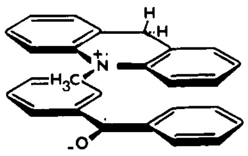
association of the negative charge on $Bph^{-\cdot}$ (located predominantly on the oxygen) with the positive charge on $NMA^{+\cdot}$ (located on the nitrogen). A structure that satisfies these requirements is shown below.



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.

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

Solvolytic Hydroperoxide Rearrangements. A New Ring Expansion Reaction

Robert C. Ronald* and Thomas S. Lillie

Department of Chemistry, Washington State University
Pullman, Washington 99164

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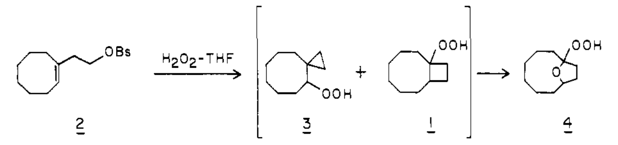
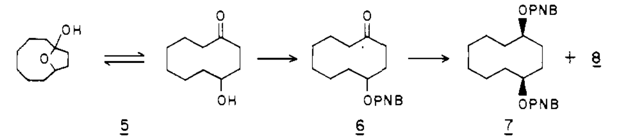
We report a new and efficient two-carbon ring expansion reaction of carbocycles that yields medium-sized rings by hydrogen peroxide mediated solvolysis of homoallylic brosylates. Reaction of cycloalkenylethyl brosylates in 1:1 90% H_2O_2–THF[1] results in solvolytically generated cyclobutyl hydroperoxides 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

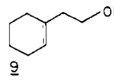
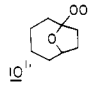
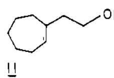
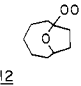
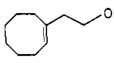
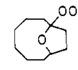
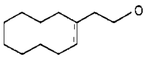
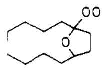
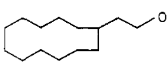
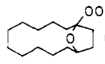


Scheme II



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	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.

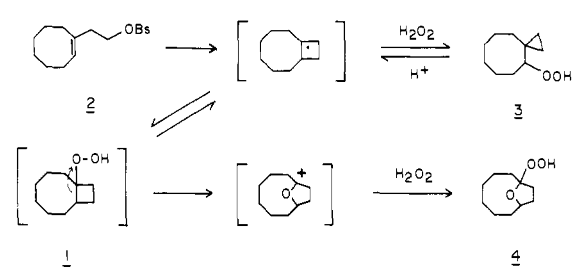
[6] Chowdhury, P.; Sharma, R.; Thyagarajan, G.; Herz, W.; Govindan, S. *J. Org. Chem.* **1980**, *45*, 4993-4997. Bohlman, F.; Zdero, C.; King, R.; Robinson, H. *Phytochemistry* **1980**, *19*, 1547-1549. Cowell, P.; Cassidy, J.; Chang, C.; Kozlowski, J. *J. Org. Chem.* **1981**, *46*, 1108-1114.

[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.

Scheme III



0 °C produced a pair of hydroxyesters that could be separated chromatographically, after *p*-nitrobenzoylation, into the cis (mp 143–145 °C)[9] and trans (mp 158–159 °C) diesters.

Optimal conversions (see Table I) of brosylates[10] are conveniently achieved by a one-pot, two-stage solvolysis procedure. Initially, the brosylate is dissolved in THF containing 1.1 equiv of powdered, suspended buffer ($K_2HPO_4{\cdot}3H_2O$). The mixture is cooled in an ice bath to avoid the small, but significant, exotherm that accompanies the mixing of high-strength H_2O_2 with organic solvents, and then the calculated amount of 90% H_2O_2 required to achieve a substrate concentration of 0.25–1.0 M in 50% THF is carefully added. The reaction vessel is then placed in a bath at the desired reaction temperature. Subsequently, when all of the brosylate has reacted, the second stage is completed by acidification with 2.1 equiv of $TsOH{\cdot}H_2O$ to convert **3** to **4**. The hydroperoxy hemiketal product is isolated by normal aqueous workup.

The oxa-bridged hydroperoxide products are only modestly stable. While they could be isolated and chromatographed on silica gel, concentrated solutions and purified samples rapidly lost H_2O_2 and became contaminated with dimeric peroxides. To facilitate handling, the crude hydroperoxides were immediately reduced (H_2/PtO_2 in THF).

The formation of **4** from **2** and **3**, as well as the homologous expansions, can be rationalized on the basis of a reversibly formed bicyclobutonium ion intermediate,[7,8] which, when trapped by H_2O_2 affording the fused cyclobutyl isomer, i.e., **1**, rapidly undergoes an irreversible Criegee type migration (Scheme III). As yet, we have been unable to observe any fused cyclobutyl derivatives directly. In the unbuffered system, the cyclopropylcarbinyl isomer, e.g., **3**, is observable by TLC[12] but remains in relatively low concentration throughout the course of the reaction. Although other modes of migration are possible from **1** and **3**, the principal if not exclusive pathway involves only the ring fusion atoms.

In addition to the brosylates we also find that the cyclopropylcarbinols are excellent substrates for ring expansion. Treatment of spiro[2.7]decane-4-ol[6] with TsOH in 1:1 H_2O_THF results in almost immediate conversion to **3** followed by reaction to form **4**. Since the cyclopropylcarbinols are readily available from cyclopropyl ketones, this provides an alternative route to ring expansion precursors; we are investigating the rearrangements of the cyclopropylcarbinols as well as other homoallylic systems to further explore this novel ring expansion reaction.

Acknowledgment. We thank the Boeing Co. for the gift of the Nicolet Technology Inc. 200-MHz NMR spectrometer. T.S.L. thanks the Graduate School of Washington State University for an assistantship.

Supplementary Material Available: Additional experimental data for brosylate **9**, **11**, **13**, and **15**, phenylurethane from **10** and **12**, *p*-nitrobenzoate from **4**, bicyclourethane from **14**, and urethane from **16** (2 pages). Ordering information is given on any current masthead page.

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[10] The brosylates were obtained in four steps from ketones by the following: $(MeO)_2POCHLiCO_2Me$ in THF/HMPA; LDA followed by 5% HCl; $LiAlH_4$; brosyl chloride in pyridine.

[11] 4-Hydroxycyclooctanone: Moell, H.; Urbanek, F. *Festschr. Carl Wurster 60. Geburstag* 1960, 91-97.

[12] Hydroperoxides and peroxides are conveniently and sensitively detected by TLC using Wurster dyes. [Solutions of 1% w/v *N,N,N',N'*-tetramethylphenylenediamine in 50% aqueous MeOH containing 1% HOAc (Smith, L.; Hill, F. *J. Chromatogr.* **1972**, 66, 101-10).] Peroxy compounds appear as blue spots; the color from hydroperoxides develops rapidly, while some peroxides require gentle heating for development of color within a few minutes.

Cis Addition of Hydride to η^2-Alkyne Complexes by Initial Reaction at an η^5-C_5H_5 Ring. Crystal and Molecular Structure of (η^5-C_5H_5)FeCO(PPh_3)(η^1-(*E*)-C(CO_2Et)=C(H)Me)

Daniel L. Reger* and Kenneth A. Belmore

Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

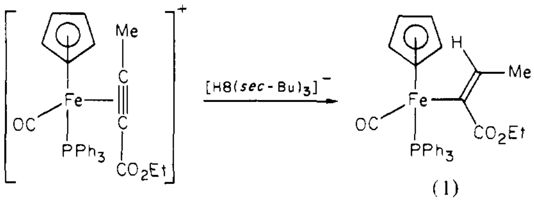
Jerry L. Atwood* and William E. Hunter

Department of Chemistry, The University of Alabama
University, Alabama 35486

Received May 2, 1983

We have reported that a variety of nucleophiles will react with $[(\eta^5\text{-}C_5H_5)FeCO(L)(\eta^2\text{-alkyne})]^+$ (L = PPh_3, $P(OPh)_3$) complexes to yield η^1-alkenyl derivatives. In our initial report,[1] trans addition of the nucleophile was assumed[2] and partially verified by ^1H nuclear Overhouser effect (NOE) enhancement experiments. Subsequently, the preparation of both the *Z* and *E* isomers of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3](\eta^1\text{-}C(Me){=}C(Ph)Me)$ coupled with the solid-state structure of the *Z* isomer definitively proved trans addition of carbon nucleophiles delivered from organocuprate reagents.[3] Although trans addition of other nucleophiles, such as $[SPh]^-$, also seems certain,[4] NOE experiments tentatively indicated that the addition of hydride was overall cis. We initially believed this result to arise from trans addition followed by a cis–trans isomerization,[1] a process shown to be reasonable for other metal–alkenyl systems.[5] We show here that the course of the hydride addition reaction is first addition to the η^5-C_5H_5 ring followed by internal cis transfer of hydrogen to the alkyne from the η^4-C_5H_6 ring that forms in the first step.

In order to definitively assign the stereochemistry of an η^1-alkenyl complex formed from hydride addition, the X-ray crystal structure of the product of reaction 1 was determined.[6] The crystal and molecular structure of **1**, illustrated in Figure 1, clearly shows that the hydrogen atom at the β-alkenyl position is disposed cis with respect to iron. The regiochemistry of the reaction, addition away from the electron-withdrawing ester substituent, is as expected from our earlier structure of $(\eta^5\text{-}C_5H_5)FeCO(PPh_3)(\eta^1\text{-}C(CO_2Et){=}CMe_2)$ (**2**).[7] Bond lengths and angles are



(1)

(1)

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[1] Reger, D. L.; McElligott, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5923.

[2] Trans addition of nucleophiles to $[CpFe(CO)_2(\eta^2\text{-alkene})]^+$ complexes has been previously demonstrated: (a) Nicholas, K. M.; Rosan, A. M. *J. Organomet. Chem.* **1975**, *84*, 351. (b) Sanders, A.; Magatti, C. V.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1610.

[3] Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101.

[4] Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *J. Am. Chem. Soc.*, submitted for publication.

[5] Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

[6] Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with cell parameters; $a = 9.075$ (4) Å, $b = 9.414$ (4) Å, $c = 30.574$ (7) Å, $\beta = 92.31$ (4)°, with $Z = 4$. A total of 2323 reflections were measured to 2θ max of 38°. Of these 1658 reflections were considered observed ($I > 3\sigma(I)$). The final R and R_w values were 0.062 and 0.068.

[7] Reger, D. L.; McElligott, P. J.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1982**, *1*, 443.