The Rearrangement of Chrysanthemyl Alcohol in Fluorosulphuric Acid

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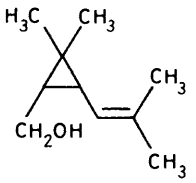
Solution of chrysanthemyl alcohol [**1**; 2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropylmethanol] in fluorosulphuric acid–sulphur dioxide at −78 °C resulted in the formation of the 2-methyl-2(3-oxabicyclo[3,1,0]hex-4-yl)-ethan-2-ylium ion (**4**). On quenching, this species underwent extensive decomposition, yielding a complex mixture of products, of which the main components were 2,2,5,5-tetramethyl-3-vinyltetrahydrofuran (**5**), 3,3-dimethyl-5-(2-methylprop-2-enyl)tetrahydrofuran (**6**), 6,6-dimethyl-5-isopropyl-2,3-dihydropyran (**7**), 3,3-dimethyl-5-(2-methylprop-1-enyl)-tetrahydrofuran (**8**), and 2,2,6-trimethyl-3,5-heptadien-1-ol (**9**). Routes to the formation of these products *via* the cyclobutonium ions derived from (**4**) are discussed. The reason why extensive rearrangement occurs during quenching, in contrast with the more usual formation of unrearranged products, is also discussed.

The (+)-*E* isomer of chrysanthemyl alcohol [1,2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropylmethanol] has been implicated in important biosynthetic pathways to irregular (*i.e.* non-isoprenoid) monoterpenes,[1] and as a result, its carbocation rearrangements have been studied.[2,3] The cyclopropane ring can be opened in any of the three possible ways,[3] the direction of a particular reaction depending on the substituent pattern, to yield the santolinyl system (3-ethyl-2,5-dimethylhexyl) the artemisyl system (2,5,5-trimethylheptyl), or the lavandulyl system (2,3,6-trimethylheptyl).

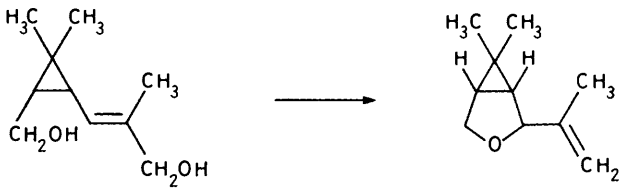
Studies of rearrangements in superacids[4] have shown that reactions can follow completely different pathways from similar reactions in dilute acids.[5] One reason for this change of behaviour[6] is the different order of reactivity of functional groups of multifunctional compounds in superacids, resulting in completely different reaction pathways for some difunctional molecules. It seemed probable that the rearrangement of chrysanthemyl alcohol in superacid would reveal a completely new rearrangement pathways to that found under more conventional conditions.

Results and Discussion

Chrysanthemyl alcohol (*Z*,*E* mixture; 40:60) was dissolved in FSO_3H–SO_2 at −78 °C. The proton NMR spectrum showed broad peaks with poor resolution, but the ^{13}C NMR spectrum, given in the Table, was well resolved. The spectrum shows a peak at δ 283 (s) typical of a carbon atom carrying almost a full positive charge. Peaks at δ 86 (d) and 70 (t) are rather low for the ranges observed[7] for carbon atoms next to oxygen in cyclic ethers studied in FSO_3H–SO_2. However, the cyclic ethers reported carry a proton on the oxygen atom in FSO_3H–SO_2, but the present ion has a charge on C-6, and it seems unlikely



(**1**)



(**2**) (**3**)

Scheme 1.

that a charge would be stable on an oxygen atom next but one to a carbocation centre.[8] The values reported are closer to those observed for cyclic ethers in neutral solvents,[7] these being in the range of δ 60–85. The peak at δ 86 is probably shifted downfield by proximity to the positive charge on carbon. We suggest that the ion is a cyclic ether, the reaction thus paralleling the conversion of (**2**) into (**3**) with toluene-*p*-sulphonic acid in benzene reported by Crombie,[3a] Scheme 1. The reaction of (**1**) with FSO_3H would be expected to be initiated at the double bond[9] to give a carbocation stabilised by the cyclopropyl group. Cyclisation would then give the ether which is the dihydro version of (**3**). Our spectrum clearly shows the positive charge to be on a carbon atom. This could arise by a hydride abstraction from this species, giving the ion (**4**). An alternative interpretation of our data would be to assume that the singlet at 22 ppm is actually a triplet, the splitting being obscured by the quartet at 21.8 ppm on the off-resonance decoupled spectrum; this would be consistent with an isomer of (**4**) in which the cyclopropane ring had been opened. However, this reaction would need to be strongly stereoselective to account for the observation of a single ion, and would be inconsistent with the products of quenching and ion reported below. We, therefore, reject this interpretation.

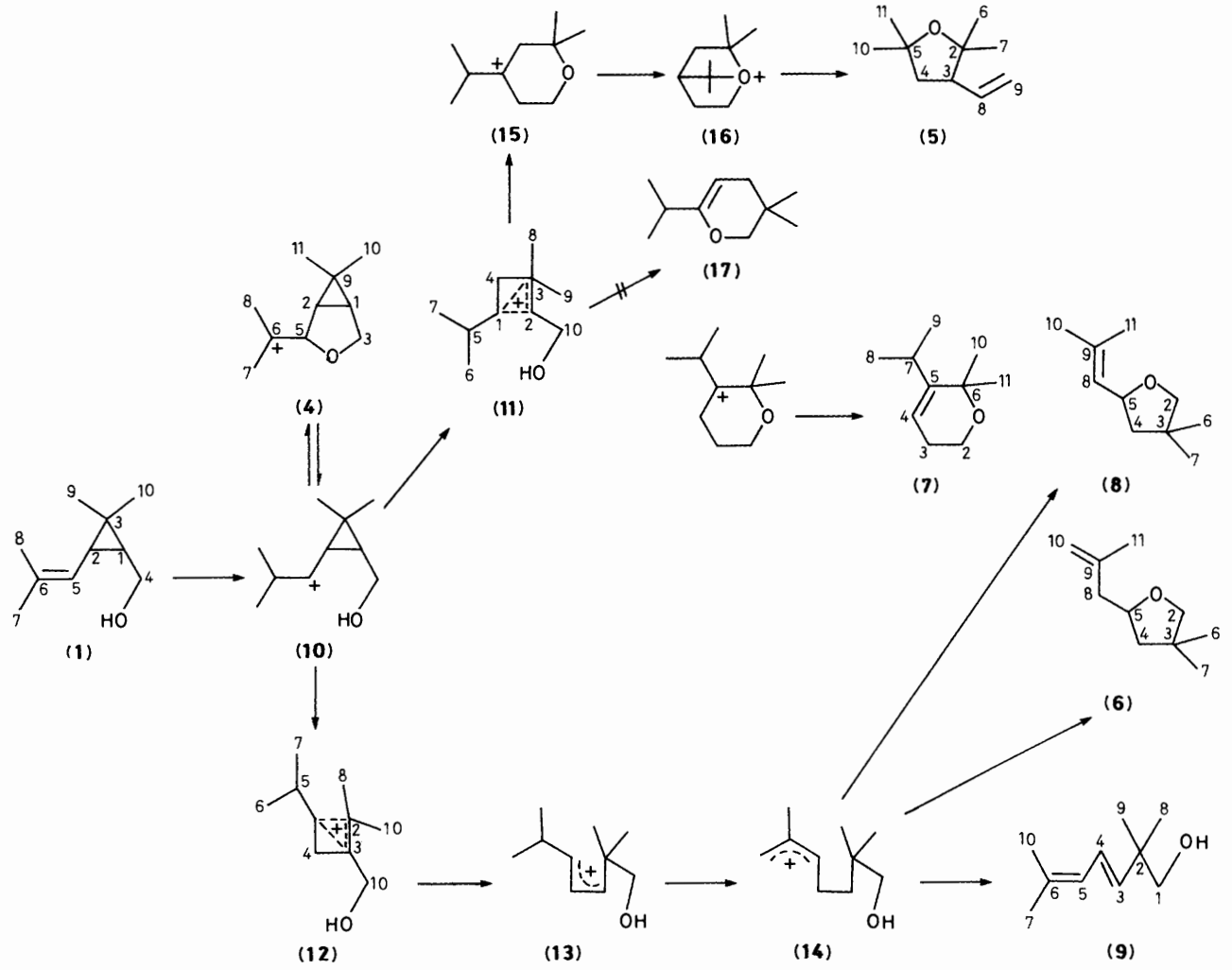
The ion appeared to be the only species present, suggesting that it was formed from both *Z*- and *E*-isomers. Formation from the *Z*-isomer is to be expected; from the *E*-isomer it may well proceed *via* the *Z*-isomer, but the mechanism of *E* to *Z* interconversion is unknown.

Reaction of chrysanthemyl alcohol (**1**) with FSO_3H in liquid sulphur dioxide at −78 °C, followed by quenching in aqueous methanol containing potassium carbonate, gave a reddish-brown oil in 80% yield which was purified by column

Table. ^{13}C NMR shifts (ppm from $SiMe_4$) measured in FSO_3H–SO_2 at −78 °C (*A*) or in $CDCl_3$ at room temperature (*B*).

Compound	Condition	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
(1)	*B*	28 d	34 d	59 s	62 t	123 d	132 s	25* q	17* q	20* q	22* q	
(4)	*A*	69 d	60 d	70 t	—	86 d	283 s	33 q	33 q	22 s	41 q	23 q
(5)	*B*	—	83 s	54 d	44 c	79 s	31* q	29* q	137 d	116 t	31* q	29* q
(6)	*B*	—	78 t	40 s	45 t	75 d	27* q	26* q	45 t	143 s	112 t	23q
(7)	*B*	—	70 s	36 t	115 d	141 s	70 s	31 d	22 q	22 q	26 q	26 q
(8)	*B*	—	80 t	40 s	48 t	76 d	26* q	27* q	126 d	135 s	18* q	26* q
(9)	*B*	72 t	39 s	124 d	125 d	126 d	138 s	26* q	18* q	23* q	24* q	

* Assignments could be interchanged.



Scheme 2.

chromatography and analysed by GLC and TLC. It contained approximately 30 compounds, five of which were present in amounts greater than 5%. Samples of these were separated by preparative GLC, and examined in order of increasing GLC retention time.

The first product, comprising 10% (w/w) of the oil was shown by elemental analysis and mass spectrometry to be $C_{10}H_{18}O$. The mass spectrum showed loss of a methyl group from M^+, followed by loss of a second methyl, then loss of C_2H_4, and loss of a third methyl group to leave $C_5H_5O^+$. The infra-red spectrum showed the presence of a carbon-to-carbon double bond.

The ^{13}C NMR spectrum (Table) showed peaks at δ 82 (singlet) and 79 (s) ppm consistent with carbon next to oxygen. It also showed the presence of four $-CH_3$ groups, and a $-CH{=}CH_2$ group. These data suggested the structure (**5**), which was confirmed by ^1H NMR. ^1H Decoupling experiments showed that the $-CH{=}CH_2$ was attached to –CH. The ^{13}C NMR chemical shifts of model compounds support the assignments of the various signals.

The second product, comprising 8% of the oil, was also shown by elemental analysis and mass spectrometry to be $C_{10}H_{18}O$. The mass spectrum has its base peak at *m/z* 99, corresponding to the loss of C_4H_7 from M^+. This was confirmed by a strong peak at *m/z* 55. Like the previous compound, a strong peak at *m/z* 81 indicates a stable C_5H_5O ion. The infra-red spectrum again showed the presence of a C=C double bond.

The ^{13}C NMR spectrum showed peaks at δ 78 (triplet) and 75 (d) ppm consistent with carbon attached to oxygen, plus three methyl groups and a vinyl group. The ^{1}H NMR spectrum showed the hydrogens on the $-CH_2$ adjacent to the ethereal oxygen to be coupled only to each other suggesting that the compound has the structure (**6**). The ^{13}C NMR assignments were again confirmed by comparing chemical shifts with those of model compounds.

The third product, comprising 19% of the oil, was isomeric with the first two, elemental analysis and mass spectrometry both indicating an empirical formula of $C_{10}H_{18}O$. The infra-red spectrum again showed the presence of a C=C double bond. The mass spectrum shows a peak at *m/z* 111 consistent with loss of C_3H_7, confirmed by a peak at *m/z* 43. Successive loss of two methyl groups from this ion gives the base peak at *m/z* 81, as observed in the previous products.

The ^{13}C NMR spectrum showed only eight signals. Peaks at δ 141 (s) and 115 (d) ppm, were characteristic of the carbon atoms of a double bond, and peaks at 70 (s) and 62 (d) ppm were within the range of carbons situated next to oxygen. The two most intense peaks were at 26 (q) and 22 (q) ppm, and probably each represents two methyl groups.

Since the substituents of this cyclic ether comprise two methyl groups (on the α-carbon atom) and an isopropyl group, it seems likely that we have a six-membered ring, in contrast to the previous compounds. This was supported by the ^{1}H NMR spectrum. A 2 H multiplet at 3.91 ($-CH_2-O-$) was shown to be coupled to a 2 H multiplet at 1.87 by decoupling. Decoupling the signal at 1.87 showed it to be coupled to signals at 3.91 and 5.37 (=CH–), indicating the structure to be (**7**).

The fourth product comprised 39% of the oil, and was isomeric with the first three by elemental analysis; mass spectrometry confirmed this result, but the mass spectrum differed considerably from those of the previous isomers. The M^+ ion readily lost a methyl group to give a peak at *m/z* 139. Loss of two further methyl groups gave peaks at *m/z* 109. An alternative pathway splits the molecule into $C_5H_9^+$ and $C_5H_9O^+$ fragments. The infra-red spectrum showed the presence of a C=C double bond. The ^{13}C NMR spectrum has signals at δ 135 (s) and 126 (d) ppm, consistent with the presence of a double bond, together with signals at 80 (t) and 76 (d) ppm consistent with carbon next to oxygen. Four peaks at 27, 26.5, and 18 ppm (all q) indicated four methyl groups. The ^{1}H NMR spectrum showed peaks at 4.54 (1 H, m) and 3.36 (2 H, AB q, *J* 8 Hz) characteristic of hydrogen on carbon atoms α to oxygen; the peak at 4.54 was coupled with a broad multiplet (2 H) at δ 1–2. These results are best explained by the structure (**8**), which is a double-bond isomer of (**6**).

The final product comprises 7% of the oil, and was again isomeric with the first four by elemental analysis and mass spectrometry. However, the mass spectrum showed a peak at *m/z* 136, resulting from loss of water and a base peak at *m/z* 123, probably resulting from loss of $-CH_2OH$. Peaks in the infra-red spectrum at 1 650 and 1 620 cm^{-1} suggested the presence of a diene, while a peak at 3 400 confirmed the presence of a hydroxy group. A UV maximum at 233 nm (ε 233 = 1.01×10^4) in cyclohexane confirmed the presence of a C=C–C=C unit. The ^{13}C NMR spectrum showed signals from four alkene carbon atoms, at 137.6 (s), 125.4 (d), 125.3 (d), 124.9 (d) ppm, and a signal at 72 (t) ppm from a carbon atom next to an oxygen. Four quartets at 26, 24, 23, and 18 ppm indicated methyl groups, while the remaining peak was a singlet at 39 ppm. These results are consistent with structure (**9**), and the ^{1}H NMR spectrum also supported the assignment, with peaks at δ 6.15 (1 H, dd, *J* 6, 8 Hz), 5.72 (1 H, d, *J* 6 Hz), 5.42 (1 H, d, *J* 8 Hz) from the diene part of the molecule and at 3.22 (2 H, s), for the $-CH_2OH$.

In previous work, we[4,7a] have found that protonated ethers in superacids are quenched to yield the unrearranged ether. Clearly, in the present case, rearrangement has taken place on quenching. In previous examples, the ether formed in superacid has been the thermodynamically stable product, but here it was formed by trapping the ion (**10**) before the cyclopropylmethyl carbocation could rearrange to form the cyclobutanium ion.[10] In the early stages of quenching, attack of the nucleophile on the ether probably gives a diol, which reverts rapidly, in a locally acid environment, to the ether *via* the carbocation; in this case rearrangement to the bicyclocyclobutonium ion provides an irreversible pathway away from the equilibrium.

The classical ion (**10**) can form a bicyclocyclobutonium ion by shift of either of two bonds to give (**11**) or (**12**). We assume that both ions are formed. The pathways by which these ions decompose must be speculative, since no reports of quenching polysubstituted bicyclocyclobutonium ions exist. In the case of (**12**), the hydroxy group could attack C-2, breaking the C-2 to C-3 bond, to yield (**7**) directly. A similar attack on C-4 is unlikely to be significant, since C-4 is unsubstituted and probably carries less charge than the other bicyclocyclobutonium carbons; attack here may give rise to an unidentified trace product. The other pathway available to (**12**) is then ring opening. A shift of C-10 from C-2 to C-3 breaks the C-1 to C-2 bond, yielding the ion (**13**) which rearranges to the more stable (**14**). This ion can then cyclise by attack of the hydroxy on C-4, yielding an ion which gives (**6**) and (**8**), or can lose a proton to give (**9**).

The other ion (**11**) should be able to follow either of the first two pathways, with attack of the hydroxy on C-1 or C-3 giving rise to cyclic ethers with 6-membered rings, but neither of these is found. Attack of the hydroxy group at C-3, followed by fission of the C-2 to C-3 bond would yield (**15**). However, shift of the carbocation centre to the side chain would permit cyclisation to the oxonium ion, (**16**). Fission of the bonds from oxygen to a substituted carbon would give stable carbocations which would revert to (**10**), but fission of the bond to the unsubstituted carbon would not give a stable ion, and elimination to yield (**5**) would be rapid. Attack of the nucleophile on C-1 would similarly give rise to (**17**), which cannot undergo similar rearrangement and so should be stable; it has not been found, but may be among the minor products. Ring opening of (**11**) is less favoured than the corresponding reaction of (**12**) since one end of the allylic ion would be primary. Ring opening may, however, yield some of the minor products.

The ions (**11**) and (**12**) can probably undergo shifts of substituents from which the large range of minor products may arise.

Our results provide a clear example of extensive rearrangement of an ion (**4**) during quenching. In anhydrous acid, the ion is stable due to the absence of nucleophiles. Addition of water sets up an equilibrium between (**4**) and (**10**), and (**10**) now has a sufficiently long lifetime to rearrange to (**11**) and (**12**). The ion (**4**) must be regarded as a kinetically stable species, favoured by its anhydrous environment so that it is in fact stable over a period of hours at −78 °C. It is a matter of speculation whether or not the cyclic ether derived from chrysanthemol could be of any significance on the biosynthetic pathway; the reaction products certainly differ in carbon skeleton from the products of rearrangement in normal acids (Scheme 2).

Experimental

The ^{1}H NMR spectra were recorded on a Varian H.A. 100 spectrometer with $CDCl_3$ as solvent and $SiMe_4$ as an internal standard. Decoupling experiments were carried out using a Muirhead–Wigan Decade Oscillator at 20–30 V. The ^{13}C NMR spectra were recorded on either a Varian XL 100 (25.2 MHz) or

a Varian CFT 20 (20.0 MHz), or a Varian XL 200 (50.3 MHz) spectrometer using $CDCl_3$ as the solvent for neutral solutions and $SiMe_4$ as an internal standard; sulphur dioxide was the solvent for superacid solutions with an external lock of [$^2H_6$]acetone of CD_3OD and external standard of $SiMe_4$ enclosed within a 5 mm NMR tube.

Infra-red spectra were measured on a Pye Unicam SP 1000 spectrometer. Ultra-violet spectra were measured on a Pye Unicam PS 1800 spectrometer. Mass spectra were recorded on either an AEI–Kratos MS9 spectrometer or a V.G. Micromass 12 F spectrometer.

Reaction mixtures were analysed by GLC using a Varian Aerograph Series 1800, a Perkin-Elmer Model F 11, or a Pye 104 gas chromatograph. Columns were either Carbowax 20 M or Carbowax 15 M (5–20% w/w) or silicone oil SE-30 coated on Chromosorb, 80–100 mesh. Preparative GLC was carried out on a Varian Model 712, using a 4 m × 1 cm column filled with Carbowax 20 M 20% Supasorb (80–100 mesh).

TLC was also used for product analysis, using plates coated with Silica gel H, Silica gel HF_{254} or silver nitrate–Silica gel H. Plates were developed in ethyl acetate–chloroform or ethyl acetate–hexane at 4 °C, and visualised with a phosphomolybdic spray, followed by heating in an oven at 110 °C for 3 min.

Chrysanthemyl Alcohol.—A commercial sample (Aldrich) was used without further purification. It consisted of 98% chrysanthemyl alcohol, 40:60 (w/w) *Z,E* mixture.

Generation of the Chrysanthemyl Carbocation.—Sulphur dioxide (1 cm^3) was condensed into a 10 cm^3 round-bottomed flask and FSO_3H (2.5 cm^3) added. The solution was cooled to −78 °C using a solid CO_2–acetone bath. Chrysanthemyl alcohol (500 mg) was dissolved in SO_2 (1 cm^3) and cooled to −78 °C, then added dropwise, down the inside of the cooled flask to the stirred FSO_3H–SO_2 mixture. After being stirred for 10 min, the solution was added to a 12 mm NMR tube cooled to −78 °C. The tube was sealed with Parafilm, removed from the cooling bath, then cleared of any residual acetone before the spectrum was measured.

Quenching of the Chrysanthemyl carbocation.—Chrysanthemyl alcohol (10 g) in carbon disulphide (40 cm^3) was added at −78 °C to a rapidly stirred solution of fluorosulphonic acid (43 cm^3) in liquid sulphur dioxide (43 cm^3) over 20 min, under an atmosphere of dry nitrogen. After being stirred for 30 min, the acid layer was trickled over a period of 25 min from a dropping funnel maintained at −78 °C down the inside wall of a vessel containing a rapidly stirred slurry of potassium carbonate (120 g, added in 20 g portions), methanol (250 cm^3), and ice (30 g) cooled to −78 °C. After completion of the addition, followed by warming of the mixture to room temperature, water (700 cm^3) was added, and the mixture filtered. The solid phase was extracted with ether. The aqueous phase was saturated with ammonium sulphate and extracted with ether (250 cm^3) and hexane (3 × 60 cm^3). Removal of solvent from the combined extracts gave 8 g (80% yield) of a reddish-brown oil.

The crude oil was purified by column chromatography to yield a yellow oil, which was fractionated by preparative GLC, with the column temperature programmed from 70–200 °C. Five fractions were collected, their purity checked by analytical GLC on two columns, and by TLC, then spectroscopically analysed.

First fraction (**5**) (Found: C, 77.6; H, 11.4. $C_{10}H_{18}O$ requires C, 77.9; 1, 11.7%); $\nu_{max.}$ 3 030 (w), 2 950 (s), 2 900 (s), 1 630 (w), 1 450 (m), 1 375–1 360 (m), 1 255 (s), 1 075 (b), 985 (w), and 805 (s) cm^{-1}; δ_H(100 MHz) 0.98 (3 H, s), 1.15 (3 H, s), 1.20 (3 H, s), 1.26 (3 H, s), 1.80 (2 H, m), 2.60 (1 H, m), 4.20 (2 H, m), and 5.64 (1 H, m). On irradiating the signal at δ 5.64, the multiplet at 4.20 gave a singlet and the multiplet at 2.60 gave a triplet. On irradiating the signal at 1.80, the signal at 5.64 gave a double doublet. The ^{13}C NMR spectrum is given in the Table; m/z, 154 (M^+, 1%), 139 (11), 133 (3), 124 (3), 121 (6), 110 (1), 109 (7), 97 (8), 96 (65), 91 (3), 82 (8). 81 (100), 80 (2), 79 (12), 77 (6), 68 (7), 67 (15), 59 (8), 58 (2), 55 (12), 53 (15), 43 (45), and 41 (28).

Second fraction (**6**) (Found: C, 77.6; H, 11.5. $C_{10}H_{18}O$ requires C, 77.9; H, 11.7%); $\nu_{max.}$ 3 025 (w), 2 970 (s), 2 890 (s), 1 625 (w), 1 460 (b), 1 380 (s), 1 370 (s), 1 260 (w), 1 065 (s), 892 (m), and 814 (m) cm^{-1}; δ_H(100 MHz) 81.06 (6 H, s), 1.71 (3 H, s), 1.60–2.34 (4 H, m), 3.31 (2 H, AB, *J* Hz), 3.99 (1 H, m), and 4.63 (2 H, s). The ^{13}C NMR spectrum is given in the Table; *m/z* 154 (M^+, 0.5%), 139 (2), 109 (1.5), 100 (7), 99 (100), 81 (44), 71 (8), 69 (10), 55 (53), 43 (87), 41 (33), and 39 (13).

Third fraction (**7**) (Found: C, 78.1; H, 11.5. $C_{10}H_{18}O$ requires C, 77.9; H, 11.7%); $\nu_{max.}$ 2 970 (s), 2 830 (s), 1 645 (w), 1 460 (br), 1 380 (s), 1 360 (s), 1 260 (w), 1 180 (m), 1 100 (s), 1 045 (m), 883 (m), 850 (m), 809 (w), and 732 (w) cm^{-1}; δ_H(100 MHz) 81.00 (6 H, d, m, *J* 8 Hz), 1.08 (6 H, s), 1.87 (2 H, m), 2.11 (1 H, m), 3.91 (2 H, m), and 5.37 (1 H, m). Irradiation of the signal at δ 5.37 caused the multiplets at 3.91 and 1.87 to collapse into triplets; irradiation of the signal at 1.87 caused the multiplet at 5.37 to collapse to a triplet and the multiplet at 3.91 to collapse to a doublet. Irradiation at 3.91 caused the multiplet at 5.37 to collapse to a triplet, and the multiplet at 1.87 to collapse to a doublet. Finally, irradiation at 2.11 caused the peak at 1.00 to collapse to a singlet, and the multiplet at 5.37 to a triplet. The ^{13}C NMR spectrum is given in the Table; *m/z*, 154 (M^+, 10%), 139 (6), 121 (4), 111 (27), 96 (37), 81 (100), 79 (11), 69 (12), 67 (12), 56 (13), 55 (15), 53 (16), 43 (44), and 41 (36).

Fourth fraction (**8**) (Found: C, 77.8; H, 11.5. $C_{10}H_{18}O$ requires C, 77.9; H, 11.7%); $\nu_{max.}$ 3 030 (w), 2 98 (s), 2 850 (s), 1 650 (w), 1 455 (s), 1 380 (s), 1 365 (s), 1 240 (w), 1 050 (s), 985 (w), 920 (w), and 870 (w) cm^{-1}; δ_H(100 MHz) 1.05 (6 H, s), 1.0–2.0 (2 H, series m), 1.64 (3 H, br s), 1.69 (3 H, br, s), 3.36 (2 H, AB, *J* 8 Hz), 4.54 (1 H, m), and 5.15 (1 H, d, *J* 6 Hz). Irradiation of the signal at δ 4.54 modified the appearance of the series of multiplets between 1.0 and 2.0. The ^{13}C NMR spectrum is given in the Table; *m/z* 154 (M^+, 13%), 140 (9), 139 (78), 123 (3), 109 (20), 95 (5), 93 (6), 85 (20), 83 (19), 81 (11), 69 (100), 67 (25), 55 (45), 53 (15), 43 (13), 42 (12), and 41 (48).

Fifth fraction (**9**) (Found: C, 78.1; H, 11.8. $C_{10}H_{18}O$ requires C, 77.9; H, 11.7%); $\nu_{max.}$ 3 400 (br), 2 900 (s), 2 870 (s), 1 650 (w), 1 620 (w), 1 460 (s), 1 370 (s), 1 360 (s), 1 050 (b), 980 (m), 965 (m), 872 (w), and 818 (w) cm^{-1}; $\lambda_{max.}$ 233 nm (ε_{233} 10 800), using a solution of 2.00 mg in cyclohexane (200 cm^3), with a path length of 1 cm; δ_H(100 MHz) 0.99 (6 H, s), 1.75 (6 H, s), 2.30 (1 H, s), 3.22 (2 H, s), 5.42 (1 H, d, *J* 8 Hz), 5.72 (1 H, d, *J* 6 Hz), and 6.15 (1 H, dd, *J* 8 Hz). The peak at 2.30 disappeared on the addition of D_2O. The ^{13}C NMR spectrum is given in the Table. The mass spectrum had *m/z* 154 (M^+, 24%), 139 (15), 136 (22), 123 (100), 121 (21), 93 (53), 91 (35), 81 (84), 79 (58), 77 (37), 69 (24), 67 (44), 55 (38), 43 (39), 41 (64), and 31 (45.

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