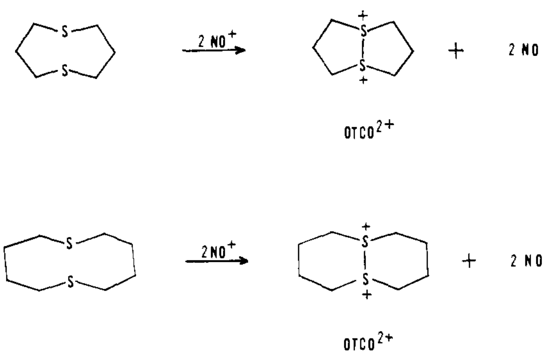


Figure 1. The reaction of DTCO and DTCD with NO$^+$

cationic species behave either as electrophiles or as two-electron oxidizing agents.

Although these dications are formed by the oxidation of dithioethers, they may also be viewed as dialkylated disulfides. However, disulfides have never been dialkylated. Only monoalkylation is achieved[1] by treatment of disulfides with the reactive alkylating agent, $(CH_3)_3O^+BF_4^-$. Therefore an oxidative coupling of two dithioether groups may provide the only route to this class of compounds.

The DTCO^{2+} dication is prepared by adding a solution of 1 mol of DTCO in acetonitrile ($\sim 10^{-1}$ M) to 2 mol of solid $NOBF_4$ on a vacuum line. As the $NOBF_4$ reacts, the solution turns yellow (the color of the cation radical, DTCO$\cdot^+$) and NO is evolved.[2] However, after all the $NOBF_4$ has reacted the solution becomes colorless and exhibits no ESR signal. The evolved NO was measured and corresponds to >95% of the theoretical amount expected for a two-electron oxidation. The color and ESR spectrum of the DTCO$\cdot^+$ cation radical can be regenerated by adding 1 mol of DTCO to the solution containing DTCO^{2+}.

$$\mathrm{DTCO^{2+} + DTCO \rightleftharpoons 2DTCO\cdot^+}$$

Fractional crystallization of the solution of DTCO^{2+} gives a colorless solid having the correct chemical analysis for $DTCO(BF_4)_2$ but exhibiting no ESR signal. The ^{13}C NMR spectrum of the dication in CD_3CN shows two peaks 53 and 35 ppm at a ratio of two to one. The ^1H NMR is also consistent with a compound having two different methylene groups but the splitting pattern is extremely complicated and could not be resolved. The DTCO^{2+} ion exhibits λ_{max} at 233 nm in acetonitrile with an extinction coefficient of 7×10^3.

The DTCO^{2+} dication reacts either as an electrophile or as an oxidizing agent depending on the added reagent. When solid $DTCO(BF_4)_2$ is treated with a saturated aqueous solution of sodium bicarbonate, 1,5-dithiacyclooctane monosulfoxide is formed in 80% yield. Conversely, when DTCO^{2+} is treated with isopropyl alcohol in acetonitrile, acetone is observed as the oxidation product in 50% yield. Likewise treatment of the dication with I^- gives I_2.

$$\mathrm{DTCO^{2+} + (CH_3)_2CHOH \rightarrow DTCO + (CH_3)_2CO + 2H^+}$$

The ten-membered ring dithioether, DTCD, also reacts with $NOBF_4$ in CH_3CN to give the dication, DTCD^{2+} (λ_{max} 232 nm, ϵ 4×10^3.) However, with DTCD the dication is formed without the intermediate cation radical being observed. Even when equimolar amounts of DTCD and DTCD^{2+} are mixed, no ESR signal is observed, and it appears that no reaction has taken place.

Solid $DTCD(BF_4)_2$ gives the correct elemental analysis and exhibits ^1H and ^{13}C NMR spectra in CD_3CN which are consistent with the proposed DTCD^{2+} dication.

Another example of a dication with an $S^+{-}^+S$ bond is found in the S_8^{2+} ion formed by oxidizing S_8 with AsF_5.[3] The crystal structure analysis of $S_8(AsF_6)_2$ shows that the eight-membered ring is fused in a cis manner to give the [3.3.0]bicyclic system.[4] At the present time the manner of ring fusion in DTCO^{2+} and DTCD^{2+} has not been determined. However, the S_8^{2+} unit should be viewed as the parent of this class of compounds with the DTCO^{2+} ion having all the nonbridging sulfurs in the eight-membered ring replaced by methylene groups.

Acknowledgment. We wish to thank Mr. David Roush for his help in obtaining the ^{13}C NMR spectra.

References and Notes

(1) H. Meerwein, K.-F. Zenner, and R. Gipp, *Justus Liebigs Ann. Chem.*, **688**, 68 (1965).

(2) W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976).

(3) R. J. Gillespie, J. Passmore, P. K. Ummat, and O. C. Vaidya, *Inorg. Chem.*, **10**, 1327 (1971).

(4) C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, **10**, 2781 (1971).

W. Kenneth Musker,* Patricia B. Roush
Department of Chemistry, University of California
Davis, California 95616

Received July 22, 1976

4-Homoadamanten-4-yl Triflate. Ring Contraction and Ion Pair Return in Trifluoroethanol

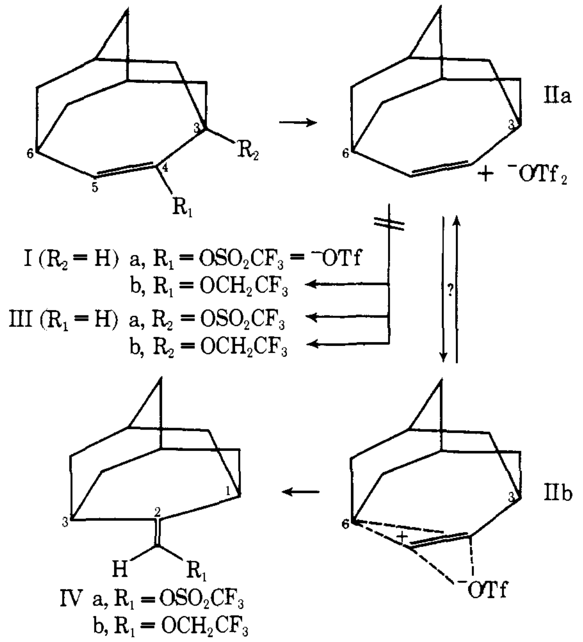
Sir:

Carbenium ions from *saturated* adamantane and homoadamantane precursors do not undergo *non*degenerate 1,2-hydride shifts,[1] presumably because of molecular rigidity and orthogonality between the vacant carbon orbital and an adjacent C–H bond.[2]

Pursuant to enticing this hydride shift we wish to report that the *unsaturated* homoadamantane Ia,[3] in which the C_4 substituent orbital is held in-plane with the tertiary C_3–H bond, solvolyzes at 100 °C to give ring contracted *primary triflate* IVa.[4] Products Ib and III, the latter resulting from to 3,4-in-plane hydride shift, were not detected.[5] Solvents used were neat trifluoroethanol (TFE) and 90% TFE in water, both buffered with pyridine, and neat pyridine. Even in the aqueous system the yield of IVa was minimally 95% and no 4-homoadamantanone was detected. At 150 °C in buffered TFE or in pyridine the initial formation of IVa was followed by slow[6] conversion of IVa to IVb.[7] There was no indication (VPC) that ring expansion of IVa to Ib occurred.

There is neither literature precedent for secondary to primary vinyl carbenium ion rearrangement,[8] for complete lack of formation of ketone hydrolysis product in aqueous solvents, nor for complete capture of the "leaving" triflate group by the "cation" [9] intermediates. Our observation of these phenomena upon solvolysis of Ia deserves comment.

Internal return and S_{N1} character are known factors in vinyl substrate solvolyses.[9] In TFE, a solvent most capable of separating ion pairs, solvent, *but not internal ion*, captured products usually predominate. The fact that the triflate group from Ia is retained in this medium, neat or aqueous, is unexpected and points to the formation of either: (1) an intimate ion pair intermediate of bent vinyl cation IIa that undergoes ring contraction[6,8] to generate a linear (stabilized[10]) but primary destabilized[8]) vinyl cation which neutralizes itself by internal return; or (2) a bridged[11] intermediate IIb in which the triflate group is transferred from the C_4 to C_5 carbon as C_6 starts to bond to C_4. Note that the geometry of Ia places the C_5–C_6 bond *in-plane and vicinally trans*[12] to the "leaving" triflate. Either reaction path speculated above would benefit by the shielding of the side of C_4 opposite the departing group



and the effect of "hiding" the developing cationic orbital between (or inside) the "cage" and $CF_3SO_3^-$.

These data alone do not clarify why antiperiplanar C_6 migration is so dominant over synperiplanar H migration. Influential factors may include substituent geometry, ring structure, and destabilization of charge on C_3 if H migration were to occur. Pyridine buffer and product structural features do not accommodate an addition-rearrangement-elimination mechanism, which, moreover, is practically unknown in related neutral media solvolyses.

A preliminary search for the independent or interconverting primary and secondary vinyl carbenium ions was inconclusive. Mixing either Ia or IVa with SbF_5-SO_2ClF at −80 °C gave an orange solution which showed only broad, partially resolved proton NMR absorptions between 2 and 5 ppm (δ).[13] Neither mixture showed significant NMR change upon warming to −10 °C.

Experiments are planned to determine activation parameters, and if the carbon-bound oxygen atom in IVa is different from that in Ia, whether C_5 undergoes inversion during the Ia to IVa rearrangement, and if the photolysis of I (R_1 = iodine) will be a source of "free" 4-homoadamanten-4-yl carbenium ion.

Acknowledgments. The author gratefully acknowledges the Clarkson College Research Fund for financial support, Dr. Herman Finkbeiner, General Electric Co., for 100 MHz NMR data, and Dr. Peter Stang, University of Utah, for commentary and encouragement.

References and Notes

(1) This statement is true only for those ions having ground-state vibrational energy. Compare R. Yamaguchi, S. Aritmatsu, and M. Kawanisi, *Chem. Lett.*, 121 (1973).

(2) M. McKervey, *Chem. Soc. Rev.*, **3**, 479 (1974).

(3) 4-Homoadamantanone, from adamantanone and diazomethane, is converted to liquid Ia (> 90%) (silica gel-pentane; M$^+$, 296. Anal. Calcd for $C_{12}H_{15}F_3O_3S$: C, 48.65; H, 5.08. Found: C, 48.82; H, 5.08. NMR (δ), 6.1 dd (1 H, vinyl), 1.7-2.7 (14 H)) by the method of ketones. P. Stang and T. Dueber, *Org. Synth.*, **54**, 79 (1974).

(4) An authentic sample of liquid IVa (silica gel-pentane elution before Ia) was prepared from adamantan-2-carboxaldehyde (J. Sharp, H. Wynberg and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **89**, 18 (1970); or, in our hands from adamantanone reacting with the Wittig reagent of CH_3OCH_2Cl followed by HCl) by the silyl ether method for aldehydes. P. Stang, M. Mangum, D. Fox, and P. Haak, *J. Am. Chem. Soc.*, **96**, 4562 (1974)): M$^+$, 296. Anal. Found: C, 48.71; H, 5.10. NMR (δ), 6.5 s (1 H, vinyl), 3.1 m (C_1-H), 2.45 m (C_3-H), 1.7-2.2 (12 H).

(5) All reactions were carried out in a glass-lined, stainless steel reactor sealed with Teflon gaskets. Product mixtures were monitored by thermal conductivity VPC.

(6) M. Imhoff, R. Summerville, P. v. R. Schleyer, A. Martinez, M. Hanack, T. Dueber, and P. Stang, *J. Am. Chem. Soc.*, **92**, 3802 (1970).

(7) Authentic IVb was not available. Our liquid IVb analyzed as follows: M$^+$, 246; NMR (δ), 6.0 s (1 H, vinyl), 4.1 q (2 H), 3.1 m (C_1-H), 2.3 m (C_3-H), 1.7-2.2 (12 H); VPC R_f IVb > IVa > Ia on OV-275 at 140 °C.

(8) Monocyclic vinyl triflates do not ring contract in S_N1 solvolyses unless the product is also secondary: W. Pfeifer, C. Bahn, P. v. R. Schleyer, S. Bocher, C. Harding, K. Hummel, M. Hanack, and P. Stang, *J. Am. Chem. Soc.*, **93**, 1513 (1971). In fact, exocyclic primary vinyl cations generated by vinyl iodide photolysis rearrange to endocyclic secondary ones: P. Kropp and S. McNeely, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975, Abstracts, ORGN 4.

(9) (a) P. Stang and T. Dueber, *J. Am. Chem. Soc.*, **95**, 2683 (1973); (b) R. Summerville, C. Senkler, P. v. R. Schleyer, T. Dueber, and P. Stang, *ibid.*, **96**, 1100, 1110 (1974); (c) Z. Rappoport and Y. Apeloig, *ibid.*, **97**, 821, 836 (1975); (d) T. Clarke, D. Kelsey, and R. Bergman, *ibid.*, **94**, 3626, 3627 (1972); (e) Z. Rappoport, E. Noy, and Y. Houminer, *ibid.*, **98**, 2238 (1976).

(10) See ref 9b and L. Radom, P. Hariharan, J. Pople, and P. v. R. Schleyer, *ibid.*, **95**, 6531 (1973).

(11) Compare S. Liggero, R. Sustmann, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4571 (1969); P. Peterson and R. Kamat, *ibid.*, **91**, 4521 (1969); G. Modena, et al., *J. Chem. Soc., Perkin Trans. 2*, 493 (1973).

(12) This has been shown to be the most desirable geometry for vinyl carbenium ion stabilization: Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **96**, 6428 (1974); D. Kelsey and R. Bergman, *ibid.*, **92**, 228 (1970).

(13) This experiment was suggested and performed by Dr. David Forsyth. Further work is in progress.

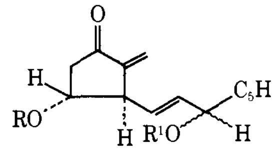
Richard Partch,* Dan Margosian
Department of Chemistry, Clarkson College
Potsdam, New York 13676

Received June 21, 1976

The Ene Reaction as a Route to 3-Hydroxycyclopentanone Derivatives. Application to the Prostaglandins

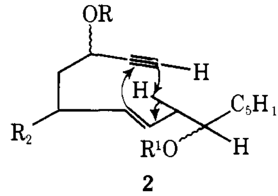
Sir:

We have previously demonstrated an efficient route to the prostaglandins via 2-methylenecyclopentanones (**1**) which were synthesized by formaldehyde trapping of the proper regiospecifically generated enolate.[1,2]

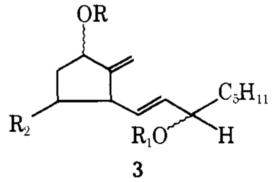


1

We now wish to report an entirely different approach to **1**: the thermal ene reaction of an appropriate acyclic enyne (e.g., **2** → **3**).[3]

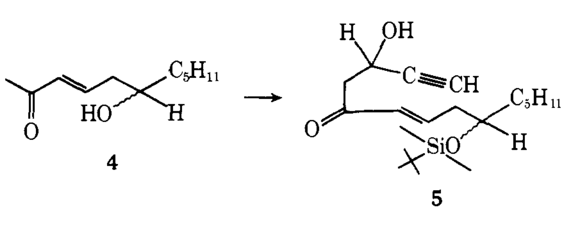


2



3

We were encouraged to examine the possibility of this transformation because arrays such as **2** are now easily accessible: the vinylogous aldol[4] **4** was protected as its *tert*-butyldimethylsilyl[5] derivative which was then submitted to the kinetic aldol reaction[6] with propynal. The usefulness of the



4 **5**