Deamination of 25-*d*.—The deuterated analog was treated with nitrous acid under the same conditions. From 1.23 g of amine hydrochloride was obtained 0.645 g of crude alcohols. The nmr spectrum showed an olefinic proton absorption centered at τ 5.81. Clearly, the upfield proton of the double band had disappeared. Since the relative areas of the carbinol proton and the olefinic proton were equal, one can conclude that the tricyclo-[3.2.1.$0^{2,7}$]octanol-4 is specifically labeled at the carbinol position.

Acetolysis of *p*-Nitrobenzoate 24.—A solution of 0.81 g of **24** in 18 ml of glacial acetic acid which also contained 0.3 g of sodium acetate was heated at reflux for 110 hr. The resulting solution was diluted with 150 ml of ice water followed by neutralization with sodium carbonate. Extraction with ether and washing of the extracts with sodium carbonate solution and water gave a solution from which 0.54 g of an oil was obtained on evaporation. The nmr spectrum revealed the presence of a small amount of unreacted *p*-nitrobenzoate (*ca.* 15%) and peaks owing to the acetate of **14**. Gas chromatography revealed only one volatile product having the same retention time as the acetate of **14** (NMP column at 120°).

Acetolyses of 23.—Acetolyses of **23** were effected at several temperatures by treatment of **23** (3.5 g, 0.012 mole) with 1.0 g of sodium acetate in 60 ml of glacial acetic acid containing 1 drop of acetic anhydride. The products were isolated as described above and analyzed as acetates on a 12-ft Carbowax 20 M column at 190°.

At Reflux (2.5 Hr).—A small amount of a hydrocarbon was isolated by collection of a peak of low retention time. The infrared spectrum was essentially that reported by Grob and Hastynek[24] for tricyclo[3.2.1.$0^{2,7}$]octene-3. The only esters detected were the acetates of *exo*-bicyclo[3.2.1]oct-2-en-7-ol and tricyclo[3.2.1.$0^{2,7}$]octanol-4 in a 2.6:1 ratio. These assignments were confirmed by comparison of infrared and nmr spectra of collected samples. At 80° (7 hr) acetates of **14** and **6** were obtained in a 2.4:1 ratio. At 25° (48 hr), a 1.1:1 ratio of the acetates of **14** and **6** was detected.

Acetolysis of 23-*d*.—The deuterated analog was solvolyzed similarly at 50° for 3 hr. The two acetate esters were formed in a ratio of one and one-half parts unsaturated ester (of **14-*d***) to one part tricyclic ester (of **6-*d***). The nmr spectrum of the ester of **14-*d*** was virtually identical with that of the protiated system, *i.e.*, no specific region appeared diminished in intensity.

The nmr spectrum of the tricyclic ester was also very similar to that of the undeuterated material. The ratio of the area of the carbinol proton at τ 5.5 to that of the upfield region was *ca.* 1:27.5 which indicates that about 0.5 proton was now present at the carbinol position.

(24) C. A. Grob and J. Hastynek, *Helv. Chim. Acta*, **46**, 1676 (1963).

Registry No.—**4**, 10058-22-7; phenylthiourea derivative of **4**, 10027-42-6; picrate of **4**, 10027-43-7; **5**, 10027-44-8; acetate of **5**, 10027-45-9; **7**, 10027-46-0; *p*-nitrobenzoate of **7**, 10027-47-1; **26**, 10027-48-2; **25**, 10039-10-8; phenylthiourea of **25**, 10027-49-3; **25-*d***, 10027-50-6; **9**, 10039-11-9; *p*-nitrophenylhydrazone of **9**, 10027-51-7; **6**, 10027-52-8; acetate of **6**, 10027-53-9; 3,5-dinitrobenzoate of **6**, 10027-54-0; **15**, 10027-55-1; **14**, 10027-56-2; *p*-nitrobenzoate of **14**, 10027-57-3; acetate of **14**, 10027-58-4.

Acknowledgments.—We are deeply indebted to the National Institutes of Health (RG 8701) for financial support of this work. J. A. B. is grateful to the same agency for a fellowship (1-F1-GM-19,553-01).

Mass Spectra of Certain Cycloalkylacetates and of Related Unsaturated Esters[1]

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Mass spectra are reported for five saturated esters and four unsaturated ones. The fragmentation patterns are interpreted in terms of mechanisms of fragmentation and the relationships of ion abundance to structural features. Starting material for synthesis of seven of the esters was α-campholenic acid (**1**). Hydrogenation of methyl α-campholenate yielded the saturated α-campholanic ester (**5**), which was in turn converted to the corresponding α,β-unsaturated ester (**24**). Rearrangement under suitable conditions of the α-campholenate yielded methyl β-campholenate (**4**) which was hydrogenated to yield the *cis*- and *trans*-β-campholanates, in turn converted to the α,β-unsaturated ester (**25**). Methyl 3-ethyl-3-methylcyclopentylacetate was synthesized from 3-ethyl-3-methylcyclopentanone, while methyl 2,6-dimethylcyclohexylacetate was synthesized from 2,6-dimethylcyclohexanone.

Although there have been published extensive investigations of the behavior of polycyclic compounds on fragmentation in an electron beam, the mass spectra of monocyclic compounds have received relatively little attention. Certain monocyclic terpenes have been examined,[2,3] as have some simple monocyclic hydrocarbons,[4] but examination of derivatives of monocyclic carboxylic acids appears to be limited to a previous investigation in this laboratory.[5] In connection with establishing the structure of a cyclopentylacetic acid isolated from a California petroleum,[6] basic information concerning the mass spectra of such structures was required. The present report concerns the mass spectra of the methyl esters of five saturated acids and four unsaturated acids, chosen to give information about several structural features.

Synthesis of Required Structures

Structures containing the polymethylcyclopentane ring with a quaternary carbon were approached *via* α-campholenic acid (**1**, 2,2,3-trimethyl-3-cyclopentenylacetic acid). This acid has been secured, together with several other compounds, by subjecting camphor oxime to the conditions of the Beckmann rearrangement;[7] however, Sauers[8] has reported that alkaline fusion of sodium 10-camphorsulfonate[9] is a superior method for preparation of α-campholenic acid. In our hands, the alkaline fusion gave a satisfactory yield of α-campholenic acid; however, this acid changed rapidly on distillation, or slowly on standing at room tem-

(1) This investigation was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

(2) R. Ryhage and E. von Sydow, *Acta Chim. Scand.*, **17**, 2023 (1963).

(3) A. F. Thomas and B. Willhalm, *Helv. Chim. Acta*, **47**, 475 (1964).

(4) P. Natalis, *Bull. Soc. Roy. Sci. Liège*, **27**, 201 (1958); **29**, 94 (1960); *Bull. Soc. Chim. Belges*, **69**, 519 (1960).

(5) J. Cason and K.-L. Liauw, *J. Org. Chem.*, **30**, 1763 (1965).

(6) J. Cason and A. I. A. Khodair, *ibid.*, **31**, 3618 (1966).

(7) J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. 2, 2nd ed, Cambridge University Press, London, 1949, pp 437–443.

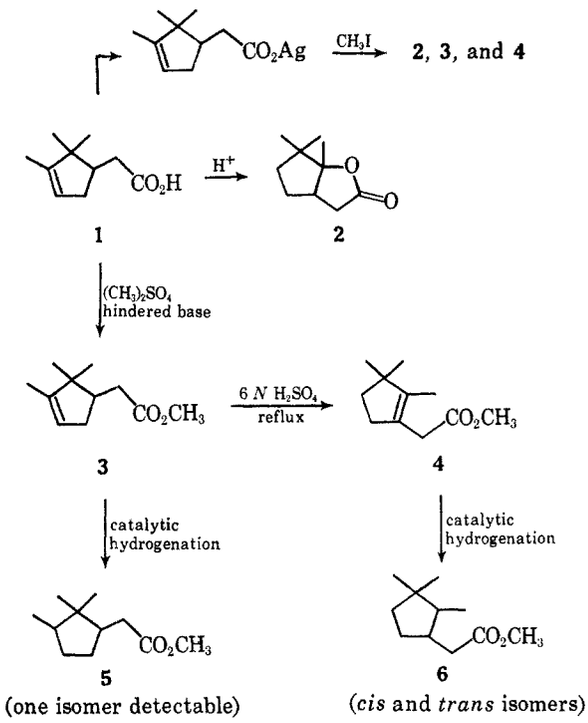
(8) R. R. Sauers, *J. Am. Chem. Soc.*, **81**, 925 (1959).

(9) J. Bredt, J. Houben, and P. Levy, *Ber.*, **35**, 1290 (1902).

perature,[10] to dihydro-β-campholenolactone (2). This facile rearrangement is ascribed to traces of sulfurous acid which remained in the α-campholenic acid, even after efforts to wash it out.

It was assumed, initially, that methyl α-campholenate (3) could be obtained without rearrangement by conversion of the silver carboxylate to the methyl ester; however, this procedure yielded the three compounds shown in Scheme 1, as well as 10% of a fourth, more volatile compound, which was probably campholene. The principal product (53.5% of total) was the lactone, 2, while the desired methyl α-campholenate was only 8.5% of the total. The cause of rearrangement under these conditions is not known; however, traces of hydrogen iodide formed during the reaction may be responsible. This acid is represented[7] as the best catalyst for the rearrangement.

SCHEME I



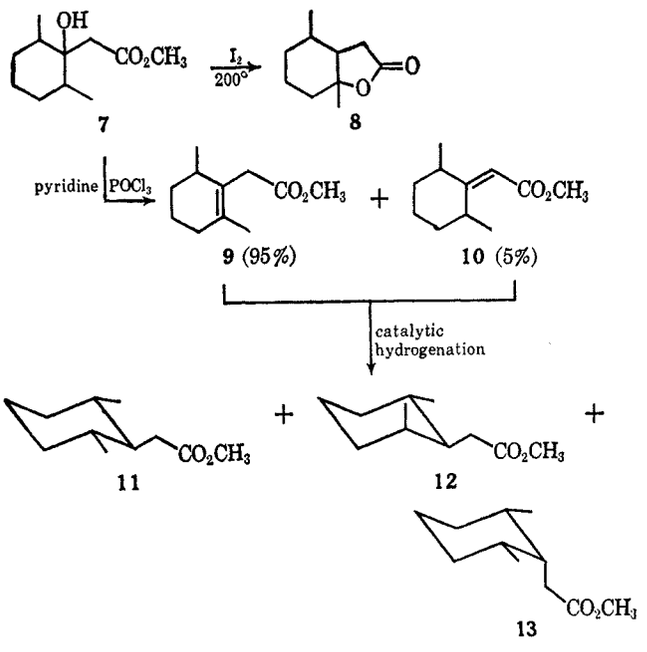
Methyl α-campholenate (3) was readily obtained in a high yield and a pure state by utilization of Stodola's base-catalyzed esterification.[11] The commercially available tris-2-hydroxypropylamine proved to function well as the hindered base. The saturated ester, methyl α-campholanate (5), obtained by hydrogenation with either platinum or palladium catalyst,[12] could not be separated into diastereoisomers by gas chromatography. The *cis* geometry is most probable, but no effort was made to establish the geometry, for isomers of this type would be expected to give the same mass spectra.[13]

Although mineral acids catalyze conversion of α-campholenic acid to lactone 2, the amide or nitrile is reported[7] to yield the corresponding β isomer. The ester also proves subject to facile rearrangement to the β isomer (*cf.* Scheme I). The reaction product consisted of 80% of the desired methyl β-campholenate (4), 17% of lactone 2, and 3% of starting material 3. The desired ester could be purified by fractional distillation.

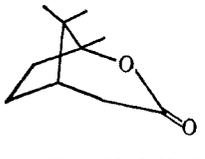
Hydrogenation of methyl β-campholenate (4) yielded the two stereoisomeric saturated esters (6), separable by gas chromatography. With platinum catalyst, expected to give a predominance of the *cis* isomer,[14] a larger amount of the ester of longer retention time resulted. With palladium catalyst, the ester of shorter retention time was predominant. A longer retention time for the *cis* isomer has previously been observed in both the cyclopentane series[6] and the cyclohexane series.[5]

Methyl 2,6-dimethylcyclohexylacetate was prepared (*cf.* Scheme II) from 2,6-dimethylcyclohexanone *via* hydroxy ester 7, which was synthesized by the Reformatsky reaction. Dehydration of this hydroxy ester by heating with iodine yielded lactone 8; how-

SCHEME II



(10) Structure 2 is assigned to the rearrangement product partly because of earlier reports[7,8] of this acid-catalyzed rearrangement, but also because a distilled and gas-chromatographed sample showed infrared absorption at 5.68 μ, which is in agreement with the γ-lactone structure. When a sample of freshly prepared α-campholenic acid was gas chromatographed on a silicone column, the collected sample showed infrared absorption above 3 μ characteristic of the hydroxyl in carboxyl, absorption at about 12.4 μ characteristic of =CH, along with *two* carbonyl bands at 5.74 μ (δ-lactone?), and 5.86 μ (carboxylic acid). Sauers[8] reported for his sample of α-campholenic acid, distilled at 0.54-mm pressure, carbonyl absorption at 5.74 μ only. Our samples of freshly prepared, unheated α-campholenic acid showed carbonyl absorption only at 5.84 μ. It seems probable that α-campholenic acid equilibrates with a δ-lactone, *via* the carbonium ion from protonation of the double bond, more rapidly than methyl migrates to lead to the more stable β-campholenic structure; however, this matter has not been further investigated by us.



(11) F. H. Stodola, *J. Org. Chem.*, **29**, 2490 (1964).

(12) It has been reported [P. Lipp, *Ber.*, **55**, 1883 (1922)] that catalytic hydrogenation of α-campholenic acid with platinum black catalyst yields exclusively the *cis* isomer, whereas hydrogenation of the amide in the same manner yields the *trans* isomer. Since stereoisomers of this type are quite unlikely to show differences in mass spectra, the stereochemical identity of our product was not investigated.

(13) W. F. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 591.

(14) S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082 (1960); **82**, 6087 (1960).

ever, a mixture of unsaturated esters **9** and **10** resulted when phosphorus oxychloride in pyridine was utilized for the dehydration. Only 5% of the exocyclic α,β-unsaturated ester resulted from the dehydration. Catalytic hydrogenation of the unsaturated ester yielded the three possible stereoisomers, **11**, **12**, and **13**, in ratios dependent on the catalyst used (*cf.* Table I).

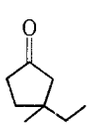
TABLE I

HYDROGENATION PRODUCTS FROM METHYL 2,6-DIMETHYLCYCLOHEXENYLACETATE

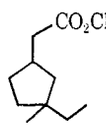
Retention time, min	Probable identity of component	—% of total, with— Pt	Pd
39.8	11	25	54
50.7	12	30	16
53.7	13	45	30

The work of Siegel and Smith[14] leads to the prediction that the component obtained in largest amount with platinum catalysis is the all-*cis* isomer, and this is consistent with the observation[5,6] that the *cis* isomer gives a longer retention time in gas chromatography. Thus, assignment of the component responsible for the 53.7-min band as isomer **13** is no doubt rather reliable. By the same reasoning, the isomer giving the shortest retention time is probably isomer **11**, with the side chain *trans* to both methyl groups; however, this assignment is less reliable, for isomer **12** differs only in having one pair of the *trans* groups not adjacent to each other. The mass spectrum was recorded only for the isomer assigned as **11**, for the *cis* and *trans* isomers of methyl 2,2,6-trimethylcyclohexylacetate gave identical mass spectra.

3-Ethyl-3-methylcyclopentanone (**14**), required for synthesis of methyl 3-ethyl-3-methylcyclopentylacetate (**15**), was obtained from β-ethyl-β-methylglutaric acid.



14



15

This acid was converted to the half-ester, which was homologated by the Arndt–Eistert procedure, and the resultant substituted adipic acid was cyclized to yield the desired ketone (**14**). Ketone **14** could be converted to ester **15** by way of either the Reformatsky reaction or by reaction with the anion of trimethyl phosphonoacetate. Each of these procedures yielded both geometric isomers of 3-ethyl-3-methylcyclopentylideneacetate. In dehydration of the Reformatsky product, it is of interest that about two-thirds of the unsaturated ester consisted of the α,β-unsaturated esters with exocyclic double bond. As expected, this is in contrast with the behavior in the cyclohexyl derivatives, wherein dehydration gave almost exclusively the endocyclic isomer (**9**), which has a tetrasubstituted double bond.

Hydrogenation of the mixture of cyclopentylidene- and cyclopentenylacetates gave a saturated ester in which stereoisomers could not be separated by gas chromatography; however, it is assumed that the two stereoisomers are present. Separation of diastereoisomers differing in such a subtle manner has previously failed in a similar structure,[6] methyl 3-ethyl-4-methylcyclopentylacetate, with the methyl and ethyl groups *trans* to each other.

Mass Spectra

Saturated Esters.—The more important ions[15] in the mass spectra of the five saturated esters appear in Table II. A considerable similarity may be noted in the spectra for the four cyclopentylacetic esters; however, striking features reveal the structures in all cases. Although the rearrangement ion, $CH_2{=}\overset{+}{C}(OH)OCH_3$, is usually the base peak in saturated esters, as is the case for the cyclohexylacetic ester in Table II, it is not the base peak for any of the cyclopentylacetic esters. Even if the ubiquitous ion of *m/e* 41 is eliminated, the rearrangement ion does not become the base peak in any of the cyclopentylacetic esters. The abundance of the rearrangement ion is especially small in the α-campholanate (**5**), which does not have a tertiary hydrogen available for elimination. This low abundance of the rearrangement ion may be ascribed to the proportionately large abundance of ions resulting from geminal substitution in the ring; however, the five-carbon ring also appears to be an important factor, for the ion of *m/e* 74 was the base peak in the spectrum of methyl 2,2,6-trimethylcyclohexylacetate.[5]

TABLE II

PARTIAL MASS SPECTRA OF METHYL ESTERS OF SATURATED $C_{10}H_{18}O_2$ ACIDS

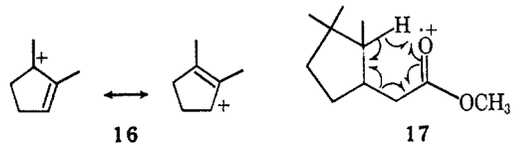
m/e (compn)[a]	*trans*-6	*cis*-6	5	15	11
41 (C_3H_5)	100	100	100	100	79
43 (C_3H_7)	31	26	26	42	36
55 (C_4H_7)	89	83	47	71	70
59 (CO_2CH_3)	21	20	19	14	17
69 (C_5H_9)	69	75	97	28	55
74 (R)	70	35	14	34	100
81 (M − R − Et)	11	10	11	96	14
83	8	13	22	9	5
84	3	12	44	3	...
95 (M − R − Me)	77	47	26	30	57
109	7	9	8	4	10
110 [M − (R + e)]	68	73	16	18	21
111 (M − $CH_2CO_2CH_3$)	85	26	4	7	60
113 (A)	35	29	2	3	6
127 (B)	0.5	6	23	...	2.5
153 (M − OMe)	7	10	9	4	5
155 (M − Et)	...	1	...	16	...
169 (M − Me)	1.1	1.6	1	1	0.5
184 (M)	0.4	0.7	5	...	2.5

[a] Composition is assigned on basis of *m/e* and interpretation of the fragmentation pattern, for which see discussion; M = molecular ion, R = rearrangement ion $CH_2{=}C(OH)OCH_3$ (74), Et = C_2H_5 (29), Me = CH_3 (15), A = $C_6H_9O_2$, **22** (*cf.* discussion), B = $C_7H_{11}O_2$, **23** (*cf.* discussion).

It is of interest that distinction between the *cis* and *trans* isomers of methyl β-campholanate (**6**) is clean-cut because of the much greater abundance in the spectrum of the *trans* isomer of the rearrangement ion (*m/e* 74) and of the highly stabilized ion **16** (*m/e* 95). The latter ion may result from loss of an electron

(15) The full mass spectra of the five saturated and four unsaturated esters appear in the Ph.D. thesis of A. I. A. Khodair, University of California at Berkeley, 1965.

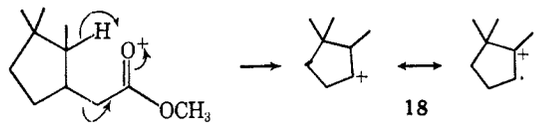
and methyl from the alkene remaining after loss of the rearrangement ion. Of course the methyl group may be lost first, or may be lost from radical ion **18**. This greater abundance of these two ions in the *trans* isomer follows logically if the transition state for loss of the rearrangement ion is the widely accepted one shown in **17**. In the *cis* isomer, in which the γ-hydrogen at the



16 **17**

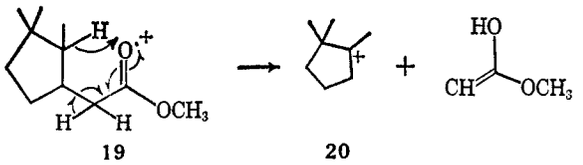
tertiary position is on the opposite side of the ring from the ester side chain, formation of the transition state (**17**) giving the more substituted alkene would be inhibited. It is of further interest that this effect is entirely absent in the six-membered ring where the flip from one conformation to the other makes formation of the cyclic transition state facile in both *cis* and *trans* isomers. In methyl 2,2,6-trimethylcyclohexylacetate,[5] the *cis* and *trans* isomers gave about the same abundance of the rearrangement ion. Furthermore, in the cyclohexylacetic ester in Table II (**11**), in which there is a tertiary hydrogen at each γ position, the ion of *m/e* 95 is in high abundance.

In the β-campholanates (**6**), the relative intensity of the rearrangement ion (*m/e* 74) is lowered by the abundance of three other ions, of which one (**16**) has already been mentioned. Whereas cleavage of the rearrangement fragment normally occurs as shown in **17**, to give the enolate as the charged fragment, in the campholanates the hydrocarbon fragment (*m/e* 110) carries as much or more of the charge. It seems necessary to assign this fragment as the resonance-stabilized radical ion (**18**) formed *via* a transition state similar to



18

17. Although it might be initially assumed that this ion is not sufficiently stable to explain such a large abundance, there is other evidence in these spectra that the tertiary carbonium ion in the cyclopentyl structure is of surprisingly low energy. For example, ion **20** (*m/e* 111), from loss of the acetic acid side chain and rearrangement of a proton, is also an abundant ion (85% of the base peak in the *trans* β-campholanate). It is striking that ion **20** is of a higher ratio in the *trans* isomer by an amount similar to the relative abundances for the rearrangement ion (*m/e* 74) and ion **16** (*m/e* 95). Furthermore, in the α-campholanate and in ester **15**, neither of which has a tertiary hydrogen adjacent to the ester side chain, the ion of *m/e* 111 is of low intensity (4 and 7%). Thus, it seems highly probable that the hydrogen at the tertiary position is lost directly to give the tertiary carbonium ion. A transition state (**19**) which is similar to **17**

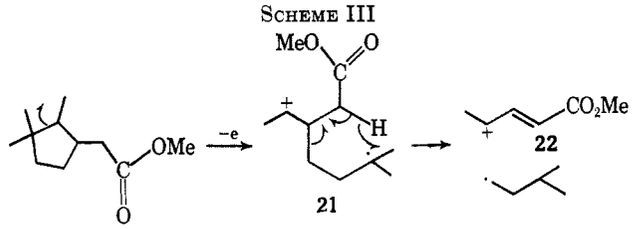


19 **20**

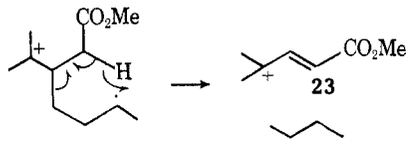
is plausible. The type of transition state shown in **19** is further supported by the abundance of the ion of *m/e* 111 in the fragmentation of ester **11**. In this cyclohexylacetic ester, the tertiary carbonium ion would result from loss of hydrogen at either γ position.

The abundance of the ion of *m/e* 113 in the β-campholanates is of considerable interest since that ion is not prominent in either the α-campholanate or the other two esters in Table II. The composition of this ion must be $C_6H_9O_2$, since alternative formulations seem impossible; so the ester function is present and part of the ring has been lost. A reasonable mechanism for this fragmentation is shown in Scheme III, wherein the initial step is loss of an electron from the ring bond between the substituents to give the radical ion **21**. Fragmentation of this ion as shown could give the resonance-stabilized ion (**22**). Although stabilization of this ion is decreased by the proximity of the

SCHEME III



positive charge to the ester group, its energy would be lowered significantly. The reality of the fragmentation shown in Scheme III is supported by the fact that the α-campholanate (**5**) in a similar fragmentation would give ion **23**, *m/e* 127. Reference to Table II reveals that the α-campholanate is the only ester therein which gives a major ion of *m/e* 127, and this ester has an ion of *m/e* 113 in low abundance.



The most striking feature of the pattern for ester **15** is the clear revelation of the presence of the ethyl group at the quaternary carbon. Since the ethyl radical is of lower energy than is methyl, the ion of *m/e* 81 (M − R − Et) should be in greater abundance than the ion of *m/e* 95, as is the case. Further, for ester **15** the ion at 155 (M − Et) is far more abundant than is 169 (M − Me) in the three compounds with geminal methyl groups.

There is little doubt that it is a mistake to attach any significance to the high abundance of the ion of *m/e* 69 in fragmentation of the cyclopentylacetic esters. This ion is also abundant in the cyclohexylacetic ester in Table II, as was the case for methyl 2,2,6-trimethylcyclohexylacetate.[5] Our investigations have revealed no instance in which useful significance could be attached to the ions representing a lower alkyl minus 2. On the other hand, serious frustrations have resulted from attempts to establish significance for these ions.

Unsaturated Esters.—As recorded[15] in Table III, mass spectra were determined for the α- and β-campholenates, which have the double bond in the ring,

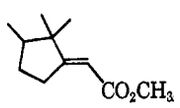
TABLE III

PARTIAL MASS SPECTRA OF METHYL ESTERS OF UNSATURATED $C_{10}H_{16}O_2$ ACIDS

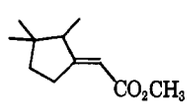
m/e (compn)[a]	3	4	24	25
41 (C_3H_5)	53	42	100	100
55 (C_4H_7)	14	15	41	46
69 (C_5H_9)	4	3	60	12
74 (R)	3	...	1	1
81	8	10	39	19
93 [M − Me − (R + e)]	53	26	22	16
107 [M − H − (R + e)]	81	100	45	35
108 [M − (R + e)]	100	13	15	12
123 (C_9H_{15})	2	12	67	21
125	3.5	8	21	6
135 (M − Me − MeOH)	5.5	5	27	11
167 (M − Me)	28	71	46	37
182 (M)	12	10	21	18

[a] M = molecular ion, Me = methyl, R = rearrangement ion.

as well as for isomers **24** and **25**, having exocyclic α,β unsaturation.[16] The latter esters were secured by α bromination and dehydrohalogenation of the α- and β-campholanic acids. In the spectra of the unsaturated esters, the near absence of the rearrangement ion of *m/e* 74 will be noted. This behavior is expected in the α,β-unsaturated esters (**24** and **25**), as well as



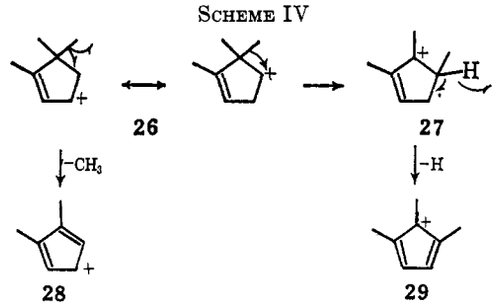
24



25

the β-campholenate (**4**), but the phenomenon is of considerable interest in the α-campholenate (**3**). Since the base peak in the α-campholenate fragmentation is at *m/e* 108, it is apparent that the rearrangement ion is not formed because the charge is retained on the hydrocarbon fragment almost exclusively. When the radical ion **26** is formed by the mechanism which has been depicted for formation of the saturated radical ion (**18**) a simple carbonium ion rearrangement would give the allylic stabilized ion, **27**, as shown in Scheme IV. Furthermore, loss of methyl from **26**

SCHEME IV

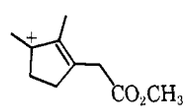


26 **27** **28** **29**

gives doubly substituted highly stabilized ion **28** (*m/e* 93, 53% of base peak), and loss of hydrogen from **27** gives triply substituted ion **29** (*m/e* 107, 81% of base peak). Thus, the opportunity for radical ion **26** to give three different highly stabilized ions, all remarkably abundant in the fragmentation pattern, appears to afford a reasonable explanation for failure of the oxygen-containing moiety to retain the charge in this fragmentation.

In the β-campholenate (**4**), in which the quaternary carbon is not adjacent to the ester side chain, the ion of *m/e* 107 becomes quite dominant, while the ions of *m/e* 108 and 93 become much less abundant than in the case of the α-campholenate (**3**). It seems necessary to ascribe structure **29** to such an abundant ion as that of *m/e* 107; however, no simple mechanism for formation of this ion is apparent. A mechanism similar to that in Scheme IV would require multiple rearrangements to arrive at **29** by fragmentation of ester **4**. Since *m/e* 107 is so dominant in the fragmentation of ester **4**, compared with **3**, some other yet-undiscovered mechanism seems more likely than a sequence related to that in Scheme IV.

The abundance of the ion of *m/e* 167 in the spectra of the unsaturated esters is expected, for loss of an electron and methyl leads directly to a resonance-stabilized allylic ion. Furthermore, this ion is most abundant in the spectrum of ester **4**, where the allylic system is triply substituted (structure **30**).

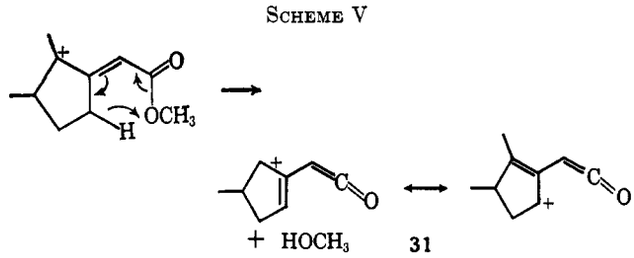


30

The ion of *m/e* 123 may be C_9H_{15}, $C_8H_{11}O$, or $C_7H_7O_2$; however, the hydrocarbon ion seems most plausible, and it is a normal ion in ester fragmentation, resulting from loss of methoxycarbonyl. For the compounds under consideration, there is apparent no predictable relationship between the abundance of this ion and structural considerations. Although ester **4** might be expected to give the greatest relative abundance of the *m/e* 123 ion, since this ion would be an allylic ion without rearrangement, the α,β-unsaturated esters actually have the largest percentages related to the base peak. This is caused, in part at least, by the lower abundance in the α,β-unsaturated esters of the ions of *m/e* 93, 107, and 108; however, other aspects of these spectra illustrate the facility of rearrangement to stable ions.

The ions of *m/e* 135 are no doubt the ketene ions resulting from loss of methanol from the ions resulting after loss of methyl. The mechanism presented in Scheme V suggests that the α,β-unsaturated esters

SCHEME V



31

should give the larger ions at 135, for this scheme requires that the other esters first rearrange to the α,β-unsaturated isomer. Furthermore, ester **24** would give the more stable ion (**31**) and hence, should give more of the ion of *m/e* 135 than would ester **25**. Since all of these expectations are realized, Scheme V receives considerable support.

(16) Gas chromatography of these esters revealed only one geometric isomer, whereas experience[6] with methyl 3-ethyl-4-methylcyclopentylideneacetates and with methyl 3-ethyl-3-methylcyclopentylideneacetate indicates that geometric isomers should be separable if present; therefore, a single isomer is probably present, and the ester group is assumed to be *trans* to the substituted side of the ring.

Experimental Section

Physical Measurements.—Distillations were through a 0.5-m simple Podbielniak-type column, and gas chromatography was with an Aerograph A-90-P under conditions specified in the individual cases. The nmr spectra were determined on a Varian Model A-60 spectrometer, in carbon tetrachloride as solvent with TMS as internal reference standard. Infrared spectra were recorded on a Perkin-Elmer Infracord 137, and ultraviolet spectra were measured on a Beckman DK-2A ratio-recording spectrometer, with heptane as solvent. Mass spectra were obtained by Miss Sherri Firth on a CEC Model 21-103C which was equipped with an ion multiplier and otherwise modified to give unit resolution at about 800; the inlet was heated to about 180°, and the ionizing voltage was maintained at 70 ev. Microanalyses were by the Microanalytical Division, Department of Chemistry, University of California at Berkeley; unless otherwise specified, all analytical samples were purified by gas chromatography.

α-Campholenic Acid (1).—To 20 g of molten potassium hydroxide, heated in a salt bath at 250°, was added slowly with stirring 20 g of commercial sodium (*RS*)-10-camphorsulfonate. After addition had been completed, heating with stirring at the same temperature was continued for an additional 20 min; then the melt was cooled and dissolved in 160 ml of water. Neutral material was extracted from the alkaline solution with two portions of diethyl ether followed by two portions of methylene dichloride, then the organic acid was liberated by acidification with hydrochloric acid and extracted with ether. Washing and drying of the extract, followed by removal of solvent, left 12 g of crude α-campholenic acid which gave infrared absorption above 3, characteristic of carboxyl, carbonyl absorption only at 5.84, and =CH absorption at 12.43 μ.

When a sample of this acid was gas chromatographed on a silicone column, the collected sample showed infrared absorption at both 5.74 and 5.86 μ. A similar infrared absorption was noted for a sample stored in ether solution over anhydrous magnesium sulfate at room temperature for 2 days. A distilled sample [bp 120–124° (6 mm)] which was then gas chromatographed showed carbonyl absorption only at 5.68 μ.

Reaction of Silver α-Campholenate with Methyl Iodide.—Following the procedure which has been described for naphthenic acids,[6] 7 g of crude, unheated α-campholenic acid was converted to the silver salt, which was in turn allowed to react with 30 g of methyl iodide in pentane solution. Injection of a sample of the neutral product (yield 4.5 g) on a silicone column (20% SE-30, 3/8 in. × 10 ft column, 148°, helium flow rate 180 cc/min) showed presence of four major bands, assigned by comparison with other samples as shown in Table IV. The β-campholenate had properties identical with those of the sample obtained by rearrangement of the α-campholenate, as described below. No effort was made to identify the band of shortest retention time, but campholene is formed by thermal decarboxylation of either campholenic acid.[7]

TABLE IV

Compd	Retention time, min	% of total
Dihydro-β-campholenolactone (2)	37	53.5
Methyl α-campholenate (3)	24.5	8.5
Methyl β-campholenate (4)	20	28
Unknown (campholene?)	7.5	10

Methyl α-Campholenate (3).—A mixture of 37 g of commercial tris-2-hydroxypropylamine, 22.4 g of distilled dimethyl sulfate, and 11.5 g of crude α-campholenic acid was heated under reflux in 20 ml of absolute methanol for 5 min. After dilution of the reaction mixture with water, and ether extraction of the neutral material, distillation yielded 7.2 g of methyl α-campholenate: bp 95° (10 mm); carbonyl absorption at 5.75 and =CH absorption at 12.46 μ. Gas chromatography to yield an analytical sample showed a single symmetrical band of retention time recorded above.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.9. Found: C, 72.1; H, 9.6.

Methyl β-Campholenate (4).—A solution of 2 g of methyl α-campholenate in 10 ml of methanol and 4 ml of 18 *N* sulfuric acid was heated under reflux for 12.5 hr. The crude product obtained by dilution of the reaction mixture and extraction with hexane was analyzed by gas chromatography (20% SE-30, 3/8 in. × 10 ft column, 160°, helium flow rate 180 cc/min) and found to be 80% methyl β-campholenate, 17% dihydro-β-campholenolactone, and 3% methyl α-campholenate. Distillation yielded 1.3 g of the β-campholenate, bp 85° (10 mm). Gas chromatography to secure the analytical sample[17] showed the distilled sample to be about 99% pure, contaminated with about 1% of the α isomer.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5. Found: C, 72.9.

For the β-campholenate, ultraviolet absorption showed λ_{max} 192.5 mμ (ε 8000); infrared absorption showed a single carbonyl band at 5.77 μ, no evidence of =CH deformation vibrations. The nmr spectrum included resonance lines of the predicted relative intensities as follows: singlet at τ 9.02 (*gem*-dimethyl), band with fine structure at 8.45 (allylic methyl), singlet at 7.05 (α-methylene also allylic), no evidence of a vinyl proton.

Methyl α-Campholanate (5).—A 7-g sample of methyl α-campholenate in 50 ml of 95% ethanol was hydrogenated at an initial pressure of 2.5 atm in the presence of 250 mg of commercial platinum oxide catalyst. Hydrogenation was complete in 30 min. Analysis of the product on either silicone or NPGS (neopentylglycol succinate) columns showed a single symmetrical band. No difference could be detected in the product obtained by hydrogenation of 168 mg of ester in 25 ml of 95% ethanol using 120 mg of 10% palladium-on-charcoal catalyst.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.8; H, 10.9. Found: C, 71.7; H, 10.9.

Methyl β-Campholanate (6).—Hydrogenation, as described for the isomer, of 1 g of methyl β-campholenate in 50 ml of 95% ethanol in presence of 200 mg of platinum oxide catalyst proceeded slowly, and hydrogen absorption ceased after 2.5 hr. Addition of a second 200 mg of catalyst and continuation of hydrogenation for 24 hr failed to complete the reduction. Gas chromatographic analysis (20% silicone grease, 3/8 in. × 10 ft column, 160°, helium flow rate 180 cc/min) revealed three components: β-campholenate, 47% of mixture, retention time 14 min; *trans*-β-campholanate, 23%, 16 min; and *cis*-β-campholanate, 28%, 19 min.

The product obtained after partial hydrogenation, as above, was next hydrogenated in 95% ethanol in the presence of 200 mg of 10% palladium-on-charcoal catalyst. Gas chromatographic analysis indicated complete hydrogenation, and the compound of longer retention time (*cis* isomer) had become the less abundant isomer (48% of total).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.8; H, 10.9. Found (for *trans* isomer): C, 71.7; H, 10.8. Found (for *cis* isomer): C, 71.8; H, 10.8.

Methyl 2,6-Dimethylcyclohexylacetate (11, 12, and 13).—A Reformatsky reaction was carried out in ether–benzene solvent in the manner which has been described in detail,[18] using 8.8 g of zinc foil, 2.8 g of 2,6-dimethylcyclohexanone,[19] and 20 g of methyl bromoacetate. Work-up yielded 6.98 g of crude methyl 2,6-dimethyl-1-hydroxycyclohexylacetate (7). Gas chromatographic analysis indicated presence of a small amount of the starting ketone and the two stereoisomeric esters.

Heating a sample of the hydroxy ester (7) with iodine at 200°, followed by distillation [bp 117–120° (13 mm)], gave a poor yield of a product which was indicated by gas chromatographic analysis to be a mixture of two isomers. Absence of significant ultraviolet absorption and infrared absorption at 5.64 μ indicate lactone 8 as the structure; so this product was not further investigated.

When a 2-g sample of crude ester 7 was dehydrated with phosphorus oxychloride and pyridine according to Rinehart and Perkins,[20] work-up and distillation yielded 0.7 g of unsaturated esters, bp 105–106° (12 mm). Gas chromatographic analysis indicated that the esters consist of 95% of the β,γ-unsaturated isomer (9), whose identity was verified by the ultraviolet absorption [λ_{max} 193 mμ (ε 9300)].

Hydrogenation of the unsaturated esters was carried out with 10% palladium-on-charcoal catalyst and 95% ethanol solvent,

(17) This analysis was performed on a 0.4-mg sample by the method depending on volumetric determination of combustion products [C. W. Koch and E. Jones, *Mikrochem. Acta*, **4**, 734 (1963)].

(18) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 470.

(19) We wish to express our appreciation to Professor W. G. Dauben and Dr. W. T. Wipke for a generous gift of this ketone.

(20) K. L. Rinehart, Jr., and E. G. Perkins, *Org. Syn.*, **37**, 37 (1957).

or with platinum oxide catalyst and glacial acetic acid solvent. Absence of ultraviolet absorption showed complete hydrogenation. Hydrogenation with platinum could not be accomplished in ethanol solvent. Isomeric distribution in the hydrogenation product is shown in Table I.

Dimethyl β-Ethyl-β-methyladipate.—β-Ethyl-β-methylglutaric acid was prepared according to Rabjohn and Farmer,[21] and converted to 3-ethyl-3-methyl-4-methoxycarbonylbutanoyl chloride by way of the methyl half-ester, as has also been reported.[22]

The above-described ester acid chloride was treated in 3-g lots with 1.7 g of diazomethane in 150 ml of ether, at a temperature of 5–10°. After the reaction mixture had stood overnight solvent was removed at reduced pressure and the residual diazo ketone was dissolved in 10 ml of absolute methanol. This mixture was treated dropwise, with stirring, with a solution of 0.43 g of silver benzoate[23] dissolved in 4 ml of trimethylamine. Addition of a few drops of catalyst solution caused evolution of nitrogen to set in, and catalyst was added intermittently as nitrogen evolution slackened. After addition had been completed, in about 2 hr, the reaction mixture was heated under reflux for 15 min. The cooled reaction mixture was treated with charcoal, and the filtrate from the charcoal was diluted with water and extracted with ether. The extracts were washed with water, 1 *N* hydrochloric acid, and again with water, then dried. Distillation of the residue remaining after solvent removal yielded 1.9 g (57%) of dimethyl β-ethyl-β-methyladipate, bp 132–134° (10.5 mm). Gas chromatography, to yield the analytical sample (20% SE-30, 3/8 in. × 10 ft column, 172°, helium flow rate 150 cc/min), indicated about 97% purity for this product; the remainder was dimethyl β-ethyl-β-methylglutarate.

Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.1; H, 9.3. Found: C, 59.7; H, 9.6.

3-Ethyl-3-methylcyclopentanone (14).—A 6.4-g sample of β-ethyl-β-methyladipic acid, obtained by alkaline saponification of the diester, was mixed with 420 mg of barium oxide and heated under the half-meter Podbielniak-type column. The bath was maintained at about 300° and the column at about 180° until distillation of the ketone had ceased after about 7 hr. The ketone was extracted with ether for separation from the water which distilled. Drying of the extract and removal of solvent through the column left 2.8 g (68%) of ketone **14**, which showed a single symmetrical band in gas chromatography; carbonyl absorption in the infrared was at 5.74 μ. This ketone has been reported[24] as of bp 174°.

Methyl 3-Ethyl-3-methylcyclopentylideneacetate. A.—A 525-mg sample of 50% dispersion of sodium hydride in mineral oil was stirred in 10 ml of dry benzene as 2 g of trimethyl phosphonoacetate was added dropwise during about 50 min. Temperature during the addition was 30–35°. Stirring was continued for 1 additional hr, then there was added dropwise during about 40 min a solution of 1.26 g of 3-ethyl-3-methylcyclopentanone in 2 ml of dry benzene. The temperature was maintained at 20–30° during the addition, then heated at 60–65° with stirring for an additional 15 min. The reaction mixture was cooled to about 10° and decanted from the precipitate. The residue was heated with four portions of benzene and each portion was decanted after cooling. Distillation of the product recovered from the extracts yielded 1.1 g (60%) of the α,β-unsaturated ester, which was identical with the sample of this ester prepared *via* a Reformatsky reaction.

B.—A 0.944-g sample of 3-ethyl-3-methylcyclopentanone was subjected to the Reformatsky reaction according to the procedure described for preparation of ester **7**, and dehydration was also accomplished as for ester **7**. Gas chromatography of the unsaturated esters (20% SE-30, 3/8 in. × 10 ft colunm, 150°, helium flow rate 150 cc/min) showed four bands, with retention times of 23 min (13% of total area), 25 min (18%), and 37 and 38 min overlapping (69%). The bands of shorter retention time are the two endocyclic β,γ-unsaturated esters [λ_{max} 192.5 mμ (ε 8850)], while the overlapping bands are the geometrical isomers of methyl 3-ethyl-3-methylcyclopentylideneacetate [λ_{max} 221 mμ (ε 11,000)], identical with the sample obtained *via* the phosphonoacetate.

Methyl 3-Ethyl-3-methylcyclopentylacetate (15).—A 0.45-g sample of the mixed unsaturated esters was hydrogenated in 95% ethanol with 10% palladium-on-charcoal catalyst. The hydrogenated product gave a single band in gas chromatography on either silicone or NPGS columns, and was indistinguishable from a sample obtained by hydrogenation in glacial acetic acid with platinum oxide catalyst.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.8; H, 10.9. Found: C, 72.1; H, 11.2.

Methyl 2,2,3-Trimethylcyclopentylideneacetate (24).—α-Campholanic acid (570 mg) obtained by saponification of ester (**5**) was α brominated and converted to the α-bromo ester according to the procedure which has been described[6] for 3-ethyl-4-methylcyclopentylacetate (naphthenic acid fraction III-2-A in previous publication[6]). The crude bromo ester, obtained in 95% yield, gave a single, symmetrical band in gas chromatography on silicone or NPGS; for the 10 ft × 3/8 in. silicone column (178°, helium flow rate 180 cc/min), retention time was 32.5 min.

The above-described sample of α-bromo ester was dehydrobrominated with quinoline by the method previously described,[6] and the product was gas chromatographed on a silicone column to give 160 mg of unsaturated ester. This ester was not pure [λ_{max} 222.5 mμ (ε 28,000)], probably contaminated with an aromatic compound. Rechromatography on an NPGS column (20% NPGS, 3/8 in. × 20 ft column, 152°, helium flow rate 180 cc/min) eliminated a small band of retention time 38 min. The pure α,β-unsaturated ester, in a band at 26 min, was collected in a yield of 122 mg (32% over-all), λ_{max} 220 mμ (ε 13,500).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.6; H, 9.9. Found: C, 72.4; H, 9.6.

Methyl 2,3,3-Trimethylcyclopentylideneacetate (25).—A 124-mg sample of *trans*-β-campholanic acid, from saponification of the ester, was converted as described above for the isomer to 135 mg (70%) of methyl α-bromo-β-campholanate. This bromo ester also gave a single, symmetrical band in gas chromatography (20% SE-30, 3/8 in. × 10 ft column, 158°, helium flow rate 150 cc/min, retention time 53.5 min).

Dehydrobromination, as described above, and chromatography on a silicone column gave 23.8 mg of ester **25**, but it was again contaminated with the "aromatic impurity;" so the material was reinjected on the NPGS column described for the isomer (133°, helium flow rate 170 cc/min). The desired ester was collected in a band at 49 min, while the impurity appeared at 73 min.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.6; H, 9.9. Found: C, 72.5; H, 9.8.

Registry No.—**3**, 7430-38-8; **4**, 7430-39-9; **5**, 7430-40-2; **6** (*cis*), 7430-41-3; **6** (*trans*), 7430-42-4; **9**, 7430-45-7; **11**, 7430-47-9; **12**, 7430-47-9; **13**, 7445-17-2; **14**, 7430-49-1; **15**, 7430-50-4; **24**, 7430-52-6; **25**, 7484-13-1; β-ethyl-β-methyladipate, 7430-46-0; methyl 3-ethyl-3-methylcyclopentylideneacetate, 7445-21-8.

(21) H. H. Farmer and N. Rabjohn, *Org. Syn.*, **36**, 28 (1956).

(22) N. Rabjohn and H. H. Farmer, *J. Org. Chem.*, **24**, 359 (1959).

(23) The excellent catalyst recommended by M. S. Newman and P. F. Beel, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

(24) J. von Braun, W. Keller, and K. Weissbach, *Ann.*, **490**, 179 (1931).