position of the homologue *N*-nitroso-*N*-*anti*-bicyclo-[3.1.0]hex-2-en-6-ylurea which rearranged via carbonium ions.

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(8) Mp 145 °C; IR (KBr) 3340, 2920, 1640, 1530, 770, 530 cm^{-1}; NMR ($CDCl_3$) δ 1.46 (2 H, m), 1.92 (4 H, m), 2.52 (1 H, m), 4.90–5.85 (3 H, m), 6.05 (1 H, m).
(9) Mp 76 °C dec; IR (CCl_4) 3250, 2920, 1730, 1510, 1390, 670 cm^{-1}; NMR ($CDCl_3$) δ 1.50 (2 H, m), 1.92 (4 H, m), 2.36 (1 H, t, J = 3, 2 Hz), 5.60 (1 H, m), 5.95–6.75 (3 H, m).
(10) IR (KBr) 2900, 2140, 1560, 1350 cm^{-1}; NMR (DMSO-d_6) δ 1.40 (2 H, m), 1.82 (4 H, m), 4.12 (1 H, t), 5.30 (1 H, m), 6.00 (1 H, m).
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(12) IR (film) 3010, 2910, 1745, 1230 cm^{-1}; NMR (CCl_4) δ 1.46 (2 H, m), 1.85 (4 H, m), 1.94 (3 H, s), 3.96 (1 H, t, J = 2.2 Hz), 5.50 (1 H, m), 6.00 (1 H, m).
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(16) IR (KBr) 3000, 1585, 1495, 1150, 770, 680 cm^{-1}; NMR (D_2O, *t*-BuOH as standard) δ 1.80 (6 H, br m), 2.70 (1 H, t, J = 3.4 Hz), 5.04 (s), 5.66 (1 H, m), 6.08 (1 H, m).
(17) Use of the corresponding trimethyloxonium salt was inconvenient because of low solubility.
(18) *m/e* 138.10459, calcd 138.10445; IR (film) 3010, 2910, 1640, 1385, 1130, 680 cm^{-1}; NMR (CCl_4) δ 1.10 (3 H, t, J = 7, 0 Hz), 1.40 (2 H, m), 1.85 (4 H, m), 3.06 (1 H, t, J = 2.1 Hz), 3.42 (2 H, q, J = 7.0 Hz), 5.30 (1 H, m), 5.90 (1 H, m).
(19) IR (film) 3010, 2920, 2840, 1640, 1220, 1130, 680 cm^{-1}; NMR (CCl_4) δ 1.40 (2 H, m), 1.85 (4 H, m), 3.06 (1 H, t, J = 2.1 Hz), 3.25 (3 H, s), 5.30 (1 H, m), 5.90 (1 H, m).
(20) Under basic conditions the following alternative mechanism is not quite excluded by our results: the diazo compound formed from **8** equilibrates with the corresponding diazonium ion. Loss of nitrogen from the latter gives the cation **17** which may rearrange to **12**; however, this would require that **17** is different from any cationic intermediate formed under acid conditions. We want to acknowledge constructive suggestions from a referee.
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(25) Mp 145 °C; *m/e* 198.0898, calcd 198.0905; IR (KBr) 3210, 2950, 2270, 1490 cm^{-1}; NMR ($CDCl_3$) δ 1.80 (2 H, m), 2.17 (4 H, m), 3.84 (1 H, m), 5.72 (1 H, m), 6.20 (1 H, m). The stereochemistry is not established.
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Detailed Potential Energy Surfaces for Carbonium Ion Rearrangements: $C_3H_7O^+$

Sir:

In earlier work,[1,2] we have emphasized that reactions occurring in the field-free regions of conventional magnetic sector mass spectrometers do so with excess energies in the transition state, which are comparable to, or less than, those present in solution reactions. Important experimental evidence for this

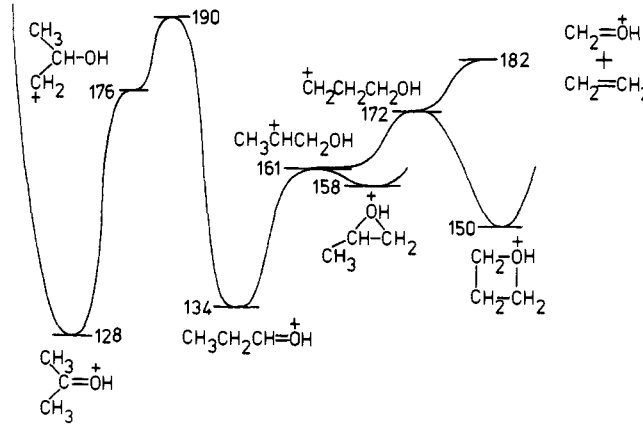
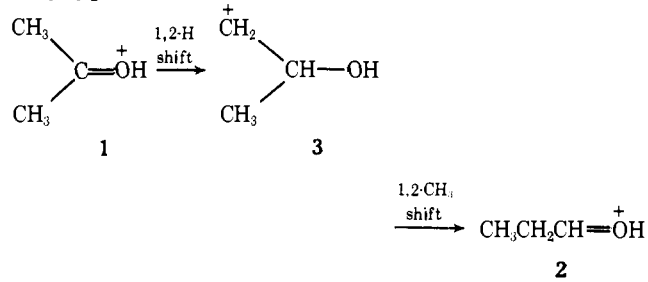


Figure 1. Potential surface for unimolecular reactions of protonated acetone and protonated propionaldehyde.

Scheme I



view is found in the occurrence of large primary deuterium isotope effects.[2-4]

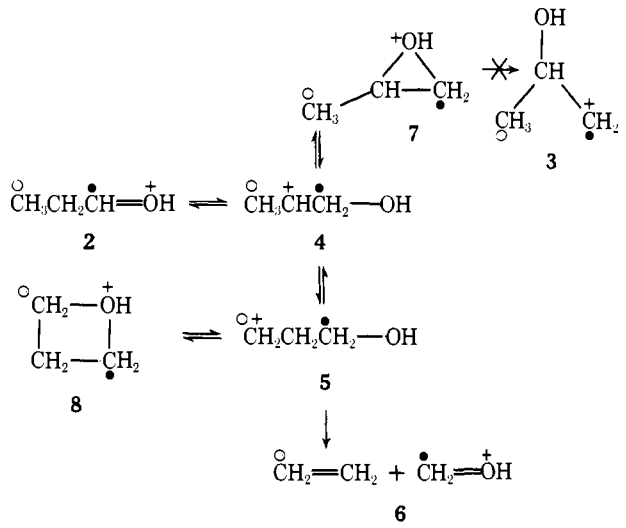
Investigations of such unimolecular reactions (i.e., those responsible for metastable peaks) have uncovered cases where isomerization of an ion is the rate-determining step, followed by more rapid dissociation from the newly formed isomeric structure.[5,6] A specific case is the rate-determining isomerization of protonated acetone (**1**) to protonated propionaldehyde (**2**) prior to dissociation.[6] The most plausible mechanism for this reaction is via the primary carbonium ion **3** as, or near to, a transition state (Scheme I). The approximate heat of formation of **3** (176 kcal mol^{-1}) can be estimated;[7] the agreement with the measured transition-state energy (190 kcal mol^{-1})[6] for the rate-determining step for isomerization of **1** prior to dissociation is satisfactory.

This scheme is incorporated into the potential energy surface shown Figure 1. A consequence of this potential surface is that ions initially generated as structure **2** should not be able to attain configuration **3.** This follows since the activation energy for elimination of C_2H_4 from **2** (~48 kcal mol^{-1}; measured transition-state energy[6]) is less than the energy (~56 kcal mol^{-1}) which would be needed to cause isomerization of **2** to **1** via **3.**

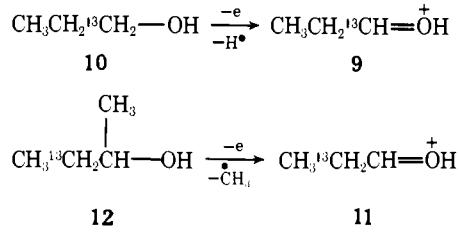
The most plausible mechanism whereby C_2H_4 loss can occur from **2** is via two successive 1,2-hydride shifts followed by cleavage of the central C–C bond in the primary carbonium ion **5.** 1,2-Hydride shifts of this type are symmetry allowed and are known from calculations[8] and solution NMR experiments[9] to proceed with negligible energy barriers, i.e., with activation energies close to the reaction endothermicities or exothermicities. Other possible isomerizations are ring closure of **4** and **5** to form the more stable protonated oxirane **7** and protonated oxetane **8,** respectively. These isomerizations, which should be rapid and reversible at energies appropriate to slow unimolecular dissociations, are incorporated into Scheme II and Figure 1.

Since we have deduced that the primary carbonium ion **3** is not accessible starting from **2,** it follows that **7,** once formed, must open exclusively to the secondary cation **4.** However,

Scheme II



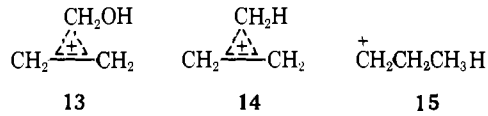
isomerization of **2** to **8**, via **4** and **5**, renders the α- and γ-carbon atoms of **2** (closed and open circles, respectively, in Scheme II) equivalent. In contrast, the β-carbon atom in **2** remains distinct insofar as it *never* becomes bound to oxygen in structures **8**, **5**, **4**, or **2**. In the dissociation step **5** → **6**, the carbon atom bound to oxygen in **5** is retained in the $CH_2{=}{}^+OH$ ion produced. This analysis results in exacting consequences for the elimination of C_2H_4 from ^{13}C-labeled ions of structure **2**. The ion **9**, produced from [1-^{13}C]propan-1-ol (**10**), should



eliminate C_2H_4 and $C^{13}CH_4$ in equal abundance in slow dissociations. This is because there is an equal probability of the label being in the α position (C_2H_4 loss) or γ position ($C^{13}CH_4$ loss) in the reacting configuration, **5**. Experimentally, the ratio of C_2H_4:$C^{13}CH_4$ loss starting from **9** is 49:51, for reactions occurring some 10^8 vibrations after generation of the ion. For ion **11**, generated from [3-^{13}C]butan-2-ol (**12**), *only* $C^{13}CH_4$ loss is expected because the labeled β-carbon atom never becomes attached to oxygen in ions of structure **5**. Experimentally, the ratio of C_2H_4:$C^{13}CH_4$ loss starting from **11** is 1:99 for dissociations occurring in the first field-free region.

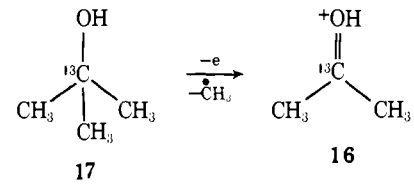
These results are in good agreement with predictions based on the potential surface (Figure 1) and mechanism (Scheme II) proposed for C_2H_4 elimination. In particular, the results indicate that the primary carbonium ion **5** is accessible starting from **2** but that the isomeric primary carbonium ion **3** is not. Use of the method,[7] based on the isodesmic substitution, for estimating heats of formation of ions reveals that **3** (which suffers inductive destabilization by an oxygen atom β to the cationic site) is less stable than **5** (which suffers destabilization by a more remote (γ) oxygen atom) by only ~4 kcal mol^{-1}. The proposed potential surface (Figure 1) emphasizes that the ability of reactions to compete, at energies appropriate to metastable dissociation, is critically dependent on the activation energies for the processes concerned.[10]

These data may also be relevant toward the energies of "bridged" carbonium ions, since the "bridged" ion **13** is not populated at energies appropriate to formation of the products **6** ($\Sigma\Delta H_f$ = 182 kcal mol^{-1}). This follows because, if **13** were



accessible, the β- and γ-carbon atoms of **5** could become equivalent via reversible isomerization to **13**; the ^{13}C-labeling results above preclude this. The data suggest that **13** is at least 10 kcal mol^{-1} less stable than the open-chain ion **5**. In this respect it is noteworthy that calculations reveal that the "bridged" propyl cation **14** has a very similar heat of formation to the classical 1-propyl cation **15**.[8]

A further consequence of the potential surface shown in Figure 1 is that, starting from **1**, the rate-determining step for C_2H_4 loss is isomerization to **2**.[6] The dissociation step itself is relatively fast and proceeds with excess energy in the transition state. Hence, once isomerization has occurred, there is discrimination against any reaction which requires a more ordered transition state than dissociation.[11,12] Relatively ordered transition states are required for the ring closures **4** → **7** and **5** → **8**. Thus there will be discrimination against the reaction which, leading to **8**, results in equivalence of the α- and γ-carbon atoms in **2**. Therefore, C_2H_4 loss from protonated acetone (**1**) should proceed by the most direct route, viz., **1** → **3** → **2** → **4** → **5** → **6**. Hence, ion **16** should lose predominantly



C_2H_4 in metastable transitions. The reported data (at least those pertaining to source reactions, which are not unambiguously relevant to the present work) are contradictory. Siegel[13] suggested that in source reactions the carbons of **16** become equivalent before ethylene loss, whereas Tsang and Harrison[14] found a predominant (89 ± 1%) loss of C_2H_4. For reactions occurring in the first field-free region, Tsang and Harrison[14] found exclusive loss of C_2H_4 from **16**. We have therefore examined independently the dissociation of **16** (produced from [2-^{13}C]-2-methylpropan-2-ol, **17**) in the first field-free region. We find C_2H_4 and $C^{13}CH_4$ losses in the ratio 89:11, reasonably close to the data of Tsang and Harrison[14] and consistent with the arguments based on the potential energy surface shown in Figure 1. On the basis of this surface, the data indicate that the 1,2-methyl shift whereby **3** produces **2** (Scheme I) is fast relative to the possible ring closure of **3** to the protonated epoxide **7**.

Acknowledgments. We wish to thank the Science Research Council for financial support. J.R.K. thanks the Eleanor Sophie Wood Foundation for a travel grant.

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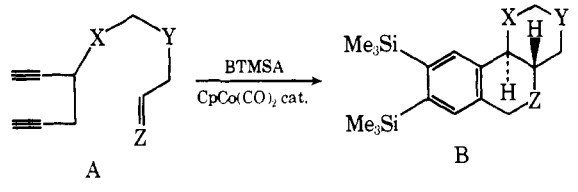
A Cobalt-Catalyzed Steroid Synthesis

Sir:

The steroid nucleus has been the target of numerous, often ingenious, synthetic schemes.[1] We recently reported the cobalt-catalyzed one-step synthesis of tricyclic ring systems B via cooligomerization of diynes A with bis(trimethylsilyl) acetylene (BTMSA) in the presence of $CpCo(CO)_2$[2] (Scheme I). In this reaction five new carbon–carbon bonds are formed with control of stereochemistry to result in what one might envisage to constitute the ABC-ring portion of the steroid moiety. We now wish to report the successful application of this scheme to the synthesis of steroidal structures.[3]

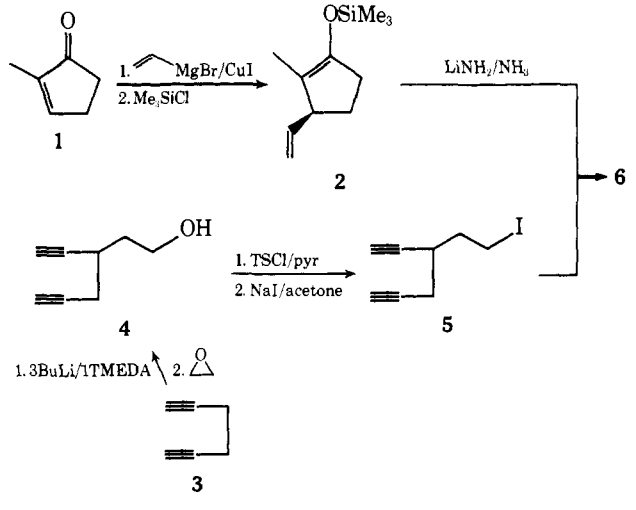
A convergent approach as outlined in Scheme II was adopted for the synthesis of the crucial 1,5-hexadiyne precursor **6**. 2-Methylcyclopent-2-enone (**1**),[4] when treated with vinylmagnesium bromide (CuI, THF; −60 to −40 °C; 45 min) followed by addition of trimethylsilylchloride (HMPA, Et_3N; −40 °C to room temperature; 30 min), gave the enol ether **2** in 89% yield.[5,6] In a parallel line of experiments diynol **4**[2] was quantitatively converted to the corresponding *p*-toluenesulfonate (TsCl, pyridine; 0 °C; 14 h),[5] which on exposure to Finkelstein conditions (45 °C; 30 h), gave iodide **5** in 96% yield.[5,6] The regiospecific enolate generated from **2** ($LiNH_2$, NH_3 (l), THF; 30 min)[7] was stereospecifically alkylated with 3 equiv of **5** to give after column chromatography (silica) 64% diynenone **6** as a mixture of diastereomers[5,6] in addition to 1.9 equiv recovered **5**. This reaction establishes the desired stereochemistry around what is to become the trans-CD-ring junction of the steroid nucleus. Although separable by chromatography, mixture **6** was reacted further as such since on

Scheme I



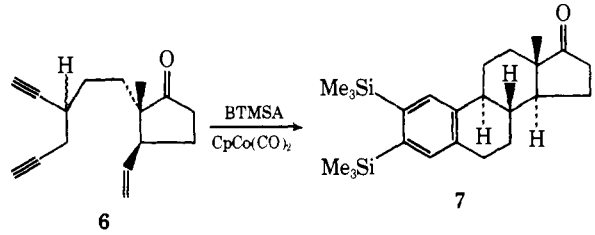
A B

Scheme II



1 2 4 5 3

cyclization and conrotatory outward benzocyclobutene ring opening both diastereomers were expected to give the same *o*-xylylene intermediate (e.g., **9**). Indeed cooligomerization



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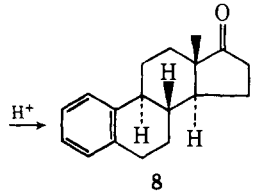

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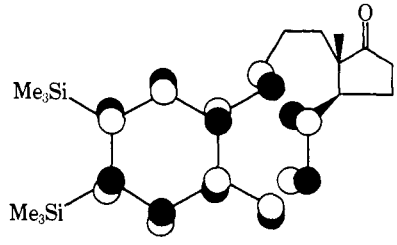

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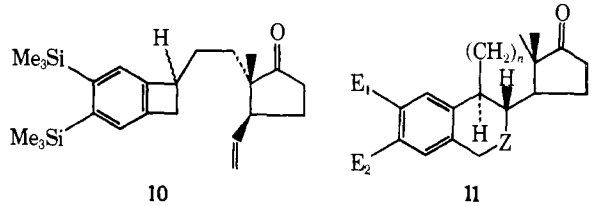
of **6** with BTMSA (solvent) in the presence of catalytic (5 mol %) amounts of $CpCo(CO)_2$ under oxygen-free conditions using syringe pump techniques (35-h addition time)[2] followed by continued heating gave racemic 2,3-bis(trimethylsilyl)-estra-1,3,5(10)-trien-17-one (**7**) in 71% yield as colorless crystals.[5,6] Shorter reaction times allowed the isolation of the two diastereomeric benzocyclobutene intermediates **10**, separated by column chromatography on silica. Slow addition of **10** to refluxing decane under N_2 cleanly gave **7**. Chemical



10 11

structural proof for **7** was obtained by quantitative protodesilylation to estra-1,3,5(10)-trien-17-one (**8**) (CF_3COOH–CCl_4–ether, 10:10:1; room temperature; 20 h) identical[8] (TLC R_f, IR, ^1H NMR, ^{13}C NMR[9], *m/e*) with an authentic sample of *d*-estratrienone.

The stereospecificity observed in the **6** → **7** transformation is remarkable and parallels that observed in other intramolecular cycloadditions to *o*-xylylenes derived from benzocyclobutenes.[10] Based on our model studies,[2] an exo-transition state leading to a trans-BC-ring junction was anticipated. Molecular models[3] as well as recent work[10] indicate that a transition state of the type shown in structure **9** (drawn as an *o*-xylylene HOMO-ene LUMO interaction) seems to be preferred. Thus, the desired trans-anti-trans arrangement in **7** is obtained rather than the trans-syn-trans form. The reason for this preference may be found in steric considerations. Thus, the other possible exo-transition state suffers from a sterically interfering methyl group, and a pseudoboat (as opposed to a pseudochair in **9**) arrangement of the carbon chain linking diene and dienophile.

To our knowledge the described approach constitutes the shortest synthesis of the steroid nucleus from an acyclic pre-