Acknowledgment. This work was supported by NIH Grant CA17918.

Registry No. **1a**, 88358-41-2; **1b**, 88358-42-3; **1c**, 87598-28-5; **1d**, 88358-43-4; **1e**, 88358-44-5; **1f**, 88358-45-6; **1g**, 88358-46-7; **2**, 77242-15-0; **3** (R′ = H; R = H), 88358-59-2; **3** (R′ = H; R = *t*-Bu), 84850-27-1; **3** (R′ = H; R = CH=CH_2), 88358-60-5; **3a**, 88358-52-5; **3b**, 88358-53-6; **3c**, 88358-54-7; **3d**, 88358-55-8; **3e**, 88358-56-9; **3f**, 88358-57-0; **3g**, 88358-58-1; **4**, 88358-61-6; **5** (R″ = H), 88358-62-7; **6** (R″ = CH_3), 5682-78-0; $PhCH_2CH_2CHO$, 104-53-0; $PhC(O)CH_2OAc$, 2243-35-8; $CH_3CH(OBr)CH(Ac)CHO$, 88358-47-8; $PhCOCH_2Cl$, 532-27-4; $PhCH_2CH_2C(SPh)$=O, 53573-33-4; cyclohexenone, 25512-62-3; cyclododecanone, 830-13-7; 2-acetoxycyclohexanone, 17472-04-7; cyclohexane-1,3-dione, 504-02-9; 2-methylnonane-3,5-dione, 88358-48-9; cyclododecanethiol, 7447-11-2; 2-(acetyloxy)cyclohexanethiol, 73921-29-6; 3-phenylpropanethiol, 24734-68-7; 2-(acetyloxy)-2-phenylethanethiol, 88358-49-0; 2-(acetyloxy)-3-(benzyloxy)butanethiol, 88358-50-3; 3-mercaptocyclohexanone, 33449-52-4; 5-mercapto-1-methylnonan-3-one, 88358-51-4; deoxybenzoin, 451-40-1; fluorenone, 486-25-9.

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Received October 17, 1983

Stable Vinyl Cations. 2.[1] Carbon-13 NMR Spectroscopic Observation of a Substituted Cyclopropylidenemethyl Cation

Summary: ^{13}C NMR spectroscopic data show the effective stabilization of the 1-cyclopropylidene-3-methyl-2-butenyl cation in solution.

Sir: The stabilizing ability of a cyclopropyl ring is well-known in trisubstituted as well as in disubstituted carbenium ions.[2] However, for vinyl cations there is a unique opportunity for stabilization by a cyclopropyl group, when one carbon of the cyclopropane ring is part of the vinyl cation, as in the cyclopropylidenemethyl cation 1.[3]

1

Cations 1 were first postulated as intermediates in the homopropargyl rearrangement.[4] The rapid solvolysis of cyclopropylidenemethyl bromide has been attributed to the high stability of the intermediate vinyl cation.[5] This conclusion is supported by ab initio and MINDO/3 calculations[6] and by experimental evidence for 1 in the gas phase.[7]

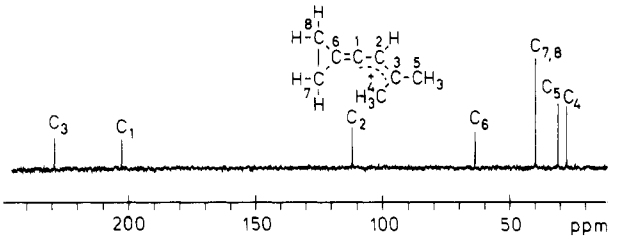
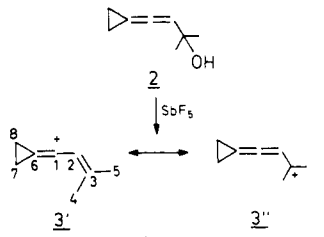


Figure 1. 100.62-MHz ^{13}C NMR spectrum of cation **3** in SO_2ClF/SO_2F_2 (2:1) at −100 °C.

Vinyl cations have been rather elusive toward direct ^{13}C NMR spectroscopic observation;[8] however, we have shown recently that α-vinyl-substituted vinyl cations can be generated from tertiary α-allenyl alcohols as stable species in solution.[1] We report here the first successful generation and NMR spectroscopic observation of the 1-cyclopropylidene-3-methyl-2-butenyl cation **3**.[9]

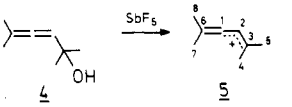
A clean yellow solution of **3** in SO_2ClF/SO_2F_2 was obtained by reaction of **2**[10] with SbF_5 by using the method already described.[11] The ^{13}C NMR spectrum (Figure 1) was recorded at −100 °C. Assignments were made by using proton-coupled spectra. Single-frequency proton-decoupled spectra were used to confirm these assignments.[12] C_3 shows long-range couplings to six methyl protons and thus could be distinguished from C_1.

Cation **3** can be considered either as a α-vinyl-β-cyclopropyl-stabilized vinyl cation (**3′**) or as a cyclopropylidene-substituted allyl cation (**3″**). The downfield



2 3′ 3″

shifts of C_1 (202.66 ppm) and C_3 (228.92 ppm)[9] indicate extensive charge delocalization between these two positions. Comparison of **3** with the analogous C_1-isopropylidene-substituted cation **5**[1] (Table I) reveals sig-



4 5

nificant differences. The corresponding allyl carbons in **5**, C_3 (257.64 ppm) and especially C_1 (245.39 ppm), are much more deshielded than those in **3**. The C_3 carbons in **3** and **5** have almost identical chemical shift values in the precursor alcohols **2** and **4**. The problem of neighboring group effects is minimized for C_3 since the substituent change is occuring at C_1, which is effectively screened from C_3.[13] We attribute the 29-ppm shielding of C_3 in **3** to the superior electron-donating capability of the β-cyclopropyl ring compared to the effect of two β-methyl groups in vinyl cation **5**. Calculations (STO-3G) have shown that a β-cyclopropyl ring stabilizes a primary

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0022-3263/84/1949-0575$01.50/0

Table I. ^{13}C NMR Chemical Shifts of Vinyl Cations 3 and 5 and Their Precursors 2 and 4[a]

compd	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
2	186.35	103.53	70.10	29.98		80.66	7.81	
3	202.66	111.72	228.92	27.18	30.62	63.66	39.63	
4[b]	197.92	99.01	69.01	29.51		97.86	20.10	
5[b]	245.39	113.97	257.64	32.43	36.44	101.55	16.29	

[a] Compounds 2 and 4 in $CDCl_3$ (77.0 ppm); 3 and 5 referenced to capillary CD_3COCl (δ_{CD_3} = 32.90 ppm); specific assignment of C_4 and C_5 in 3 and 5 tentatively analogous to allyl cations. [b] Reference 1.

vinyl cation by 14 kcal/mol more than two β-methyl groups[6] do.

In 3 the two methyl groups at C_3 are nonequivalent as in other allyl cations.[13] The observed smaller downfield shifts, compared to the precursor, reflect less need for hyperconjugative stabilization from these methyl groups due to less positive charge at C_3 in 3 as compared to 5. Electron donation from the cyclopropyl ring at C_1 decreases electron density at C_3, thus leading to less deshielding for this carbon than that in 5. C_1 is 31 ppm upfield from that in 5 even if a 12-ppm correction for the different shift in the precursors is taken into account.

Charge delocalization away from C_1 and C_3 into the β positions C_7 and C_8 of the cyclopropyl ring is indicated by the shift of the signals for these carbons (39.63 ppm), which is 32 ppm downfield from the precursor. This downfield shift for the β-cyclopropyl carbons is of similar magnitude to that in α-cyclopropyl-stabilized allyl cations,[13] whereas the α-cyclopropyl carbon C_6 in 3 cannot be compared because it is unique to this type of vinyl cation.

At first glance, the upfield shift for the unsaturated cyclopropyl carbon C_6 from 80.66 ppm in 2 to 63.66 ppm in 3 is surprising. In α-cyclopropyl-substituted trigonal cations[13] and also in α-cyclopropyl-substituted vinyl cations,[14] both C_α and C_β ring carbons exhibit considerable downfield shift. The unusual shift for C_6 in 3 may be related to the unusual shift in 2, where C_6 is both terminal allenic and part of a cyclopropyl ring.

The shift of C_6 may also be rationalized by taking into account the unique structure of cyclopropylidenemethyl cations 1, which can be looked upon as the unsaturated analogues of cyclopropylcarbinyl cations. In valence bond terminology there is a difference between 1 and α-cyclopropylcarbinyl cations in that the resonance structures of 1 include homopropargylic cation resonance forms (which of course would be given very unequal weights) whereas cyclopropylcarbinyl resonance structures would be homoallylic. In 3 this would partially change the bond between C_6 and C_1 to a triple bond, giving C_6 some sp character. Calculations on 1 show the C_α–C_β distance became significantly shorter than that of a double bond.[6] In 3 the mutual shielding of the two sp carbons C_6 and C_1 might give rise to the substantial upfield shifts observed for these carbons.

Alternatively, the upfield shift for C_6 in 3 could be explained by polarization effects. The β carbons of vinyl cations are negatively charged,[15] but preliminary calculations for model cations of type 1 and 3 do not show significant differences from 5.[16]

The ^{13}C NMR spectroscopic data of 3 presented here show the first direct experimental proof obtained for a stable vinyl cation in solution utilizing the unique and unusually effective stabilization of such a cation by a β-cyclopropyl ring. These data are in agreement with theory and give additional support to the interpretation of the solvolytic studies of these systems.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Registry No. 3, 88295-38-9.

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Received October 24, 1983

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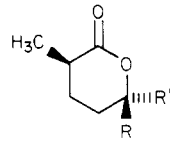
A Convergent Asymmetric Synthesis of (-)-Malyngolide and Its Three Stereoisomers

Summary: (-)-Malyngolide, an antibiotic of algal origin, and its stereoisomers (+)-malyngolide and (+)- and (-)-epimalyngolide have been synthesized asymmetrically in high diastereomeric and enantiomeric purity.

Sir: Since the antibiotic (-)-malyngolide (1) was isolated from marine algae and its structure, including relative and absolute configuration, established in 1979,[1] a number of syntheses[2-5] have been reported. The majority of these lack stereoselectivity, the product being a mixture of (±)-malyngolide and its diastereomer, (±)-epimalyngolide (2), which can be separated by chromatography.[3] One



1, R = n-C_9H_{19}; R' = CH_2OH
2, R = CH_2OH; R' = n-C_9H_{19}

synthesis[4] produces racemic malyngolide stereoselectively and two others produce a mixture of (-)-malyngolide and (+)-epimalyngolide, either by total asymmetric synthesis[5a] or by derivation from a chiral starting material, D-glucose.[5b] We report here a convergent asymmetric synthesis in which either chiral center is produced in one or the other of the two possible configurations. In this way, not only (-)-malyngolide and (+)-epimalyngolide but also their enantiomers were produced in high diastereomeric and enantiomeric purity.

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