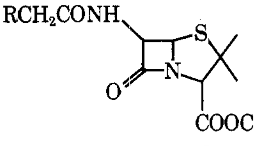
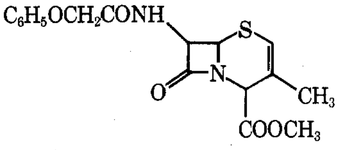
consistent with observations on small molecules.[2a] Thus, introduction of an oxygen γ to a nitrogen causes an upfield shift (**1a** vs. **1b**) comparable with that observed in analogous ^{13}C spectra.[10] When **1a** is converted to its sulfoxide (**5**) both nitrogens experience upfield shifts but to different extents, probably reflecting both geometrical (cis vs. trans) and structural (sulfonyl vs. oxygen) contributions. Insofar as **3** and **6** are appropriate models, ionization of the 4-carboxyl group appears to have a larger effect on the chemical shift of the lactam nitrogen than would be observed for a carbon at the analogous position.[11]



1a, R = C_6H_5O
1b, R = C_6H_5



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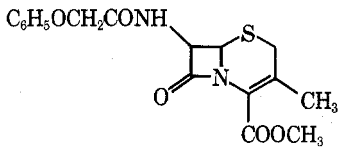

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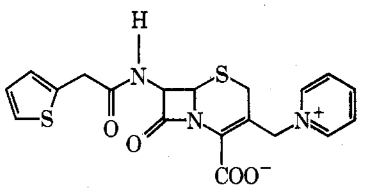

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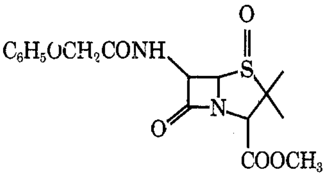

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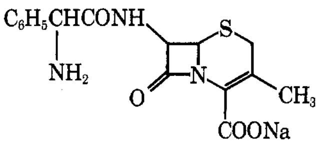

6

Of special interest are the lactam nitrogen resonance positions in **1**–**3**. The 30-ppm change in conversion from the five- to the six-membered ring (**1** vs. **2**) is not readily explicable. Because the lactam nitrogen in **2** is essentially planar,[12] increased amide conjugation would be expected to have induced a downfield shift. The corresponding nitrogen in **3** is less planar than in **2**, with concomitant decreased amide conjugation. Here, however, enamine-type conjugation is possible, and indeed the difference in resonance positions between **2** and **3** is comparable with that between cyclohexylamine and aniline.[2a] It may be that the nitrogen resonance position is insensitive to minor changes in the degree of amide delocalization.

Work is in progress to determine if the nitrogen chemical shifts of this class of compounds, including commercially available ones such as **4** and **6**, may be correlated with biological and pharmacological properties.

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Silver(I)-Promoted Reactions of Strained Hydrocarbons. Oxidation vs. Rearrangement

Summary: The reaction between silver trifluoroacetate and quadricyclene in methanol has been studied with the aid of an interfaced GC–MS data acquisition system. In addition to a Bronsted acid and silver metal, the products include norbornadiene (**2**), 3-methoxy-5-norbornene (**3**), 3-methoxynortricyclene (**4**), 3-trifluoroacetoxy-5-norbornene (**5**), 3-trifluoroacetoxynortricyclene (**6**), three isomeric 3,5-dimethoxynortricyclenes (**7**, **8**, and **9**), 3-methoxy-5-trifluoroacetoxynortricyclene (**10**), 3-methoxy-5-hydroxynortricyclene (**11**), and methyl trifluoroacetate. The formation of the various products as a function of time was monitored by gas chromatography. Finally, the formation of **7**, **8**, **9**, **10** and **11** along with acid and Ag^0 is interpreted as a two-electron redox reaction.

Sir: We wish to present evidence that oxidation occurs when certain strained hydrocarbons are treated with Ag(I) salts. Such a process was first proposed in 1971 by Kaiser, Childs, and Maitlis, who studied the action of various Lewis acids on tri-*tert*-butylprismane,[1] but their suggestion has since received little attention. We have been investigating some Ag(I)-promoted reactions of various quadricyclenes and have been impressed by the ability of those compounds to reduce Ag(I) to the metallic state. For example, we recently reported that treatment of quadricyclene (1) with silver trifluoroacetate in methanol leads to 89% reduction of Ag(I) to Ag^0 and to Bronsted acid production.[2] Three organic products were tentatively identified (2, 3, and 4), but they provided no clue to the origin of silver metal. It is intriguing that while other strained hydrocarbons such as the bicyclo[1.1.0] butanes, cubanes, homocubanes, and tricyclo[4.1.0.0^{2,7}]heptanes undergo rearrangement in the presence of silver ion, they have not been reported to reduce Ag(I) to Ag^0.[3]

The reaction between silver trifluoroacetate (0.19 M) and 1 (0.24 M) in methanol at room temperature leads to a complex mixture of organic products. However, by utilization of an interfaced GC–MS data acquisition system, we have finally completed a detailed product study and have identified a group of materials which are intimately linked to Ag(I) reduction and to acid production. The products include norbornadiene (2), 3-methoxy-5-norbornene (3), 3-methoxynortricyclene (4), 3-trifluoroacetoxy-5-norbornene (5), 3-trifluoroacetoxynortricyclene (6), the isomeric 3,5-dimethoxynortricyclenes (7, 8, and 9), 3-methoxy-5-trifluoroacetoxynortricyclene (10), 3-methoxy-5-hydroxynortricyclene (11), and methyl trifluoroacetate.


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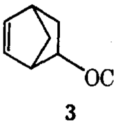

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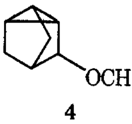

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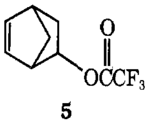

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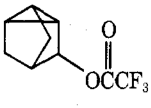

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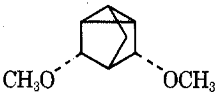

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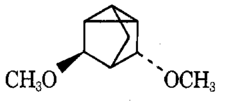

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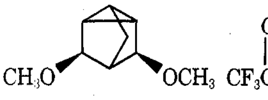

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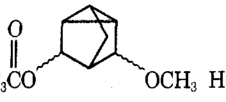

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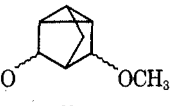


11

All products were initially identified by GC–MS analysis of crude product mixtures. Molecular ions were observed for all compounds except 5 and 6, which yielded low quality spectra under the experimental conditions. The isomeric relationship between 7, 8, and 9 is clearly revealed in the similarity of their mass spectra, each of which exhibits a base peak at m/e 75 $(CH_3OCHOCH_3)\cdot^+$. The structures of 2, 3, 4, 5, 6, 8, and 9 were subsequently confirmed by comparison of their GC retention times and mass spectra (except for 5 and 6) with those of authentic materials. Further, a small quantity of 9 was isolated and subjected to NMR analysis (microcell), and the molecular formulas of 8 and 9 were rigorously established by mass measurement of their molecular ions: 8 (154.0990), 9 (154.0982). The structure assigned to 7 was inferred from its molecular formula (mol wt 154.0997), its obvious relationship to 8 and 9, and a GC demonstration that it is not the dimethyl ketal of nortricyclanone.[4] The structure of 11 was confirmed by mass measurement of its molecular ion (140.0820), and by ir and NMR analysis of a small collected sample. Finally, the structure assigned to 10, based initially on its mass spectrum, was verified by GC observation of its ultimate conversion, under the reaction conditions, to the alcohol 11. That this is possibly a transesterification reaction was indicated by GC–MS detection of methyl trifluoroacetate in the reaction mixture.

The progress of the reaction was followed by GC analysis of injected aliquots, peak areas being determined by electronic integration and taken from digital output. It was necessary to utilize two separate columns to resolve the product groups 1–6 (SE-30) and 7–11 (Carbowax). The results are summarized in Figure 1. It can be seen that 1 was largely reacted after 2 h and that 11 is clearly a secondary product. Further, some norbornadiene is consumed in secondary reactions, possibly through conversion to 5 and 6 by reaction with trifluoroacetic acid, also a reaction product.

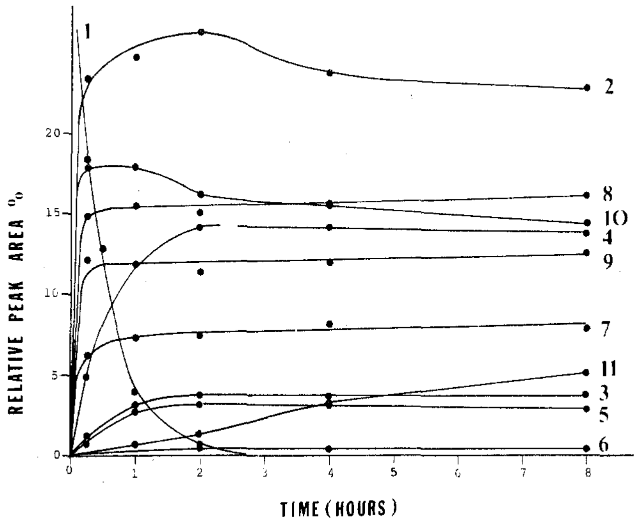
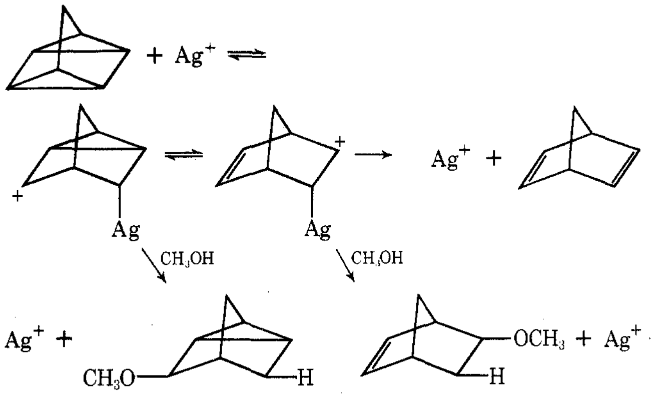
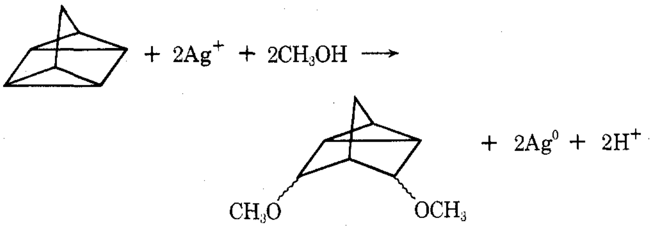


Figure 1. Product composition with time for the reaction of 1 with silver trifluoroacetate in methanol.

The formation of 2, 3, 4, 5, and 6 is consistent with the conventional argentation–deargentation pathway below. It



is significant, however, that this mechanism does not account for Ag(I) reduction or for acid production, but that Ag(I) is ultimately returned to the reaction medium. Moreover, the formation of 7, 8, 9, 10, and 11 cannot be so rationalized. Instead, a two-electron oxidation accounts for the precipitation of Ag^0, the production of protic acid, and for the observed organic products. A very recent study by



Brettle and his co-workers[5] of the anodic oxidation of 1 in methanolic sodium methoxide corroborates this view. Diethers 8 and 9 were identified as the major products.

Finally, inspection of *adiabatic* ionization potentials allows a prediction as to when oxidation of strained hydrocarbons by Ag(I) should be important. For example, recently reported ionization potentials for 1,[6] cubane,[7] and tricyclo[4.1.0.0^{2,7}]heptane[6] are 7.40, 8.74, and 8.15 eV, respectively. Hence, the reduction of silver ion to Ag^0 (IP 7.57 eV) should be energetically favorable with 1 but not with the latter two hydrocarbons. We note, however, that oxidation potentials in methanol, when they are measured, may not follow the same trend as gas-phase ionization potentials, and the above data must be regarded as merely indicative.

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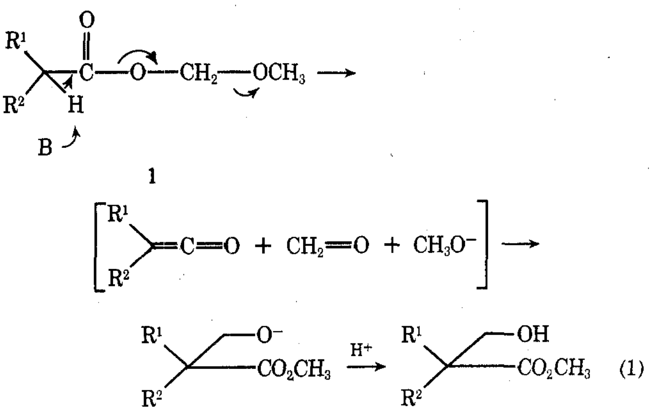
Fragmentation–Recombination of Methoxymethyl Ester Enolates. A Novel Method for Preparation of Hydracrylic and Glycidic Esters

Summary: Methoxymethyl ester enolates undergo fragmentation to ketenes, formaldehyde, and methoxide ion which recombine to give hydracrylic and glycidic esters in good yield.

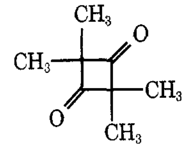
Sir: A variety of ester enolates have been prepared by reaction of lithium *N*-dialkylamides with esters at low temperature.[1] Although solutions of these ester enolates were considered to be stable even at room temperature, an interesting opportunity for reaction exists with enolates generated from methoxymethyl esters, (eq 1). Thus, heterolytic fragmentation[2] might be expected to occur as shown; in principle, recombination of the fragments should give the more stable hydracrylate ion. Herein, we report the realization of such a fragmentation–recombination and briefly discuss the mechanism and synthetic potential of the process.



(1)

Methoxymethyl esters were conveniently prepared in excellent yield by reaction of sodium carboxylates (sodium hydride + carboxylic acid) with chloromethyl methyl ether in refluxing tetrahydrofuran (THF)–hexamethylphosphoric triamide (HMPA, 1 equiv).

Addition of a THF solution of the methoxymethyl ester derived from isobutyric acid (**1**, $R^1 = R^2 = CH_3$) to 1.1 equiv of lithium diisopropylamide (LDA) in THF at −78° followed by quenching with D_2O at −78° cleanly gave recovered **1** (50% D incorporation).[3] On the other hand, warming the solution of ester enolate to room temperature resulted in isolation of hydracrylate **2** ($R^1 = R^2 = CH_3$, 69% yield). Two minor reaction components were isolated and identified as dimethylketene dimer **3**[4] (~10%) and diester **4** (15%).[5] In similar fashion, except that HMPA was added to LDA before generation of the ester enolate,[6] the methoxymethyl ester derived from tiglic acid **5** gave the α-vinyl hydracrylate **6** in 61% isolated yield.



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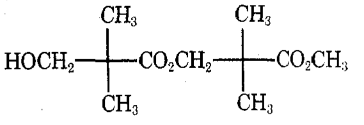

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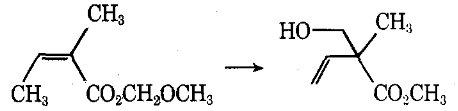
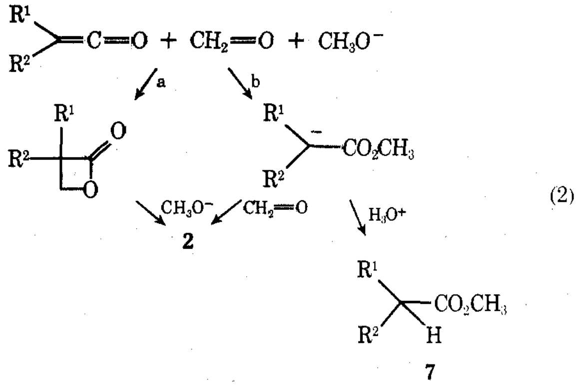


5 **6**

That a free alkoxide ion is involved in the process **1** → **2** was convincingly demonstrated by fragmentation–recombination of the ester enolate of **5** in the presence of ethoxymethyl ester enolate **1′** (OCH_3 replaced by OCH_2CH_3, $R^1 = R^2 = CH_3$); VPC comparison of the reaction components with previously isolated materials showed that four hydracrylic esters were present in about equal proportions and that these corresponded to the methyl and ethyl esters of **2** ($R^1 = R^2 = CH_3$) and **6**. Thus, intermediates derived from **1** and **5** must react indiscriminately with either methoxide or ethoxide generated in a fragmentation of the ester enolates (eq 1).[7]

At least two possible recombination paths to **2** have been considered (eq 2): a thermally allowed cycloaddition of ketene with formaldehyde and subsequent methoxide opening of the β-lactone (path a),[8] or ketene attack by methoxide to generate an ester enolate followed by trapping with formaldehyde (path b).



(2)

We do not favor path a for two important reasons. First, in all cases of fragmentation–recombination of **1**, trace to significant amounts of untrapped methyl ester **7** were detected; most dramatically, with **1** ($R^1 = CH_3$; $R^2 = OCOC_6H_5$), only methyl ester **7** ($R^1 = CH_3$; $R^2 =$