N,N-dimethylmethacrylamide, 6976-91-6; methyl vinyl ketone, 78-94-4; *n*-butyl methacrylate•methyl methacrylate copolymer, 25608-33-7; ethyl acrylate•methyl methacrylate copolymer, 9010-88-2; allyl methacrylate•*n*-butyl methacrylate•methyl methacrylate copolymer, 51053-21-5; *n*-butyl methacrylate-glycidyl methacrylate•methyl methacrylate copolymer, 25766-58-9; poly(*N,N*-dimethylmethacrylamide), 81665-88-5; poly(methyl vinyl ketone), 25038-87-3; [(4,5-dihydrofuran-2-yl)oxy]trimethylsilane, 51425-66-2; tris(dimethylamino)sulfur [α,α-bis(trifluoromethyl)benzenemethanolato]fluoromethylphenyl silicate, 79218-03-4.

Picosecond Observation of Kinetic vs. Thermodynamic Hydrogen Atom Transfer

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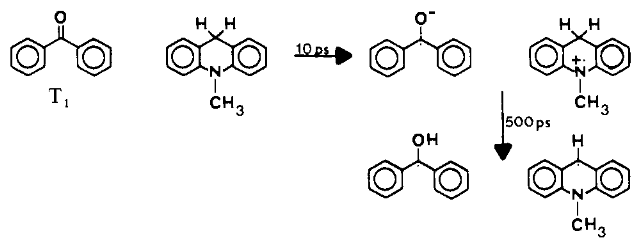
In an earlier paper,[1] it was demonstrated that the photoinduced reduction of benzophenone (Bph) by *N*-methylacridan (NMA) occurs via an electron–proton–electron mechanism (Scheme I). The initial step (within 10 ps after 355-nm laser excitation in benzene) is electron transfer from NMA to ^{3}Bph yielding the corresponding radical ions Bph$^{-}\cdot$ and NMA$^{+}\cdot$, which have visible absorbances with λ_{max} of 720 and 640 nm, respectively. Subsequent to electron transfer, proton transfer occurs from NMA$^{+}\cdot$ to Bph$^{-}\cdot$ ($t_{1/2}$ = 500 ps) yielding the benzophenone ketyl radical (λ_{max} = 550 nm) and the *N*-methylacridanyl radical (λ_{max} = 520 nm). Previously,[1] it was assumed that proton transfer occurred from the 9-position of NMA$^{+}\cdot$ (rather than from the *N*-methyl position) since the more stable, and observed, acridanyl radical would be the immediate product.[2] We now report that initial proton transfer occurs from the *N*-methyl position of NMA$^{+}\cdot$, followed by a fast ($t_{1/2}$ < 500 ps) intramolecular [1,5] proton shift yielding the acridanyl radical.

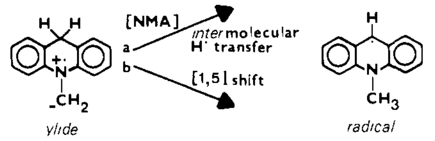
The experimental procedure for obtaining absorption spectra of photolysis intermediates with a time resolution of 25 ps has been described in detail.[1,4] Three systems observed simultaneously contained 0.05 M Bph and 1.0 M either NMA or the two deuterated analogues NMA-*9,9*-d_2 and *N*-(methyl-d_3)acridan.[5]

The rate of proton transfer from NMA$^{+}\cdot$ and NMA$^{+}\cdot$-*9,9*-d_2 were identical (within 3% as determined by the disappearance of Bph$^{-}\cdot$ and NMA$^{+}\cdot$); however, the *N*-(methyl-d_3)acridan gave a slower rate of proton transfer yielding $k_H/k_D = 1.4 \pm 0.05$. These results indicate that initial proton transfer occurs from the *N*-methyl position rather than the 9 position of NMA$^{+}\cdot$. The ratios of ketyl radical to *N*-methylacridanyl radical (determined by the ratio of the 550- and 520-nm peaks) were constant for all three systems studied indicating that although initial proton transfer occurs from the *N*-methyl position, the *N*-methylacridanyl radical appears at a rate similar to ketyl radical formation.

Scheme I

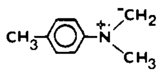


Scheme II



Further evidence that initial proton transfer occurs from the *N*-methyl position with subsequent formation of the acridanyl radical was obtained by NMR analysis. A solution of 1 M Bph with 0.015 M *N*-(methyl-d_3)acridan in C_6D_6 was photolyzed to ~50% conversion of the acridan. The remaining starting material contained >20% *N*-(methyl-d_2)acridan. Furthermore, the 9,9′-acridanyl dimer (one of the major products) contained ~100% *N*-methyl-d_2 groups.[7]

Initial proton transfer from the *N*-methyl position will create an ylide. Since the acridanyl radical appears as fast as the ketyl radical, the ylide must be converted to the acridanyl radical within 500 ps. Two mechanisms can account for conversion of the ylide to the radical, paths a and b, Scheme II. Path a is an *inter*molecular hydrogen atom transfer from the 9-position of acridan to the ylide yielding acridanyl radical and acridan. If path a is occurring, we anticipate that other ylides similar to the NMA ylide will also abstract a hydrogen atom from NMA. *N,N*-Dimethyl-*p*-toluidine (DMT) undergoes electron–proton transfer to ^{3}Bph in C_6H_6 at rates similar to those for NMA. Proton transfer from DMT$^{+}\cdot$ to Bph$^{-}\cdot$ will create a DMT ylide similar to the NMA ylide. Laser excitation of 0.05 M Bph with 1 M NMA and 1 M DMT in C_6H_6 showed the same amount of ketyl radical (5 ns after excitation) as a solution with only 1 M NMA but showed only half as much acridanyl radical. This result shows that the DMT ylide does not abstract a hydrogen atom from acridan and rules out path a as the mechanism for acridanyl radical formation. By exclusion pathway b, an *intra*molecular [1,5] sigmatropic shift, must be occurring.



DMT–*ylide*

The reason for kinetically favored proton abstraction from the *N*-methyl group rather than the thermodynamically favored 9-position must be due to the geometry of the ion pairs in solution. It is anticipated that the favored geometry would allow maximum π system overlap between the two aromatic systems and strong

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[†] Camille and Henry Dreyfus Teacher-Scholar and Alfred P. Sloan Fellow.

(1) Peters, K. S.; Pang, E.; Rudzki, J. *J. Am. Chem. Soc.* **1982**, *104*, 5535.

(2) Mass spectral analysis of NMA and NMA-*9,9*-d_2 has shown that hydrogen atom loss occurs predominantly from the 9 position.[3] Our mass spectral analysis of NMA, NMA-*9,9*-d_2, and *N*-(methyl-d_3)acridan confirm this previous conclusion, indicating that <1% of the hydrogen loss occurs from the *N*-methyl position in the gas phase.

(3) Clark, J.; Bakavoli, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1966.

(4) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.*, in press.

(5) NMA was prepared as described previously.[6] The NMA-*9,9*-d_2 was prepared by $NaBD_4$ reduction of *N*-methylacridone in 2-propanol at 80 °C, 14 h, 75% yield, NMR and mass spectrum indicated it was >93% d_2, ~6% *d*H, and <1% H_2. *N*-(methyl-d_3)acridan was prepared similar to NMA using CD_3I rather than CH_3I. NMR and mass spectrum indicated it was >99.8% methyl-d_3.

(6) Colter, A. K.; Saito, G.; Sharom, F. J. *Can. J. Chem.* **1977**, *55*, 2741.

(7) Photolysis was done with a 300-W medium-pressure Hg arc lamp filtered through a 330-nm cutoff filter. NMR analysis of the mixture (1.0 M Bph and 0.015 M *N*-(methyl-d_3)acridan in C_6D_6) before photolysis showed a peak at 3.66 ppm due to the methylene bridge protons (9 position) and a very small peak at 2.80 ppm due to the <0.2% *N*-(methyl-d_2)acridan in the starting material (along with many peaks between 6.5 and 8 ppm due to the Bph and NMA aromatic protons). After photolysis to 50% conversion, *N*-(methyl-d_2)acridan (2.80 ppm, pentet) accounts for >20% of the remaining starting material and pentets appear at 2.69 and 2.60 ppm. We assign the pentet at 2.60 ppm to the 9,9′-(*N*-(methyl-d_2)acridanyl) dimer (a sample of 9,9′-(*N*-methylacridanyl) dimer shows a singlet at 2.63 ppm). The pentet at 2.69 is possibly due to the mixed dimer from the acridanyl and ketyl radicals. The position of the *N*-methyl-d_2 NMR peaks in the starting material (2.80 ppm) and in the 9,9′-acridanyl dimer (2.60 ppm) are shifted upfield from the *N*-methyl groups in the corresponding compounds, 2.84 and 2.63 ppm, respectively. Isotope shifts of these magnitudes for CHD_2 vs. CH_3 groups are common in proton NMR.[8] NMR spectra were recorded on a Bruker 300 MHz.

(8) Gutowsky, H. S. *J. Chem. Phys.* **1959**, *31*, 1683.

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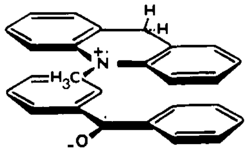
association of the negative charge on Bph$^{-\cdot}$ (located predominantly on the oxygen) with the positive charge on NMA$^{+\cdot}$ (located on the nitrogen). A structure that satisfies these requirements is shown below.



It is apparent that interaction between the oxide center and the methylene protons of NMA$^{+\cdot}$ requires major restructuring of the complex, whereas interaction with the *N*-methyl protons, to give the observed proton transfer, can readily occur.

Future studies will involve other systems that can show proton transfer from more than one position to see if the reported phenomenon is general. Also of interest is whether other exothermic proton shifts (e.g., [1,7] shift) occur as fast as this [1,5] shift.

Acknowledgment. This work is supported by a grant from the National Science Foundation CHE-8117519. K.S.P. acknowledges support from the Henry and Camille Dreyfus Foundation and the Alfred P. Sloan Foundation.

Registry No. NMA, 4217-54-3; ^{3}Bph, 119-61-9.

Solvolytic Hydroperoxide Rearrangements. A New Ring Expansion Reaction

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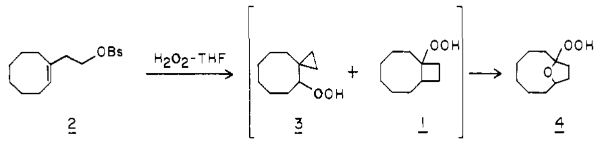
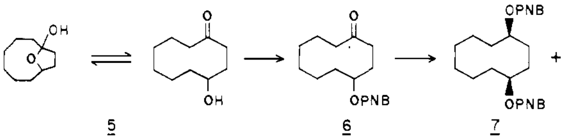
We report a new and efficient two-carbon ring expansion reaction of carbocycles that yields medium-sized rings by hydrogen peroxide mediated solvolysis of homoallylic brosylates. Reaction of cycloalkenylethyl brosylates in 1:1 90% H_2O_2–THF[1] results in solvolytically generated cyclobutyl hydroperoxides that undergo facile Criegee type rearrangement[2] affording oxa-bridged, hydroperoxy hemiketals[3] of the corresponding 4-hydroxy ketones augmented by two methylene groups (Scheme I).

The Criegee[2] perester–hydroxy ketone rearrangement of decalin hydroperoxide has long been known to produce an oxa-bridged bicyclic product; however, this reaction has received little attention other than investigation of its rather unusual mechanism.[4,5] Our interest in this rearrangement arose from synthetic considerations involving sesquiterpenes[6] that are formally oxa-bridged hemiketal derivatives of 4-hydroxycyclodecanones. It occurred to us that Criegee type rearrangements in appropriately substituted bicyclo[6.2.0]decanes such as **1** would result in the basic bicyclic ring system of these natural products.

Scheme I

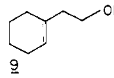
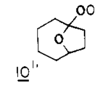
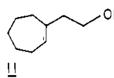
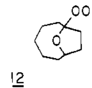
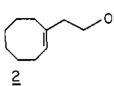
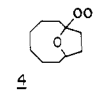
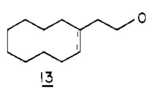
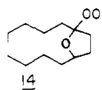
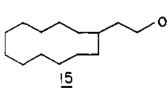
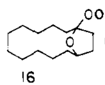


Scheme II



PNB = p-nitrobenzoyl

Table I. Two-Stage Solvolytic Expansions of Brosylates

entry	time (temp, °C)	product (yield, %)	derivative mp
 9	0.5 (25)	 (78) 10[10]	95-96°C[a,b]
 11	1 (25)	 (72) 12	83-84°C[a,b]
 2	3 (25)	 (84) 4	92-94°C[a,c]
 13	26 (40)	 (47) 14	109.5-110°C[b,d]
 15	72 (37)	 (81) 16	132-133°C[a,b]

[a] Of corresponding hydroxyketone. [b] Phenylurethane. [c] p-Nitrobenzoate. [d] Bicyclic hemiacetal.

To this end, we investigated the preparation of **1** by solvolysis in the presence of H_2O_2 of the readily available brosylate **2**.[7] Solvolysis (2 h) of **2** at 25 °C in 1:1 90% H_2O_2–THF[1] buffered with 1.1 equiv of K_2HPO_4 resulted in the formation of **3** (59%) and **4** (10%). While the ratio of **3** to **4** is quite similar to the ratio of cyclopropylcarbinyl to cyclobutyl products observed by other workers,[7,8] the presence of a one-proton resonance at δ 4.65 clearly indicated that the minor product was not the expected cyclobutyl isomer. In the absence of the K_2HPO_4, **4** is the principal reaction product; but it is accompanied by almost an equal amount of an as yet unidentified polar peroxy compound. The cyclopropylcarbinyl hydroperoxide **3** is stable under the solvolysis conditions; however, if the mixture is acidified **3** is converted to **4** in 84% yield.

That **4** is indeed the ring expansion product was confirmed by conversion to the known[9] *cis*-1,4-cyclodecandiol bis(*p*-nitrobenzoate) **7** (Scheme II). Hydrogenation of **4** (H_2/PtO_2 in THF) afforded a mixed hemiketal–hydroxy ketone **5**, which upon treatment with *p*-nitrobenzoyl chloride in pyridine gave a single keto ester **6** (mp 92–94 °C). Reduction of **6** with BH_3·THF at

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(1) Concentrated H_2O_2 (90%) is available from FMC corp. Investigators should read FMC Technical Bulletin 46 for information on the safe handling and disposal of high-strength H_2O_2. In addition, investigators should read: Shanley, E. S.; Perrin, J. R. *Jet Propul.* **1958**, *28*, 382–385. A reprint of this article is contained in FMC Bulletin 46. The vigorous decomposition of H_2O_2 is catalyzed by heavy metals and heavy metal ions. Care should be exercised to exclude these materials and dust particles from H_2O_2 reaction mixtures.

(2) Criegee, R. *Ber. Dtsch. Chem. Ges.* **1944**, *77*, 722–726. Criegee, R.; Kasper, R. *Liebigs Ann. Chem.* **1948**, *560*, 127–135. Criegee, R.; Dietrich, H. *Ibid.* **1948**, *560*, 135–141. Criegee, R.; Schnorrenberg, W. *Ibid.* **1948**, *560*, 141–148.

(3) Investigators should familiarize themselves with the precautions for handling peroxy compounds outlined in Swern's excellent treatise on organic peroxides. See: D., Ed. "Organic Peroxides"; Wiley-Interscience, New York, 1970.

(4) Bartlett, P. D.; Kice, J. *J. Am. Chem. Soc.* **1953**, *75*, 5591–5595. Goering, H.; Olson, A. *Ibid.* **1953**, *75*, 5853–5859. Denny, D. B.; Denney, D. G. *Ibid.* **1957**, *79*, 4806–4808.

(5) Hedaya, A.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 1661–1672. Yoblokov, V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1980**, *49*, 833–842.

(6) Chowdhury, P.; Sharma, R.; Thyagarajan, G.; Herz, W.; Govindan, S. *J. Org. Chem.* **1980**, *45*, 4993–4997. Bohlman, F.; Zdero, C.; King, R.; Robinson, H. *Phytochemistry* **1980**, *19*, 1547–1549. Cowell, P.; Cassidy, J.; Chang, C.; Kozlowski, J. *J. Org. Chem.* **1981**, *46*, 1108–1114.

(7) Paquette, L.; Henzel, K. *J. Am. Chem. Soc.* **1975**, *97*, 4649–4658.

(8) Hanack, M.; Scheider-Bernlohr, H.; Schneider, H. J.; Huttinger, R.; Wentrup, G. *Leibigs Ann. Chem.* **1968**, *717*, 41–53.

(9) *cis*-1,4-Cyclodecanediol bis(nitrobenzoate) has been prepared via the hydroboration of *cis,trans*-1,5-cyclodecadiene. Mehrotra, I.; Devaprabhakara, D. *Tetrahedron Lett.* **1973**, 1885–1886.

0002-7863/83/1505-5709$01.50/0