relatively rapidly by isomerization or during decomposition to form $C_5H_5^+$.

It would obviously be of interest to be able to obtain data at higher energies (shorter lifetimes) in order to reduce or even eliminate such scrambling reactions. Meyerson has pointed out that doubly charged toluene molecular ions exhibit a much lower degree of scrambling on decomposition,[11] which is consistent with their high ionization potential (24.5 eV).[15] Field ionization offers a method to study ions of very short lifetimes.

Experimental Section

All of the data were determined on a Hitachi RMU-7 double-focusing mass spectrometer. Abundance values were measured with a "bright" ion source, Model MS-101, with 70 eV electron energy (unless otherwise stated), 100 μA total electron emission current, 185° sample reservoir system, and ion source thermocouple reading of 180°. Measurements in the field-free drift region between the ion source and the electrostatic analyzer were made using the Barber-Elliott-Major defocusing technique.[30] All the abundance ratios for which an error is quoted represent the average of ten separate values and the quoted error is the standard deviation. All abundances are corrected for ^{13}C. Appearance potentials were determined using the semilogarithmic plot method[31] with Ar and Xe as standards. For collision-induced metastable measurements, the argon pressure in the first drift region was 2×10^{-4} Torr.

Toluene-α-d_3 (**6**) and -*ring*-d_5 (**7**) were commercial samples of greater than 98.5% isotopic purity. 2,4,6-Trideuteriotoluene (**8**) was prepared from *m*-toluidine by exchanging the hydrochloride with deuterium oxide in a sealed tube,[32] followed by reduction of *m*-toluidinediazonium-d_3 salt with alkaline formaldehyde.[33] The **2,4,6-trideuteriotoluene** so formed possessed an isotopic purity (confirmed by low-voltage mass spectrometry) of d_3, 96.5%; d_2, 2.6%; d_1, 0.9%.

Cycloheptatriene-7-d_1 (**9**)[34] was found to have an isotopic content of d_1, 94.4%. For cycloheptatriene-1,2,3,4,5,6-d_6 (**10**)[34] the isotopic content was d_6, 96.6%; d_5, 3.4%.

Acknowledgments. We are grateful to the Army Research Office (Durham) and to the National Institutes of Health (GM-16609) for generous financial support.

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(30) F. W. McLafferty, J. Okamoto, H. Tsuyama, Y. Nakajima, T. Noda, and H. W. Major, *Org. Mass Spectrom.*, **2**, 751 (1969).

(31) F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

(32) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 239 (1946).

(33) R. Q. Brewster and J. A. Poje, *J. Amer. Chem. Soc.*, **61**, 2419 (1939).

(34) We are indebted to Dr. M. J. Goldstein, Cornell University, for providing samples of the deuterated cycloheptatrienes, **9** and **10**.

Electron Impact Induced Rearrangements in Isoprenoids[1]

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Abstract: Several isoprenyl ketones in which the first isoprene unit is saturated were synthesized and their mass spectra were examined. Due to extensive hydrogen migration, double bond mobility was observed, indicating the limitations of mass spectrometry for detection of the position of a saturated isoprene unit in polyisoprenoids. Corresponding hydrocarbons and alcohols also show hydrogen migration and double bond lability upon electron impact.

Recently mass spectrometry has been used extensively in structural studies of various naturally occurring isoprenoids which contain one saturated unit.[2–4] For example, a C_{43}-isoprenoid ketone containing one saturated unit has been isolated from tubercle bacilli, and from mass spectral data it was concluded that the saturated isoprene unit was the third one from the keto group.[3] A similar C_{43} ketone (I) was isolated[2] from the photooxygenation of the naphthoquinone of *M. phlei*, MK-9 (II, H_2). Low-resolution mass spectral data (Table I) for this compound established that the fragmentation pattern was very similar to that reported[3] for the C_{43} ketone from tubercle bacillus. However, there appeared to be a discrepancy in the assignment of the position of the saturated unit.

Table I. Partial Mass Spectrum of C_{43} Ketone (I) Resulting from Photooxygenation of MK-9 (II, H_2)

M − (69 + 68*n*) series			(69 + 68*n*) series		
m/e	*n*	Rel abundance	*m/e*	*n*	Rel abundance
604		3.5	409	5	0.9
535	0	1.0	341	4	1.0
467	1	2.0	273	3	1.2
399	2	2.4	205	2	1.7
331	3	1.4	137	1	23
263	4	5.0	69	0	100
195	5	0			

The main fragmentation pattern in the high mass region for this type of polyisoprenoid compound reflects the successive loss of units of mass 68, due to diallylic cleavage, resulting in a series of peaks of *m/e* [M − (69 + 68*n*)] for $n = 0$–4, together with two minor series resulting from *m/e* [M − (15 + 68*n*)] and [M − (43 + 68*n*)]. Another important but less prominent series, *m/e* (69 + 68*n*) for $n = 0$–5, also is observed. The absence of a peak at *m/e* 195, due to diallylic

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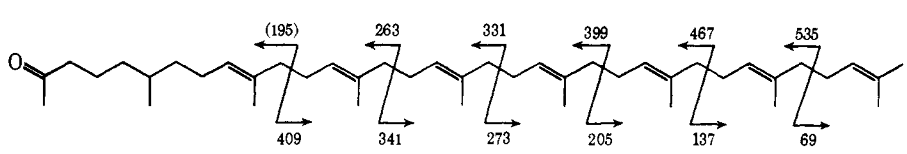
* Address correspondence to this author.

(1) Supported in part by Grant No. AM 13688 from the National Institutes of Health, U. S. Public Health Service.

(2) C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, **91**, 731 (1969).

(3) L. Coles and N. Polgar, *J. Chem. Soc. C*, 2376 (1968).

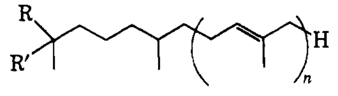
(4) (a) K. J. I. Thorne and E. Kodicek, *Biochem. J.*, **99**, 123 (1966); (b) Y. Higashi, J. L. Strominger, and C. C. Sweeley, *Proc. Natl. Acad. Sci. U. S.*, **57**, 1878 (1967).



I, mol wt 604

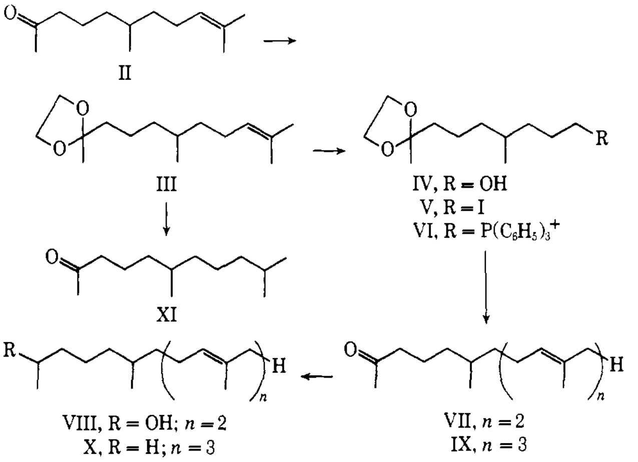
cleavage, in the main series for these two ketones indicated that the saturated isoprene unit was second from the keto group, and not third as suggested by Coles and Polgar.[3]

On the other hand, the second series (69 + 68*n*), *n* = 0–5, suggested that the first unit is saturated. Careful degradation[2] of the ketone from photooxygenation of MK − 9 (II, H_2) established that in fact it was the first unit that was saturated, contrary to the structure assigned on the basis of the frequently used [M − (69 + 68*n*)] series. Since this type of mass spectral data is being increasingly used as the sole basis for assigning structures to important biological compounds it was considered of interest to explain this anomaly; hence syntheses and mass spectral studies of model compounds of types A, B, and C were undertaken.



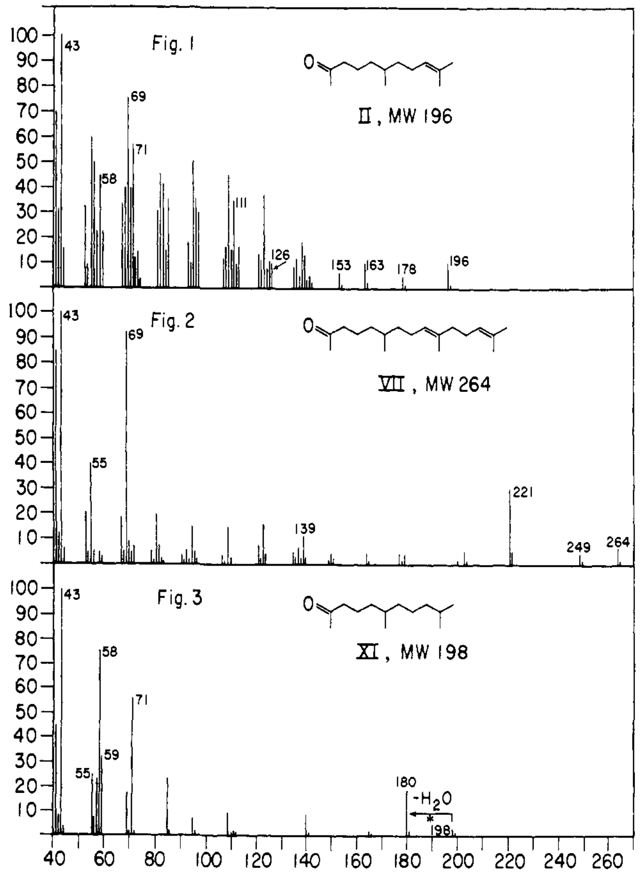
A, R, R' = ═O
B, R = H; R' = OH
C, R = R' = H

Syntheses. The various model isoprenoids were all prepared from the common intermediate 6,10-dimethyl-9-undecen-2-one (II) which was prepared from citronellol[5] *via* the bromide and condensation with ethyl acetoacetate.[6] Protection of this ketone as its ethylene ketal III followed by ozonolysis and reduction gave the ketal alcohol IV which was converted to iodide V *via* the tosylate and thence to phosphonium salt VI. The action of butyllithium on phosphonium salt VI generated the ylide, and reaction with 6-methyl-5-hepten-2-one in the one case and with geranylacetone in the other gave ketones VII and IX, respectively, after hydrolysis of the ethylene ketal. Both compounds were obtained as cis–trans mixtures at the new double bond and were separated cleanly by glpc.



The alcohol VIII was prepared by borohydride reduction of ketone VII, and hydrocarbon X was formed by the action of borohydride on the tosylhydrazone of ketone IX. Finally, the saturated ketone XI was prepared from unsaturated ketal III by hydrogenation followed by hydrolysis.

Mass Spectra. The mass spectral data[7] are presented in Tables I and II and Figures 1–5.



Figures 1, 2, and 3. Mass spectra of 6,10-dimethyl-9-undecen-2-one (II, Figure 1), *trans*-6,10,14-trimethyl-9,13-pentadecadien-2-one (VII, Figure 2), and 6,10-dimethylundecan-2-one (XI, Figure 3).

Table II. High-Resolution Mass Spectra of Some Isoprenyl Ketones: 6,10-Dimethyl-9-undecen-2-one (II), 6,10,14-Trimethyl-9,13-pentadecadien-2-one (VII), and 6,10,14,18-Tetramethyl-9,13,17-nonadecatrien-2-one (IX)

II ($C_{13}H_{24}O$)		VII ($C_{18}H_{32}O$)		IX ($C_{23}H_{40}O$)	
Peak *m/e*	Composition	Peak *m/e*	Composition	Peak *m/e*	Composition
196	$C_{13}H_{24}O$	264	$C_{18}H_{32}O$	332	$C_{23}H_{40}O$
178	$C_{13}H_{22}$	249	$C_{17}H_{29}O$	317	$C_{23}H_{37}O$
163	$C_{12}H_{19}$	221	$C_{15}H_{25}O$	289	$C_{20}H_{33}O$
153	$C_{10}H_{17}O$	139	$C_9H_{15}O$	277	$C_{19}H_{33}O$
141	$C_9H_{17}O$	43[b]	C_3H_7	263	$C_{18}H_{31}O$
139	$C_9H_{15}O$		C_2H_3O	137	$C_{10}H_{17}$
126[a]	C_9H_{18}			71	C_4H_7O
	$C_8H_{14}O$			69	C_5H_9
111	$C_7H_{11}O$				
71	C_4H_7O				

[a] 25% C_9H_{18}, 75% C_8H_{14}. [b] 10% C_3H_7, 90% C_2H_3O.

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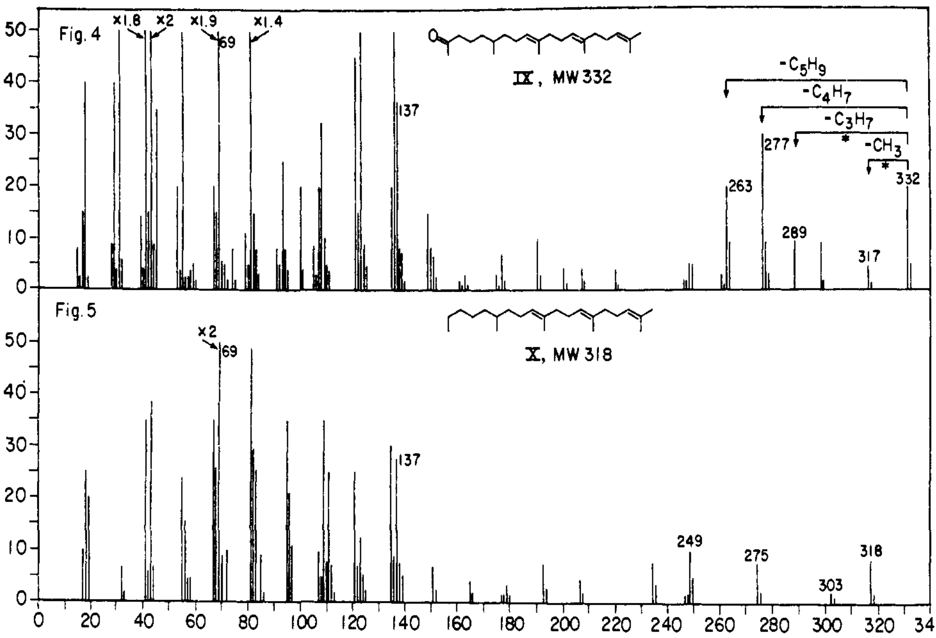
(5) The citronellol was a kind gift from Givaudan Corp.

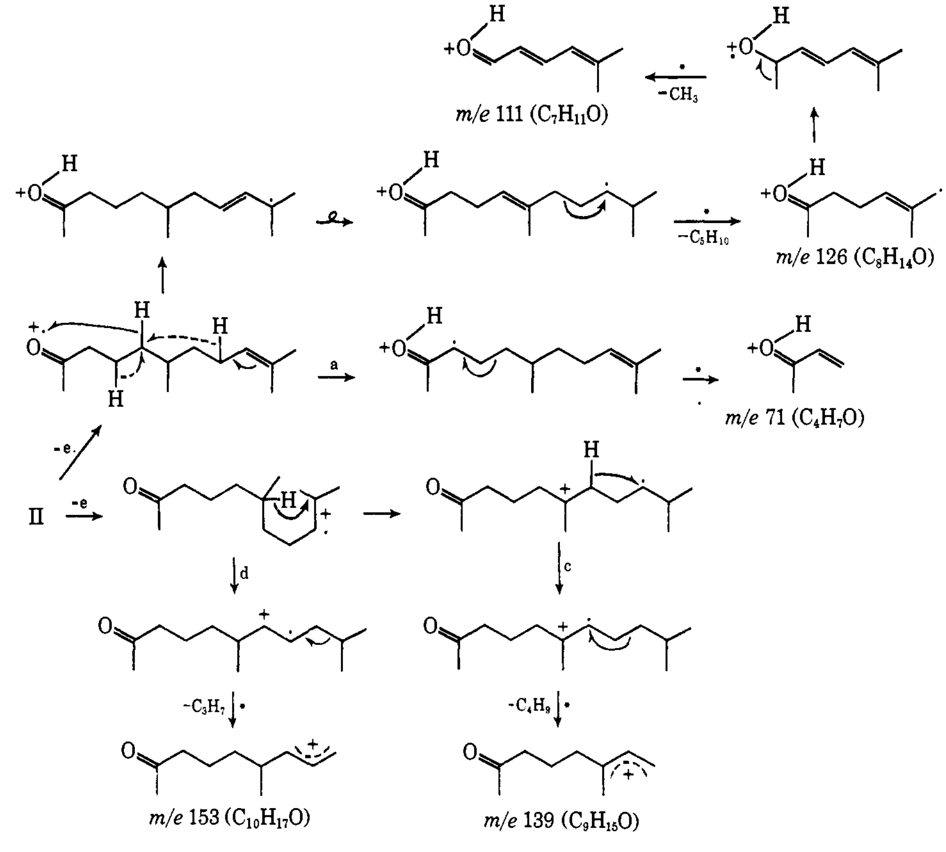
(6) R. Azerad and M. O. Cyrot, *Bull. Soc. Chim. Fr.*, 3740 (1965).

(7) We are indebted to Dr. Charles W. Koch and the Analytical Laboratory, U.C., Berkeley, for the mass spectral data.



Figures 4 and 5. Mass spectra of *trans*-6,10,14,18-tetramethyl-9,13,17-nonadecatrien-2-one (IX, Figure 4) and *trans*-2,6,10,14-tetramethyl-2,6,10-nonadecatriene (X).

Scheme I



6,10-Dimethyl-9-undecen-2-one (II). The important fragments in the mass spectrum (Figure 1) of this C_{13} ketone in which the first isoprenoid unit is saturated and the second unsaturated are *m/e* 196 (M^+), 178, 163, 153, 141, 126, and 111. The low mass region is abundant with masses arising from α cleavage (43), McLafferty rearrangement (58),[8] allylic cleavage (69), and "γ cleavage + 1" (71).[9,10] Examination of the origin of masses 178, 153, 139, and 126, using the technique[11] of decoupling the ion acceleration on the CEC-21-110B spectrometer for metastable spectra, indicated that all these fragments originated from the molecular ion. The mass 163 arises from the two masses 196 and 178, while the mass 111 comes directly from the mass 126. These data together with exact mass measurements

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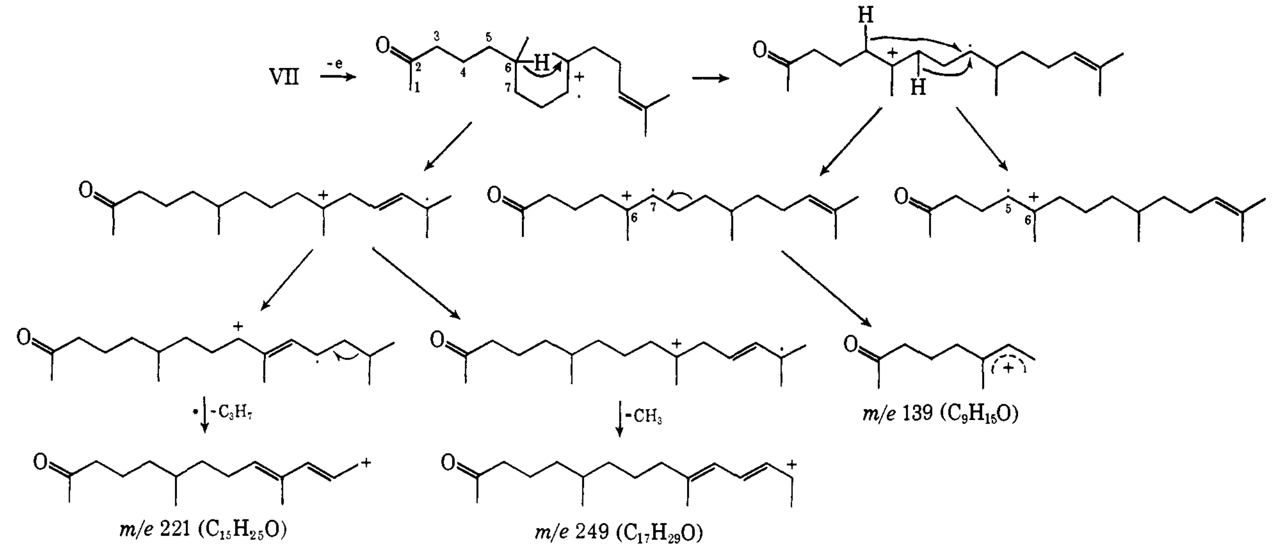
(8) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(9) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 160 (1968).

(10) A. N. H. Yeo and D. H. Williams, *ibid.*, **91**, 3582 (1969).

(11) (a) T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967); (b) J. H. Markgraf and C. W. Koch, *J. Heterocycl. Chem.*, **7**, 235 (1970).

Scheme II

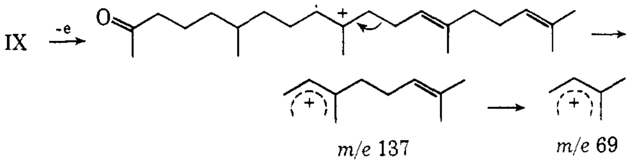


(Table II) support the fragmentation pattern proposed in Scheme I. The data clearly reflected double bond migration (pathways c and d) after ionization, but before fragmentation, arising from 1,2-hydrogen shifts[12] and also longer, energetically favorable 1,5-hydrogen[13] shifts.

6,10,14-Trimethyl-9,13-pentadecadien-2-one (VII). For this C_{18} ketone in which the first of the three isoprene units is saturated, the main peaks in the high mass region are *m/e* 264 (M^+), 249 (M − 15), and 221 (M − 43). The low mass region shows prominent fragments at *m/e* 41, 43, 55, and 69 (Figure 2). Absence of a *m/e* 195 peak, whose presence would be anticipated due to diallylic cleavage, again reflected double bond migration. The low ion current carried by the two fragments *m/e* 58 (4%) and 71 (5%), arising from β cleavage with abstraction of a γ-hydrogen of the methyl ketone (McLafferty rearrangement)[8] and "γ cleavage + 1" processes,[9,10] respectively, indicated that the γ-hydrogen was not readily available for such migration. For a large number of methyl ketones studied[14a] and for the C_{13} ketone (II), the fragment *m/e* 58 carries *ca.* 40% of the ion current; however, in isoprenoid ketones (and for example 4-methylhept-6-en-3-one[14b]), this fragment *m/e* 58 carries much less of the ion current. The only γ-hydrogen available is vinylic; hence such abstraction of a γ-hydrogen with expulsion of an allene fragment clearly is not a favorable process. Furthermore, in a model compound, 6,10-dimethylundecan-2-one (XI), relative abundances of *m/e* 58 and 71 were 75 and 48% (Figure 3),[15] respectively.

A fragmentation mode for C_{18} ketone VII is presented in Scheme II. Of the two positions (C-5 and C-7) adjacent to the trisubstituted C-6 in the saturated first isoprene unit, the contribution arising from double bond migration to the 5,6 position could be large since the ion current carried by the two fragments *m/e* 58 and 71 is low, while the contribution arising from the migration into the 6,7 position is also present, leading to the mass 139. This together with the high-resolution data (Table II) again supported double bond migration, after ionization but before fragmentation, as indicated in Scheme II. Such 1,2- and 1,5-hydrogen migrations are enhanced in isoprenoids whenever there is a vacant (saturated) isoprene unit present in the molecule; furthermore, we have illustrated the complexity that can arise as the result of several double bond migrations.

6,10,14,18-Tetramethyl-9,13,17-nonadecatrien-2-one (IX). The mass spectrum of the C_{23} ketone IX in which the first of the four isoprene units is saturated is presented in Figure 4 and Table II. It lends support to the observations made above. As expected, the spectrum shows the fragment resulting from diallylic cleavage at *m/e* 263 with loss of a C_5H_9 unit, but the fragment resulting from the second diallylic cleavage which should have been at *m/e* 195 was absent. Again the relative abundances of fragments *m/e* 58 (4%) and 71 (6%) were low. These results arise due to migration of the double bond from the 9,10 position in the second isoprene unit to the other trisubstituted position (C-6) in the first isoprene unit *via* a 1,5-hydrogen shift. The other diallylic fragmentation pattern of the C_{23} ketone IX before migration, which is also observed for the C_{43} ketone I, then could be very useful in assigning the position of the saturated isoprene unit in such systems.



Participation of the ketonic function in any fashion in enhancing the migration of the double bond from the second isoprene unit was ruled out since *all-trans-2,6,10,14-tetramethyl-2,6,10-nonadecatriene* (*X*) showed a similar type of migration. This hydrocarbon, consisting of a propyl group followed by a saturated isoprene unit and then three unsaturated isoprene units, shows the

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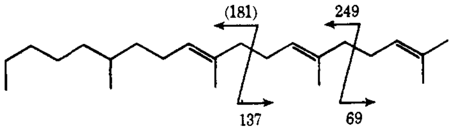
[12] (a) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, 31, 115 (1966); (b) B. J. Millard and D. F. Shaw, *J. Chem. Soc. B*, 664 (1966).

[13] After completion of this work, a report [A. F. Gerrard and C. Djerassi, *J. Amer. Chem. Soc.*, 91, 6008 (1969)] elegantly showed the double bond mobility upon electron impact due to 1,2, 1,3, and 1,5 shifts in 1-phenylheptenes, in which the phenyl nucleus greatly influences the fragmentation pattern.

[14] (a) A. G. Sharkey, Jr., J. L. Shultz, and R. A. Friedel, *Anal. Chem.*, 28, 934 (1956); (b) L. Ahlquist, R. Ryhage, E. Stenhagen, and E. von Sydow, *Ark. Kemi*, 14, 211 (1959).

[15] The spectrum showed a large $M^+ - 18$ (18%) peak for the loss of water. Recently, A. N. H. Yeo and D. H. Williams, [*Org. Mass Spectrom.*, 2, 331 (1969)] also noted considerable loss of water from aliphatic ketones having more than seven carbon atoms in the chain.

first diallylic fragment at *m/e* 249 (10%), but the second diallylic fragment at *m/e* 181 was totally missing (Figure 5). The other fragments arising from 1,2-allylic hydrogen migration, *m/e* 303 (25%) and 275 (10%), were present. The second series (69 + 68*n*) was present as seen from the peaks at *m/e* 137 and 69.



X

The C_{18} alcohol VIII also shows a strong peak at *m/e* 69, but the diallylic fragment at *m/e* 197 is absent as in the case of the C_{18} ketone. The other fragment due to double bond mobility, $M^+ - 43$, *m/e* 223.2048 ($C_{15}H_{27}O$), is also present. These results clearly indicate that spectra of isoprenyl alcohols as well must be interpreted with the same caution.

The mass spectra discussed here were determined on all-trans compounds but the corresponding cis isomers also showed similar fragmentation patterns. Our data indicate that there are considerable 1,2 and 1,5 shifts and double bond migrations in isoprenoids; hence the assignment of position to a saturated unit based only on mass spectral evidence should be made with great caution. The series [M − (69 + 68*n*)] which has usually been relied upon would invariably lead to the wrong conclusion when such a saturated unit is present because of double bond migration. However, assignments made with the aid of the series (69 + 68*n*) should be more reliable when the first unit is saturated. However, if the saturated unit is elsewhere in the chain, this technique also should be applied with caution. In this regard, it is now evident that the structure assigned to the C_{55} alcohol, bactoprenol,[4a] based on mass spectral interpretations is unreasonable since a loss of 70 mass units has been related to the presence of a saturated isoprene unit.

Experimental Section[16]

6,10-Dimethyl-9-undecen-2-one Ethylene Ketal (III). 6,10-Dimethyl-9-undecen-2-one (II) was prepared from citronellol[5] as reported[6] and 24 g (0.14 mol) was dissolved in 200 ml of dry benzene. Ethylene glycol (19.2 g, 3 mol) and a trace of *p*-toluenesulfonic acid were added and the mixture was stirred and refluxed under a nitrogen atmosphere, using a Dean–Stark trap to remove water. After 8 hr the solution was poured into ether and washed with sodium carbonate solution and then with water. The organic phase was dried over sodium sulfate and evaporated to give 27 g (92%) of ethylene ketal III: nmr δ 5.1 (br, t, 1, C=C*H*R), 3.9 (s, 4, OCH_2CH_2O), 1.2–2.0 (m, 11, CH_2), 1.60–1.66 (br, 6, C=CCH_3), 1.3 (s, 3, $\geqslant$$CCH_3$), 0.88 (d, 3, >CHC$H_3$); mass spectrum *m/e* 204 (M^+, 22), 87 (100).

Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.9; H, 11.6. Found: C, 74.9; H, 11.7.

9-Hydroxy-6-methylnonan-2-one Ethylene Ketal (IV). A solution of 24 g of ethylene ketal III in 150 ml of methanol was cooled to −75°. Ozone, 0.163 mmol/min, was bubbled through the solution until no more ozone was taken up after which the solution was flushed with oxygen and then with nitrogen and allowed to reach room temperature. It then was added dropwise to a solution at 5° of 7.7 g of sodium borohydride and 6.4 g of sodium hydroxide dissolved in 50 ml of methanol and 20 ml of water. The mixture was stirred at 25° for 10 hr and then refluxed for 20 min. Removal of methanol gave an oily mixture which was chromatographed on silica gel using 10% ethyl acetate in benzene as eluent and gave 16 g (74%) of alcohol ketal IV: glpc retention time 28 min, 11 sec, 175°; nmr δ 3.9 (s, 4, OCH_2CH_2O), 3.6 (br, 1, OH), 3.5 (t, 2, HOCH_2), 1.2–1.8 (m, 11, CH_2), 1.3 (s, 3, $\geqslant$$CCH_3$), 0.88 (d, 3, >CH–C$H_3$); mass spectrum *m/e* 216 (M^+, 40), 87 (100).

Anal. Calcd for $C_{12}H_{24}O_3$: C, 66.5; H, 11.2. Found: C, 66.6; H, 11.2.

9-Iodo-6-methylnonan-2-one Ethylene Ketal (V). A solution of alcohol ketal IV (10.4 g) dissolved in pyridine (30 ml) was stirred at 5° and to it was added *p*-toluenesulfonyl chloride (15 g). The reaction mixture was stirred for 4 hr at room temperature and then poured onto ice water and extracted with methylene chloride. Evaporation of the organic phase *in vacuo* until the odor of pyridine could not be detected was followed by solution in 100 ml of dry acetone and addition of sodium iodide (15 g). The reaction mixture then was stirred for 2 hr and stored in the dark for 10 hr. Dilution with water and extraction into methylene chloride gave an oil after removal of solvent and distillation gave 11.59 g (74%) of iodide ketal V, bp 70–72° (2 mm); nmr δ 3.9 (s, 4, OCH_2CH_2O), 3.2 (t, 2, ICH_2), 1.2–1.8 (m, 11, CH_2), 1.3 (s, 3, $\geqslant$$CCH_3$), 0.89 (d, 3, >CH–C$H_3$).

Anal. Calcd for $C_{12}H_{23}O_2I$: C, 44.2; H, 7.0; I, 39.0. Found: C, 44.6; H, 6.6; I, 39.0.

Ketal Phosphonium Salt VI. Sublimed triphenylphosphine, 2.4 g, and 3 g of ketal iodide V were mixed and heated to 80° with 2 ml of benzene. After 6 hr, the reaction mixture was cooled to room temperature and stirred with anhydrous ether. Solvent was removed and the resulting solid phosphonium salt VI was dried at 80° (1 mm) for 10 hr.

***trans*-6,10,14-Trimethyl-9,13-pentadecadien-2-one (VII).** The ketal phosphonium salt VI (2.8 g) was dissolved in dry DMSO (40 ml) and the solution was stirred under a nitrogen atmosphere. Butyllithium (3 ml, 1.6 *M*) was added dropwise, the solution was stirred for 1.5 hr, 6-methyl-5-hepten-2-one (640 mg) was then added dropwise, and the reaction mixture was stirred for 24 hr. Addition of water and extraction with hexane gave crude product which was chromatographed on silica gel with 3% ethyl acetate in benzene as eluent. The cis–trans mixture of 450 mg of ketals thus obtained was dissolved in acetone (10 ml), dilute phosphoric acid (2 ml) was added, and the solution was stirred for 4 hr. Addition of water and extraction with ether gave a mixture of the *cis,trans*-ketones VII which were separated by glpc at 200°; *cis*-ketone VII, retention time 45 min 7 sec; *trans*-ketone VII, retention time, 50 min 45 sec; mass spectrum *m/e* 264.2439 (M^+, $C_{18}H_{32}O$) for both cis and trans isomers.

***trans*-6,10,14,18-Tetramethyl-9,13,17-nonadecatrien-2-one (IX).** The ketal phosphonium salt VI (2.8 g) in dry DMSO (40 ml) was stirred at room temperature, butyllithium in hexane (7 ml, 1.6 *M*) was added dropwise, the solution was stirred for 1.5 hr, *trans*-geranylacetone[17] (920 mg) was then added dropwise, and the reaction mixture was stirred for 24 hr. Addition of water and extraction with hexane gave crude product which was chromatographed on silica gel using 3% ethyl acetate in benzene to elute the mixture of ketals. Treatment with dilute phosphoric acid (5 ml) in acetone (15 ml) for 5 hr, removal of solvent, addition of water, and extraction into methylene chloride gave a mixture of Δ^9-*cis*,*trans*-Δ^{13}-*trans*-ketones IX which were separated by glpc at 240°: Δ^9-*cis*-Δ^{13}-*trans*-ketone IX, retention time 45 min 35 sec; *all-trans*-ketone IX, retention time 51 min 18 sec; mass spectrum *m/e* 332.3022 (M^+, $C_{23}H_{40}O$) for both isomers.

***trans*-6,10,14-Trimethyl-9,13-pentadecadien-2-ol (VIII).** A mixture of *cis,trans*-ketones VII (50 mg) dissolved in methanol (2 ml) was added to a well-stirred solution of sodium borohydride (48 mg) in methanol (12 ml) at 0°. The reaction mixture was stirred for 6 hr, decomposed by addition of water, and then extracted with ether. Removal of solvent gave 35 mg (69%) of the cis,trans mixture of alcohols VIII which was separated by glpc at 180°: *cis*-alcohol VIII, retention time 31 min 18 sec; *trans*-alcohol VIII, retention time 37 min 21 sec; mass spectrum *m/e* 226.5283 (M^+, $C_{18}H_{34}O$) for both isomers.

***trans*-2,6,10,14-Tetramethyl-2,6,10-nonadecatriene (X).** *all-trans*-Ketone IX (66 mg) and tosylhydrazine (35 mg) were refluxed

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(16) Microanalyses were performed by the Analytical Laboratory, University of California, Berkeley; glpc analyses were done on an Aerograph Model A-90-P using a 10 ft × 1/4 in. column packed with 30% QF-1 on firebrick at temperatures ranging from 175 to 240° and a helium flow rate of 60 cc/min. Mass spectra were recorded on M66 (Varian), CEC 21-103C, and CEC 21-110B instruments at 70 eV; nmr spectra are reported in $CDCl_3$ as δ units relative to internal TMS (δ 0).

(17) O. Isler, R. Ruegg, L. Chopard-dit-Jean, H. Wagner, and K. Bernhard, *Helv. Chim. Acta*, **39**, 897 (1956).

for 4 hr in methanol (25 ml) under a nitrogen atmosphere at which time all of the ketone had been converted to tosylhydrazone as shown by tlc. The solution was concentrated to 5 ml, added at 0° to $NaBH_4$ (40 mg) in methanol (10 ml), stirred for 6 hr at room temperature, and heated at reflux for 1 hr. Removal of solvent and glpc at 170° gave *all-trans*-hydrocarbon X, retention time 18 min 18 sec; mass spectrum *m/e* 318.3285 (M^+, $C_{23}H_{42}$).

6,10-Dimethylundecan-2-one (XI). Ketal III (100 mg) was dissolved in 25 ml of ethanol and hydrogenated over 20 mg of 5% Pd/C. Filtration, addition of dilute phosphoric acid, evaporation of the ethanol, addition of water, extraction into ether, and evaporation of the ether gave saturated ketone XI.

Anal. Calcd for $C_{13}H_{26}O$: C, 78.4; H, 13.3. Found: C, 78.7; H, 13.2.

Synthesis and Polymerization of 1-Bicyclobutanecarbonitriles

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Abstract: 1-Bicyclobutanecarbonitrile and its bridge deuterated, 2,2-dimethyl, and 2,2,4,4-tetramethyl derivatives have been synthesized *via* base-induced elimination reactions of the corresponding 3-chlorocyclobutanecarbonitriles or 3-cyanocyclobutyl benzenesulfonates. They readily undergo free-radical or anionic homopolymerizations to form high polymers containing 1,3-cyclobutane links in the chain. The tetramethyl polymer also contains ketenimine links, arising from propagation through N and caused by steric hindrance. Facile copolymerizations with the usual vinyl monomers also occurred, again incorporating cyclobutane rings into the polymer chain. The nature of the substituents at the 3 position determined their effect on polymerizability. The 3-methyl- and 2,2,3-trimethyl-1-bicyclobutanecarbonitriles did not polymerize well with radicals, but anionic polymers could be made. The 3-phenyl derivative also did not polymerize well. On the other hand, 1,3-bicyclobutanedicarbonitrile and 3-chloro-1-bicyclobutanecarbonitrile polymerized and copolymerized well under radical or anionic conditions. 1-Bicyclobutanecarbonitrile dimerized in solution at 80° and trimerized at 150°.

Ring-opening polymerization of compounds containing cyclopropane rings has been explored briefly in the past. Cyclopropane itself has not been reported to polymerize well, and 1,1-dimethylcyclopropane[2] and isopropylcyclopropane[3] give only low polymers. Ketley,[4] Takahashi,[5] Lishanskii,[6] and their colleagues have shown that 1,1-dichloro-2-vinylcyclopropane polymerizes. Several bicyclic compounds containing three-membered rings also undergo polymerization. Pinazzi[7] has described low polymers from bicyclo[*n*.1.0]alkanes and spiropentane is claimed to polymerize.[8] Of direct interest in the present connection, Wiberg and coworkers[9] have shown that methyl and ethyl 1-bicyclobutanecarboxylate polymerize when left at room temperature. This series of articles will explore the synthesis and polymerization of selected bicyclic monomers and show that polymerization of bicyclo[*x*.*y*.0] compounds with opening of a strained single bond constitutes a new area of polymer chemistry. The present article deals with 1-bicyclobutanecarbonitriles.

Synthesis of Monomers. Convenient access to most of the required compounds was provided by cycloaddition of allene or 1,1-dimethylallene to acrylonitrile.[10] Conversion of the resulting methylenecyclobutanecarbonitriles to the corresponding 3-methyl-1-bicyclobutanecarbonitriles has already been described by Blanchard and Cairncross.[11] Alkyl groups at the reaction center usually diminish polymerizability, so we wished to prepare the corresponding compounds lacking the 3-methyl substituent. We used oxidation with sodium metaperiodate–osmic acid[12] for 3-methylenecyclobutanecarbonitrile, and the more reactive ozone for the hindered and less-soluble 2,2-dimethyl compound[10] to obtain 3-oxo-1-cyclobutanecarbonitrile and 2,2-dimethyl-3-oxo-1-cyclobutanecarbonitrile. Exhaustive methylation of either of these compounds using sodium hydride and methyl iodide in *N*-methylpyrrolidone solution gave 2,2,4,4-tetramethyl-3-oxocyclobutanecarbonitrile. Reduction of the three ketones by sodium borohydride in water gave the corresponding alcohols in good yields. 3-Hydroxycyclobutanecarbonitrile was smoothly converted by thionyl chloride to 3-chlorocyclobutanecarbonitrile,[13] while the methylated hydroxynitriles were converted to the corresponding benzenesulfonates using benzenesulfonyl chloride in

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