C BDEs are lowered by 11-12 kcal/mol, relative to the $H\text{–}CH_3$ bond, presumably because of delocalization of the odd electron in the radical into the

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(1) Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714–1718.

(2) Bordwell, F. G.; Harrelson, J. A., Jr.; Lynch, T.-Y. *J. Org. Chem.* **1990**, *55*, 3337–3341.

(3) Bordwell, F. G.; Algrim, D. J.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5904–5906.

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Table I. Resonance Stabilization of Allylic-Type Radicals

no.	compd	pK_{HA}[a]	radical	$E_{ox}(A^-)$[c]	BDE[d]	ΔBDE[h]
1	$CH_2{=}CHCH_2{-}H$	(44)[b]	$C{=}C{-}C^\bullet$		86[e]	19
2	$PhCOCH_2{-}H$	24.7	$O{=}C{-}C^\bullet$	−0.607	93[f]	12
3	$CH_3CO_2{-}H$	12.3	$O{=}C{-}O^\bullet$		106[e]	−2
4	$PhCONH{-}H$	23.35	$O{=}C{-}N^\bullet$	0.074	107[g]	0[i]
5	$PhC(NH_2){=}NH$	26.7	$N{=}C{-}N^\bullet$	−0.348	102	5[i]
6	camphor	30.4	$O{=}C{-}C^\bullet$	−0.856	95	10
7	thiocamphor	17.3	$S{=}C{-}C^\bullet$	−0.584	83	22
8	$PhCSNH{-}H$	16.9	$S{=}C{-}N^\bullet$	−0.251	90[g]	17[i]
9	$PhCH_2CONMe_2$	26.6	$O{=}C{-}\dot{C}{-}Ph$	−1.023	86	19
10	$PhCH_2CSNMe_2$	21.3	$S{=}C{-}\dot{C}{-}Ph$	−0.789	84	21
11	$CH_3CH{=}NOH$	28.5	$O{=}N{-}C^\bullet$	−0.613	98	6
12	$PhCH{=}NOH$	20.2	$O{=}N{-}\dot{C}{-}Ph$	−0.342	90	14

[a] Values measured in DMSO by an overlapping indicator method; present work or ref 7, unless otherwise noted. [b] Estimated (ref 8). [c] Irreversible potentials measured in DMSO by cyclic voltammetry;[8] the values given are relative to the ferrocene/ferrocenium couple.[9] [d] Calculated from the equation BDE(kcal/mol) = $1.37\mathrm{p}K_{HA} + 23.06E_{ox}(A^-) + 73.3$, unless otherwise noted. In ref 9 we present a list of 31 compounds in which the BDEs of acidic H-A bonds have been established to ±2 kcal/mol, or better, by this method. [e] Reference 5. [f] Reference 1. [g] Reference 3. [h] Relative to BDE = 105 kcal/mol ($H{-}CH_3$) for H–C acids, BDE = 107 kcal/mol ($H{-}NH_2$) for H–N acids, and a BDE = 104 kcal/mol (RO–H) for H–O acids. [i] There is little or no effect in replacing Ph by Me, which isn't surprising since these groups are attached to the central atom of the heteroallylic system.

$C{=}O$ group.[1] On the other hand, in the carboxamides, acetamide and benzamide, where $C{=}X$ is also a carbonyl group ($H{-}N{-}C{=}O$ system), the H-N bond weakening is negligible, relative to the H-NH_2 bond.[2] But in the thiocarboxamides, thioacetamide, and thiobenzamide, where $C{=}X$ is a thiocarbonyl group ($H{-}N{-}C{=}S$ system), the H-N BDEs are lowered by 16-17 kcal/mol, relative to H-NH_2.[3] Although we have rationalized these differences in other ways,[2,3] it now appears likely that a major factor controlling these ΔBDEs may be the degree of resonance stabilization in the radicals, which changes depending on the electronegativity of the atoms at the termini of the heteroallylic radical.[4] According to calculations made by Borden and his colleagues,[4] the C–O bonds in the formyloxyl radical, $O{=}C(H){-}O^\bullet$, show no tendency to equalize, as is demanded by allylic-type resonance. The absence of any appreciable resonance energy in $O{=}C(R){-}O^\bullet$-type radicals is manifested also by the near equivalence of the BDEs of the O–H bonds in carboxylic acids and alcohols, e.g., CH_3CO_2–H, BDE = 105.8 kcal/mol vs RO–H, BDE = 104 ± 2 kcal/mol.[5] It appears, then, that resonance is unimportant in the allylic-type radicals $O{=}C{-}O^\bullet$ and $O{=}C{-}N^\bullet$ where both terminal atoms are strongly electronegative,[4,6] whereas resonance is important in the allylic-type radicals $O{=}C{-}C^\bullet$ and $S{=}C{-}N^\bullet$, where one of the terminal atoms has a relatively low electronegativity. We have now tested this postulate further by making estimates of the BDE of the sp^3 H-N bond in benzamidine, $PhC(NH_2){=}NH$, ($H{-}N{-}C{=}N$), and the BDEs of the acidic H-C bonds in (a) camphor ($H{-}C{-}C{=}O$), (b) thiocamphor ($H{-}C{-}C{=}S$), (c) the carboxamide $PhCH_2CONMe_2$ ($H{-}C{-}C{=}O$), (d) the thiocarboxamide $PhCH_2CSNMe_2$ ($H{-}C{-}C{=}S$), and (e) the oximes $CH_3CH{=}NOH$ and $PhCH{=}NOH$ ($H{-}O{-}N{=}C$). The results are summarized in Table I.

Examination of the first three entries in the Table I shows the following: (a) that changing one of the terminal atoms in $C{=}C{-}C^\bullet$ from carbon to oxygen causes the resonance energy, as judged by ΔBDE, to decrease by 7 kcal/mol, and (b) that changing both the terminal atoms in $C{=}C{-}C^\bullet$ from carbon to oxygen causes the resonance energy to drop to zero. Examination of entries four and five shows that changing one terminal atom in $C{=}C{-}C^\bullet$ to oxygen and one to nitrogen, as in $O{=}C{-}N^\bullet$, also causes the resonance energy to drop to zero, but that changing both terminal carbon atoms to nitrogen, as in $N{=}C{-}N^\bullet$, leads to retention of about 5 kcal/mol of resonance energy. The change of one terminal atom in $C{=}C{-}C^\bullet$ to oxygen, as in camphor, causes a decrease in resonance energy of 9 kcal/mol, but a change to sulfur, as in thiocamphor, $S{=}C{-}C^\bullet$, causes an *apparent increase* in resonance energy of 3 kcal/mol. The change of one terminal atom in $N{=}C{-}N^\bullet$ from nitrogen to sulfur, as in $S{=}C{-}N^\bullet$ (entry 8), also causes an *apparent* increase in resonance energy (from 5 to 17 kcal/mol). We have described the increases in ΔBDEs caused by replacement of a carbon, nitrogen, or oxygen atom by a sulfur atom as *apparent* increases in resonance energies because the larger size and polarizability of the sulfur atom may render other means of stabilization possible.

Analysis of the effects in the entries 9 and 10 in Table I is more complex in that a Ph group, which strongly stabilizes the radical and therefore moderates the influence of the heteroallylic system, is attached to the terminal carbon atom. The effect of replacing the carbonyl by a thiocarbonyl group causes only a 2 kcal/mol decrease in BDE. The effect of the thiocarbonyl group is moderated, not only by the effect of Ph, but also by the attachment of a Me_2N group to the carbon atom of the $C{=}S$ moiety. Comparison of the BDE of the acidic H-C bond in CH_3CSNMe_2, which has been found to be 92 kcal/mol (ΔBDE = 13 kcal/mol),[10] with the ΔBDE of 22 kcal/mol for the acidic H-C bond in thiocamphor, shows that this moderating effect is large.[11]

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(4) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459–1460. Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513–2519.

(5) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(6) Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 6853–6854. The authors concluded from an ESR study that resonance involving a nitrogen radical and an adjacent carbonyl group is unimportant.

(7) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

(8) Bordwell, F. G.; Harrelson, J. A., Jr.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101–3105.

(9) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.*, accepted for publication.

(10) Zhang, X. Unpublished results.

(11) Although the combined effect of the donor Ph and acceptor $C({=}S)NMe_2$ groups on the stability of this carbon-centered radical is large (ΔBDE = 21 kcal/mol), it is still 9 kcal/mol less than the sum of the individual effects on the methyl radical (30 kcal/mol).

The final two entries in Table I provide another example where the terminal atoms are oxygen and carbon, but with nitrogen as the center atom. Here ΔBDE is 6 for $CH_3CH{=}NOH$, but increases to 14 when CH_3 is replaced by Ph.

To the best of our knowledge these are the first quantitative experimental results to support the conclusion drawn from theoretical calculations[4] that resonance energies in heteroallylic radicals are closely associated with the electronegativities of the atoms at the termini.

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Articles

Synthesis of Novel Perhalo 1,3-Heterodienes from *N*-Bromoperhalo-1-alkanimines

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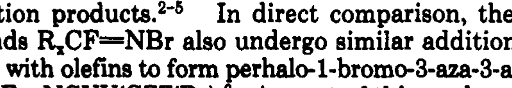
The hydrolysis of several perhalo-1-bromo-3-aza-3-alkenes ($R_xCF{=}NCF_2CF_2Br$, R_x = CF_3, C_2F_5, $ClCF_2$) affords the corresponding acid amide ($R_xCONHCF_2CF_2Br$) in excellent yield. Dehydrofluorination of the amides using active KF gives the novel 1,3-heterodienes, perhalo-1-bromo-3-aza-4-oxo-2-alkenes ($R_xCON{=}CFCF_2Br$), in high yield. Details on the synthesis and properties of the new compounds are given along with some reaction chemistry of the dienes.

Introduction

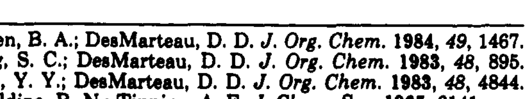
Recently, we have reported that highly halogenated *N*-bromo-1-alkanimines ($R_xCF{=}NBr$) can be prepared in excellent yields by treatment of the corresponding perhalogenated nitrile with bromine and activated cesium fluoride.[1]



$$R_xC{\equiv}N + CsF + 2Br_2 \longrightarrow (R_x)(F)C{=}N{-}Br + CsBr_3$$

This one-step general synthesis combined with the good thermal stability of the imines has allowed us to investigate the chemistry of these compounds in some detail.

Previous studies of other *N*-halo compounds have shown that the N–X (X = Cl, Br) bond is very labile, and as a result, such compounds react quite readily under mild, thermal conditions with halogenated olefins to give 1,2-addition products.[2-5] In direct comparison, the compounds $R_xCF{=}NBr$ also undergo similar addition reactions with olefins to form perhalo-1-bromo-3-aza-3-alkenes ($R_xCF{=}NCYY'CZZ'Br$).[6] As part of this work, we have prepared a series of these addition products by treating various *N*-bromoperhalo-1-alkanimines with tetrafluoroethylene.



$$(R_x)(F)C{=}N{-}Br + CF_2{=}CF_2 \xrightarrow[24\ hr.]{140°C} (R_x)(F)C{=}N{-}CF_2CF_2Br$$

R_x = CF_3, C_2F_5, $ClCF_2$

The above compounds were typically prepared as indicated by heating the $R_xCF{=}NBr$ (5 mmol) and a 2-fold excess of $CF_2{=}CF_2$ in a Pyrex vessel. The products were easily separated from excess olefin and any unreacted *N*-bromo imine by vacuum-line fractionation. Although there exists the possibility of syn and anti isomerism about the C=N bond, previous NMR studies indicate that only one isomer is formed, and it is assumed on steric grounds that the observed isomer is, in each case, the one with both perhaloalkyl groups anti to each other.[6]

Further investigation of the reaction chemistry of the perhalo-*N*-alkyl-1-alkanimines, in particular their use as precursors to a series of highly halogenated 1,3-heterodienes, has been carried out, and the results of some of these studies are discussed herein.

Results and Discussion

Hydrolysis of $R_xCF{=}NCF_2CF_2Br$. Previous studies of other perhaloalkanimines have shown that they usually undergo complete or partial decomposition with H_2O at 20 °C. For example, $CF_3N{=}CF_2$ decomposes to give CO_2, NH_4F, and HF,[7] whereas $C_3F_7N{=}CF_2$ is converted to C_2F_5CN and $C_2F_5CONH_2$. With less than stoichiometric amounts of H_2O, hydrolysis is incomplete and a low yield of the corresponding isocyanate is formed.[8]

Hydrolysis of the perhalo-1-bromo-3-aza-3-alkenes in our study was carried out by shaking with an equimolar amount of H_2O at room temperature for 2–4 h. The products formed were all low-melting, white crystalline solids and were easily identified by both infrared and NMR spectroscopy as the corresponding acid amides (eq 1). The full characterization of these compounds is given

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[1] O'Brien, B. A.; DesMarteau, D. D. *J. Org. Chem.* **1984**, *49*, 1467.

[2] Chang, S. C.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 895.

[3] Zheng, Y. Y.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 4844.

[4] Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc.* **1965**, 6141.

[5] Bauknight, C. W., Jr.; DesMarteau, D. D. *J. Org. Chem.* **1988**, *53*, 4443.

[6] O'Brien, B. A.; DesMarteau, D. D. *Rev. Chim. Miner.* **1986**, *23*, 621.

[7] Barr, D. A.; Haszeldine, R. N. *J. Chem. Soc.* **1955**, 1881.

[8] Barr, D. A.; Haszeldine, R. N. *J. Chem. Soc.* **1956**, 3416.