with the molecular ion of cyclopentanone, while eq 3–5 are not. We conclude that the average lifetime of the enolic product ion IIa is on the order of $1-5 \times 10^{-8}$ sec, and that it rearranges to a form characterized by the same chemistry as the molecular ion of cyclopentanone, i.e., reketonizes.

The m/e 84 ion in the spectrum of 2-ethyl-5-propyl-cyclopentanone (III), which arises from two consecutive McLafferty rearrangements (eq 9), behaves like an enol
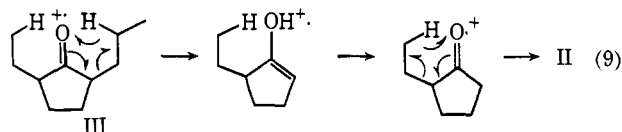
at short lifetimes as expected from earlier studies of consecutive rearrangements,[4] but at τ_T ca. 10^{-1} sec, this ion also behaves like a keto form, undergoing, for example, eq 7.

Straight-chain aliphatic ketones produce McLafferty products which do not reketonize on such a scale that they can be detected by icr. For example, the acetone enol ion formed from 2-hexanone still undergoes reactions typical of the enolic form, e.g., protonation of acetone-d_6, even for τ_T on the order of 10^{-1} sec with ionizing voltages in the range of 13 and 20 V. The lifetime of the acetone enol ion is thus in excess of 10^{-1} sec when the total population of McLafferty products is considered, even though it may be[2] on the order of $10^{-5}-10^{-6}$ sec for the metastable fraction losing methyl.

In the presence of a collision gas (air) at 10^{-5} Torr, the reaction product of I retains its enolic structure even at residence times on the order of $10^{-2}-10^{-1}$ sec. The presence of the collision gas may alter the residence time of the ion, and we are conducting experiments to distinguish between this and chemically more interesting explanations relating to collisional stabilization of the enol form.

The difference in reactivity between I and 2-hexanone suggests that the reketonization process is a function of ion structure even within nonaromatic ketones. We are beginning to examine other systems in order to determine whether information about the preferred geometry of the activated complex for reketonization may be gathered in this way.

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Silver(I)-Assisted Methoxyl Group Ionization. Some Mechanistic and Synthetic Considerations Derived from the Behavior of endo-2-Methoxytricyclo[4.1.0.0^{3,7}]heptanes[1]

Sir:

Although Ag$^+$ is now recognized to be capable of catalyzing spectacular bond rearrangements of bicyclo[1.1.0]butane derivatives under exceedingly mild conditions,[2] bicyclo[2.1.0]pentane is characterized by inertness toward this noble metal ion.[3,4] Consistent with this reactivity order are our more recent findings that 1[5a,b] and 2[5c] are likewise unreactive toward catalytic amounts of silver perchlorate in benzene.[6]
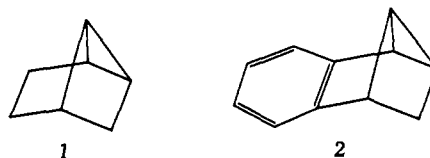
As regards ether **5a**, however, quantitative rapid isomerization exclusively to *anti*-7-methoxynorbornene (**6a**) occurs under these conditions. We have now devised a general synthesis of *endo*-2-methoxytricyclo-[4.1.0^{3,7}]heptanes (**5**) which permits: (a) conclusive demonstration of the fact that this rearrangement and the general **5 → 6** isomerization proceed by initial ionization of the methoxyl substituent and not by any Ag$^+$-strained bond interaction; and (b) realization of facile synthetic entry to a variety of formerly elusive anti-7-substituted norbornenes.

The brief synthetic scheme is founded upon stereoselective dibromocarbene addition[7] to readily available 3-methoxycyclohexenes (**3**) and subsequent stereoselective carbene–hydrogen insertion (**4 → 5**).[8–10] The very characteristic nmr features of **5a**, particularly the low-field quartet ($J_{1,2} = 3.5$ and $J_{2,3} = 7.0$ Hz),[11] are also readily apparent in the spectra of **5c** and **5d**. Independent confirmation of structure **5c** was derived from catalytic hydrogenation (Pd/C, ethanol, 1 atm) to *endo*-1-methyl-3-methoxynorbornane (100%). As a result of their inherent structural features, this low-field

(1) Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds·XI. For the previous paper, see L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Amer. Chem. Soc.*, 94, 4739 (1972).

(2) (a) L. A. Paquette and S. E. Wilson, *ibid.*, 93, 5934 (1971), and earlier work; (b) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, 93, 4611 (1971), and preceding papers.

(3) L. A. Paqeutte, *Accounts Chem. Res.*, 4, 280 (1971).

(4) Appropriate substitution with labilizing substituents does result, however, in skeletal rearrangement: L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, 94, 3653 (1972).

(5) (a) H. C. Brown and H. M. Bell, *ibid.*, 85, 2324 (1963); (b) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, 85, 2324 (1963); (c) R. Edman, *ibid.*, 91, 7103 (1969).

(6) G. Zon, unpublished observations.

(7) D. Seyferth and V. A. Mai, *J. Amer. Chem. Soc.*, 92, 7412 (1970).

(8) W. R. Moore and B. J. King, *J. Org. Chem.*, 36, 1877, 1882 (1971); W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, 83, 2019 (1961).

(9) Not unexpectedly, methoxyl-substituted tricyclo[4.1.0.0^{2,7}]heptanes are also produced in this step. The relative yields of such products vary with substitution. Complete details will be elaborated upon in a future full paper.

(10) Satisfactory combustion analyses have been obtained for all new compounds described herein except for the deuterium-labeled substrates for which accurate mass spectral determinations were secured.

(11) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, 88, 864 (1966); (b) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, 88, 3135 (1966). We thank Dr. Tanida for a copy of the nmr spectrum of **5a**. High resolution nmr spectra reveal that each component of this doublet of doublets is further split ($J \cong 0.5$ Hz) by long-range coupling.

signal appears as a doublet ($J_{2,3} = 7.0$ Hz) in the spectrum of **5b** and is expectedly lacking in that of **5e** and **5f**.[12]

3

4

5

6
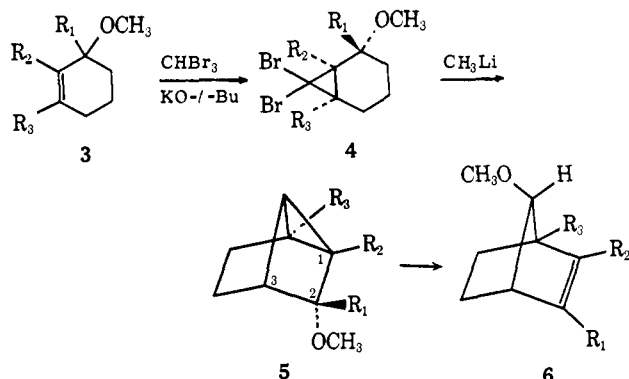
a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = H$; $R_3 = CH_3$
d, $R_1 = R_2 = H$; $R_3 = D$
e, $R_2 = R_3 = H$; $R_1 = D$
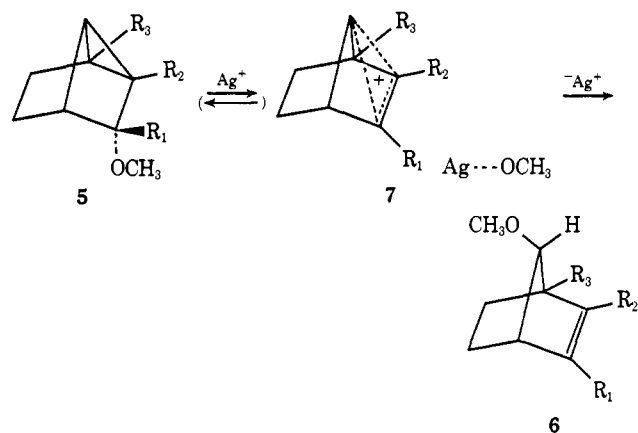f, $R_1 = D$; $R_2 = H$; $R_3 = CH_3$

When treated with 1–3 mol % of silver perchlorate in anhydrous benzene, the various tricyclic ethers **5** were converted cleanly to **6**. Generally speaking, such isomerizations were complete in less than 12 hr at 40°; precise rate constants were not obtainable because of difficulties arising from complexation of Ag$^+$ to the norbornene product as it was formed.[13] Nevertheless, the stereospecificity of product formation and ultimate positioning of deuterium label in **6d**, **6e**, and **6f** suggest that the mechanism shown in Scheme I is operative. In particular, the exclusivity of attack at C-7 from the anti direction is consistent with intervention of cation **7**.[14] Further support for this pathway was secured from Ag$^+$-catalyzed rearrangement of **5a** (1 mmol) in ethanol (20 mmol)–benzene (90:10); *anti*-7-ethoxynorbornene and **6a** were formed in a *ca.* 20:1 ratio. Appropriate control experiments served to demonstrate that **6a** and its syn counterpart are entirely stable to such reaction conditions. Also, the possible involvement of *endo*-2-ethoxytricyclo[4.1.0^{3,7}]heptane was not in evidence (vpc studies). Thus, these data provide the perspective that the methoxyl group experiences exceedingly facile ionization, presumably as the result of

prior coordination to silver(I). Silver methoxide, the coproduct attending the formation of cation **7**, is to our knowledge a yet uncharacterized substance;[14a] notwithstanding, in the present circumstance it clearly serves as the source of methoxide ion responsible for the ultimate trapping of **7**.

It has been shown previously that **5a** experiences the same rearrangement under conditions of acid catalysis.[11a,15] However, the catalytic influence of proton donors has been found to be significantly less effective than that of Ag$^+$. For example, exposure of **5b** to 6 mol % of *p*-toluenesulfonic acid monohydrate in benzene at 40° did cause isomerization to **6b**, but at a rate some 50 times slower than that observed with AgClO$_4$. Also, treatment of **5e** with 1 mol % of trifluoroacetic acid in benzene at 40° produced no detectable amount of **6e** after 28 hr at 40°. In this connection, attempts to induce the rearrangement of **5a** with other transition metal catalysts such as bis(benzonitrile)palladium chloride and rhodium dicarbonyl chloride dimer also failed.

The findings here presented, which reveal that the customarily highly endothermic ionization of neutral ethers is substantially facilitated by prior coordination to Ag$^+$, under conditions of virtually neutral pH and in nonnucleophilic solvents (*e.g.*, benzene) of low dielectric constant, have important general implications for our understanding and control of carbonium ion behavior. Thus, systems which exhibit complications due to proton sensitivity (or insensitivity) and/or solvolysis during synthesis may be readily examined by utilization of the present anhydrous AgClO$_4$–benzene method, or some suitable modification of it. More specifically, methoxyl derivatives, which invariably are of greater stability than the corresponding sulfonate esters particularly in highly reactive molecular types, could prove superior in the exploration of certain carbonium ion processes. Also, in those many instances such as the present situation where ethers are synthetically more accessible than the derived alcohols, this option could prove particularly useful. There exists, of course, the customary dependence of ease of methoxyl ionization on structural features. The ready reactivity of the tricyclic ethers **5** and the inertness of the *anti*-7-methoxynorbornenes (**6**) to silver perchlorate in eth-

Scheme I

5

7

Ag···OCH$_3$

6

(12) The following summary of nmr data is presented to confirm the positioning of isotopic label in the deuterated substrates: for **5b**, $\delta_{TMS}^{C_6D_6}$ 3.47 (d, $J = 7$ Hz, 1, H-2), 3.07 (s, 3, OCH$_3$), 2.56 (v br d, $J \approx 7$ Hz, 1, H-3), 1.10–2.20 (m, 6), and 1.20 (s, 3, CH$_3$); for **5c**, 3.55–3.79 (d with fine splitting, $J = 7$ Hz, 1, H-2), 3.01 (s, 3, OCH$_3$), 2.35–2.71 (m, 1, H-3), 1.56–1.99 (m, 6), and 1.00 (s, 3, CH$_3$); for **5d**, 3.63 (d of d, $J = 7.0$ and 3.7 Hz, 1, H-2), 3.03 (s, 3, OCH$_3$), 2.55 (v br d, $J \approx 7$ Hz, 1, H-3), and 1.35–2.35 (m, 6); for **5e**, 3.04 (s, 3, OCH$_3$), 2.57 (v br s, 1, H-3), and 1.18–2.23 (m, 7); for **5f**, 3.05 (s, 3, OCH$_3$), 2.52 (m, 1, H-3), 1.54–2.39 (m, 6), and 1.03 (s, 3, CH$_3$); for **6b**, 5.39–5.59 (m, 1, vinyl), 3.12 (br s, 1, H-7), 3.05 (s, 3, OCH$_3$), 2.50–2.73 (m, 1, bridgehead), 2.10–2.30 (m, 1, bridgehead), 1.73–2.10 (m, 2, exo methylenes), 1.60 (d, $J = 1.5$ Hz, 3, CH$_3$), and 0.74–1.27 (m, 2, endo methylenes); for **6c**, 5.73–6.06 (m, 2), 3.06 (s, 3), 2.78 (br s, 1), 2.50–2.71 (m, 1), 1.59–2.03 (m, 2), 1.22 (s, 3), and 0.76–1.21 (m, 2); for **6d**, 5.88 (d, $J = 2$ Hz, 2), 3.02 (s superimposed on br m, 4), 2.57 (m, 1), 1.71–2.05 (m, 2), and 0.79–1.09 (m, 2); for **6e**, 5.90 (br d, $J \approx 2.5$ Hz, 1), 3.03 (s superimposed on br m, 4), 2.58 (m, 2), 1.59–2.12 (m, 2), and 0.79–1.10 (m, 2); for **6f**, 5.90 (s, 1), 3.06 (s, 3), 2.78 (br s, 1), 2.50–2.71 (m, 1), 1.59–2.03 (m, 2), 1.22 (s, 3), and 0.76–1.21 (m, 2).

(13) C. F. Wilcox, Jr., and W. Gaal, *J. Amer. Chem. Soc.*, **93**, 2453 (1971), and references contained therein.

(14) J. J. Tufariello and R. J. Lorence, *ibid.*, **91**, 1546 (1969); J. Lhomne, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969).

(14a) Note Added in Proof. A summary of a study of the properties of silver methoxide has just made its appearance: R. S. Macomber, *16th Annu. Rep. Petr. Res. Fund*, 88 (1972).

(15) A. Diaz, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3133 (1966). See also, J. J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Commun.*, 1202 (1967).

anol–benzene (90:10) at 40° define rather broadly at this time the limits of reactivity under relatively mild conditions. Putting this another way, in the reactions of ethers promoted by Ag+, successful rearrangement due to methoxyl group ionization could conceivably occur if the resulting carbonium ion is at least 10^4 times more kinetically accessible than the cyclohexyl cation.[16] Since many molecular types do fall into this category, the implications are potentially far-reaching. These implications are currently under active study.[17] It should be emphasized, however, that our data now serve as a caveat regarding the validity of mechanistic interpretations based on the nature of ether products derived from silver ion promoted reaction of strained-ring hydrocarbons in the presence of alcohol trapping agents.[2b] The structure of such ether products need not reflect that of a true carbonium ion intermediate, if one exists, since they may result from secondary transition metal catalyzed reaction of ephemeral trapping product(s) *via* carbon–oxygen bond heterolysis.

Acknowledgment. The financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Cancer Institute is gratefully acknowledged.

(16) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955).
(17) As examples of the generality of such reactions we cite the Ag+-catalyzed conversion of i to cycloheptatriene[6] and of ii to 2-methyl-2-

i   ii
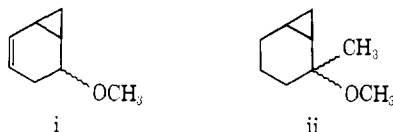
norcarene (S. E. Wilson, unpublished).

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N,N,N',N'-Tetramethylphosphorodiamidate Group. A Useful Function for the Protection or Reductive Deoxygenation of Alcohols and Ketones[1]

Sir:

We recently reported[2] that the lithium–amine reduction of enol diethyl phosphates prepared by phosphorylation of enolate anions was an efficient method for the regiospecific formation of olefins. Further investigation of the scope of this reduction reveals that the diethyl phosphates (DEP) and N,N,N',N'-tetramethylphosphorodiamidates (TMPDA) of alcohols, as well as ketone enolates, are also readily reduced in high yield by lithium–ethylamine solution. In addition to making possible the direct cleavage of the hydroxyl function the two-step process for the reductive removal of a ketone, *i.e.*, RCOR' → RCHOHR' → RCH₂R', has certain advantages over the Wolff–Kishner reduction in some cases. Also, the TMPDA grouping appears to be a useful blocking group for the hydroxyl function, as it

is stable to a variety of reaction conditions, and yet the original alcohol may be regenerated in near quantitative yield under relatively mild conditions.

The DEP and TMPDA derivatives are readily prepared by phosphorylation of the corresponding enolate or alcoholate anions. The former may be generated from α,β-unsaturated ketones by lithium–ammonia reduction[3] or conjugate organometallic addition or from saturated ketones by enolization with lithium-diisopropylamide. The latter are simply prepared from an alcohol by treatment with a slight molar excess of *n*-butyllithium. For the phosphorylation of these anions we have used 1 equiv of diethylphosphorochloridate or a fivefold excess of the less reactive N,N,N',N'-tetramethyldiamidophosphorochloridate[4] and found that the best solvent system for the reaction is 4:1 dimethoxyethane- (or tetrahydrofuran-) N,N,N',N'-tetramethylethylenediamine. In general, the reaction is complete after stirring for 1–2 hr at 25°, and chromatography and/or crystallization of the product after work-up afforded the desired ester. The yields of these phosphorylations are uniformly high, and the choice of which ester is formed depends on the proposed subsequent use.

While either derivative is satisfactory for the reductive formation of olefins from the enol system, the TMPDA grouping is more necessary for the deoxygenation of primary and secondary alcohols. More by virtue of its greater ease of formation than a significant difference in the reduction stage, the DEP grouping appears better for the reductive removal of tertiary alcohols.

The reductive cleavage of either the DEP or TMPDA groups may be accomplished by the addition of a solution of the derivative and 2–4 equiv of *tert*-butyl alcohol in tetrahydrofuran to an ice-cooled, argon-protected solution of 10 equiv of lithium in dry ethylamine. After stirring for 20–30 min, the reaction mixture is quenched with water, and the product isolated by ether extraction. Chromatography and/or crystallization of the crude product affords the reduced material in high yield. The reduction is very fast and in the absence of a proton source the TMPDA group is reduced without concomitant reduction of an anisole ring. When the immediate objective is the removal of an oxygen function, this reduction procedure may be performed on unpurified phosphorus ester without any adverse effect on the yield.

The following examples[5] (Chart I) serve to document these generalizations and provide a basis for evaluation of the scope of the process.

The utility of this sequence for the reductive removal of a ketone function is illustrated by the cases in Chart II. In neither case was it necessary (or advantageous) to purify material at the intermediate stages, although in each instance this was done initially. In both instances the indicated transformations were not as satisfactorily accomplished by other means due to the acid–base

(2) R. E. Ireland and G. Pfister, *Tetrahedron Lett.*, 2145 (1969); see also, M. Fetizon, M. Jurion, and N. T. Anh, *Chem. Commun.*, 112 (1969).
(3) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Amer. Chem. Soc.*, 87, 275 (1965).
(4) E. Crunden and F. Hudson, *J. Chem. Soc.*, 3591 (1962); H. G. Cook, J. D. Ilett, B. C. Saunders, G. J. Stacey, H. G. Watson, I. G. Wilding, and S. J. Woodcock, *ibid.*, 2921 (1949).
(5) All new compounds were characterized by ir and nmr spectroscopy and behavior on glpc and tlc, and had satisfactory (±0.2%) combustion analyses.