of the substance (in $CHCl_3$) displayed two resonances in a ratio of 1:4 at 9.09 and 3.00 ppm downfield from tetramethylsilane due to the aldehydic and methylenic hydrogens, respectively. In benzene solution the methylenic hydrogens appeared as an eight-line AA'BB' pattern. An analytical sample was prepared by an additional short-path distillation at 0.03 mm: bath 80–95°; $n^{23}D$ 1.5452. This material (12 mg) was reconverted to its semicarbazone in the usual way, mp and mmp 189° dec.

On investigating V, it was found to dissolve promptly in anoxic ammonia (4.3 mg in 146 mg) and the clear solution at 25° displayed a greenish tint in 3 min and became deep emerald green within 15 min. At −78° the color changed to light orange and the deep green color returned at 25°. An appreciable quantity of a colorless microcrystalline material appeared in a few minutes. This suspension was solidified by liquid nitrogen, the tube was opened, and transferred to chilled liquid ammonia in a large tube flushed with oxygen, and then the outer tube was sealed. On warming to 25° the yellow color in the small tube changed to a greenish color momentarily, then disappeared entirely in less than 1 hr while the ammonia deposited additional opaque colorless material on the walls of the inner tube.

The solution of V in anoxic ethylenediamine (5 mg in 137 mg) at 25° displayed a yellow color which changed to emerald green after 16 hr. Chilling the solution to −78° formed a canary yellow solid and returning to 25° restored the green color. On opening the tube in air at 25° the green color disappeared within 12 hr, leaving a light yellow solid.

Similarly, 5.8 mg of V in 180 mg of 1,1,3,3-tetramethylguanidine displayed first yellow then emerald green in 3 min at 25°. Chilling to −78° caused it to become faintly greenish yellow while warming restored the intense emerald green color. On opening the tube to the air the green color disappeared within 12 hr but retained a light cherry red color.

Registry No.—Ia, 2790-85-4; Ib, 13961-87-0; Ic, 13961-90-5; Id, 6513-21-9; IIa, 6367-15-3; IIb, 3693-95-6; IIc, 5673-91-6; IId, 13961-95-0; IIf, 13961-96-1; IIg, 13976-38-0; IIh, 13028-62-1; III, 13976-40-4; IIn, 13976-41-5; IIIa, 13976-42-6; IIIc, 13976-43-7; IV, 13976-44-8; V, 13976-45-9; semicarbazone of V, 13976-46-0; $HSCMe_2CH(NHAc)CONHCH_2CO_2Et$, 13976-47-1; $CH_2(SCH_2CH(NHCOC_6H_5)CO_2CH_3)_2$, 13976-48-2; $AcSCH_2CH_2CH{=}NNHCONH_2$, 13976-49-3; $CH_3COSCH_2CH_2COCH_3$, 13976-50-6; $AcSCH_2CH_2C(CH_3){=}NNHCONH_2$, 13976-51-7; $(SCH_2CH_2C(CH_3){=}NNHCONH_2)_2$, 13976-52-8.

Acknowledgments.—The author wishes to thank the members of the faculty of the Department of Chemistry, College of Arts and Sciences, Northwestern University, for their many valuable suggestions during this investigation and for providing laboratory facilities which made this study possible.

Isolation of the 11-Carbon Acyclic Isoprenoid Acid from Petroleum. Mass Spectroscopy of Its *p*-Phthalimidophenacyl Ester[1]

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Gas chromatographic examination of appropriate distilled fractions of methyl naphthenates from a California petroleum failed to reveal the presence of any of the C_{10} isoprenoid acid, 3,7-dimethyloctanoic acid. The ester of the C_{11} isoprenoid acid, methyl 4,8-dimethylnonanoate, was isolated but only to the extent of 0.04% of the naphthenate mixture. Final purification by crystallization of the *p*-phthalimidophenacyl ester was necessary and this ester proved satisfactory for structural determination by mass spectrometery. Features of the fragmentation pattern of this type of ester are described. For comparison with the isolated product, 4,8-dimethylnonanoic acid was synthesized from citronellol.

Recent investigations in this laboratory of the component acids in a California petroleum have resulted in the identification of only one nonisoprenoid structure—geometric isomers of 3-ethyl-4-methylcyclopentylacetic acid.[2] In addition to one cyclic isoprenoid acid, 2,2,6-trimethylcyclohexylacetic acid,[3] the C_{14}, C_{15}, C_{19}, and C_{20} acyclic isoprenoid acids have been isolated.[4] The C_{14} and C_{19} acyclic acids could arise by degradative oxidation of the C_{15} and C_{20} acids;[5] however, such oxidation from the chain end could not yield the C_{12}, C_{13}, C_{17}, or C_{18} acids by a simple direct route. These four acids must be present in extremely low concentration, if at all, in the California petroleum under investigation, for our efforts have not yet resulted in their isolation. In contrast the C_{11} and C_{16} acyclic isoprenoid acids could arise by oxidation from the chain end. Examination of fractions in which the C_{10} and C_{11} isoprenoid acids should be located is the subject of the present report. A search for the C_{16} isoprenoid acid, which resulted in isolation of a C_{12} bicyclic acid, will be reported subsequently.

The stereoisomers of 3-ethyl-4-methylcyclopentylacetic acid were isolated[2] from a fraction of methyl naphthenates boiling in the range 97–107° (11.5 mm). A prominent band in the glpc of this ester fraction (refer to Figure 1 of the cited publication, 33-min band) was at the retention time expected for the ester of the 11-carbon acyclic isoprenoid acid; however, rechromatography of the material collected in this band showed the presence of a particularly formidable mixture. Examination of higher boiling fractions suggested a less difficult separation, and the desired component was eventually isolated, as described in the Experimental Section, with somewhat less difficulty from the fraction which had bp 107–118° (11.5 mm). The second fraction from glpc on neopentyl glycol succinate (NPGS) was rechromatographed on silicone. The second and third fractions (IV-2-B and IV-2-C) from this second chromatography were examined in some detail.

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

(2) J. Cason and A. I. A. Khodair, *J. Org. Chem.*, **31**, 3618 (1966).

(3) J. Cason and K.-L. Liauw, *ibid.*, **30**, 1763 (1965).

(4) J. Cason and D. W. Graham, *Tetrahedron*, **21**, 471 (1965).

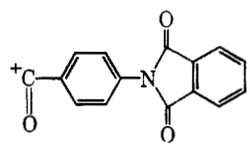
(5) In principle, the C_{15} and C_{20} acyclic isoprenoid acids could arise by terminal oxidation of the hydrocarbons farnesane and phytane; however, it is also possible that the hydrocarbons arise by reduction of the analogous acids. The latter route has been proposed as the origin of the normal hydrocarbons [J. E. Cooper and E. E. Bray, *Geochim. Cosmochim. Acta*, **27**, 1113 (1963)].

Fraction IV-2-B proved to consist principally of the esters of two monocyclic C_{11} acids, neither of which was the previously reported[3] methyl 2,2,6-trimethylcyclohexylacetate. The latter ester has a retention time on silicone which is somewhat greater than that of methyl decanoate, whereas the retention time of fraction IV-2-B is slightly less than that of methyl decanoate. Furthermore, the mass spectra of the IV-2-B esters show significant differences from the spectrum of methyl 2,2,6-trimethylcyclohexylacetate. Considerable effort failed to effect a separation of the IV-2-B esters; however, repeated glpc accomplished sufficient enrichment in different fractions that two fragmentation patterns developed in the mass spectra. Specific structural assignments have not been accomplished; however, comparison with the mass spectra of a series of compounds of known structure[6] indicates that both of the IV-2-B esters are polyalkylcyclopentylacetates. One ester has an ethyl substituent, while the other alkyls are methyl, and each ester probably has a *gem*-dimethyl grouping. Completion of the proof of structure of these compounds will probably require a more effective means of separation.

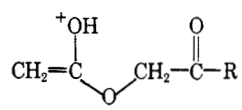
Spectral analysis indicated the presence of the C_{11} isoprenoid acid in fraction IV-2-C; so further purification was effected by an additional chromatography on NPGS. The once-distilled, thrice-chromatographed fraction IV-2-C-2 (about 0.04% of the naphthenic acid mixture) proved to have four molecular ions in its mass spectrum (*m/e* 198, 200, 210, and 212). Conversion of the methyl ester to the *p*-phthalimidophenacyl ester and four crystallizations of this derivative yielded the ester of the C_{11} acyclic acid, containing only small amounts of the derivative of a C_{11} monocyclic acid.

Fraction IV-2-C-2 shows no significant ultraviolet absorption above 195 mμ, while the nmr spectrum[7] shows no vinyl hydrogens and a total of 24 hydrogens (reference to the cleanly defined resonance for the methoxyl hydrogens located at τ 6.4). Thus, an acyclic structure is indicated, and is supported by the relatively narrow methylene peak at about τ 8.8. An unsymmetrical triplet centered at about τ 7.8, with an area equivalent to two hydrogens, shows the presence of a methylene group α to the ester group and flanked by a second methylene group; therefore, the absence of substituents on both α and β carbons is indicated. A doublet in the methyl region, centered at about τ 9.1, with a coupling constant of 6 cps, has an area equivalent to that of ten hydrogens, and, hence, represents three methyl groups.[8] This doublet, whose downfield peak is much the larger of the two, is consistent only with a structure in which no methyl group, including the terminal methyl, is adjacent to methylene. Thus, the principal component of fraction IV-2-C-2 must have the isopropyl end group and a third methyl more remote from carboxyl than the β position. Mass spectrometry was utilized to locate the chain-substituted methyl in the γ position.

Since the methyl ester of the acid under investigation could not be purified sufficiently to allow reliable deduction of structure from the mass spectral fragmentation pattern, the solid *p*-phthalimidophenacyl ester[9] was utilized for purification. This ester has also proved useful for structure determination, by examination of features of the fragmentation pattern which have been developed in a study of methyl esters.[10] For all *p*-phthalimidophenacyl esters, the ion of *m/e* 250 is in overwhelming abundance; no other ion of *m/e* greater than 43 amounts to as much as 10% of the 250 ion.



1 (*m/e* 250)



2, R = *p*-phthalimidophenyl (*m/e* 323)

This abundant ion, structure **1** (one of many resonance forms), arises from simple cleavage between carbonyl and methylene. Loss of carbonyl from ion **1** would give an ion of *m/e* 222, which was also prominent (6% of abundance of **1**). This fragmentation of ion **1** is supported by the occurrence of a metastable peak centered at *m/e* 197 (calcd, 197).

The ion of *m/e* 323 is assigned structure **2**, which is the rearrangement ion from fragmentation of the phenacyl ester of an acid with no α-substitution. Although the 323 ion is only about 0.3% of the abundance of the 250 ion, it is, nevertheless, relatively prominent compared to most ions produced in fragmentation of *p*-phthalimidophenacyl esters. For examination of the fragmentation pattern of interest, it is convenient to refer to the rearrangement ion as the base peak, as has been done[11] in Table I. Purification of the ester by crystallization may be followed by reference to the mass spectrum. The ions of *m/e* 337 and 351, the rearrangement ions for esters with α-methyl and α-ethyl substitution, respectively, are noted to decrease as the sample is recrystallized until their abundances in the thrice crystallized sample are near that in the synthetic ester. In contrast, the molecular ion of the ester of the monocyclic C_{11} acid (*m/e* 447) is not eliminated by the crystallization process. The relative abundance of this ion is much higher (probably by a power of ten) than the relative concentration of the ester, for the molecular ion of the monocyclic ester is much more stable to fragmentation than is that of the acyclic ester.

The significant ion of mass corresponding to M − 29 has been shown by deuterium labeling in acyclic methyl esters[12] to arise almost entirely from elimination of the α and β carbons along with an additional hydrogen.

(6) J. Cason and A. I. A. Khodair, *J. Org. Chem.*, **32**, 575 (1967).

(7) The Ph.D. Thesis of A. I. A. Khodair, University of California at Berkeley, 1965, contains tracings for the nmr spectra of this isolated sample of ester as well as the synthetic sample.

(8) The excess of area for three methyl groups may represent the effect normally observed for polymethylalkanoates, but this overlap with the methylene band has been noted previously in more highly branched acids [J. Cason and G. L. Lange, *J. Org. Chem.*, **29**, 2107 (1964)]. In the present case, the broadening of the resonance lines, as well as the excess of hydrogen in the methyl region, is most reasonably ascribed to the presence of impurities containing a larger number of methyl groups (three additional molecular ions observed in the mass spectrum).

(9) We were advised of the usefulness of the *p*-phthalimidophenacyl ester by Dr. F. H. Stodola prior to his publication concerning it [F. H. Stodola, *Microchem. J.*, **7**, 389 (1963)]. This ester has proved to be of great value for forming crystalline derivatives of the naphthenic acids.

(10) A useful analysis of the mass spectra of carboxylic esters is that of R. Ryhage and E. Stenhagen in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 399.

(11) The full mass spectrum of this ester is depicted graphically in the Ph.D. Thesis of A. I. A. Khodair; see ref 7.

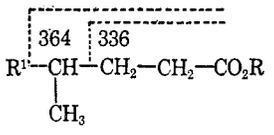
(12) Ng Dinh-Nguyen, R. Ryhage, S. Ställberg-Stenhagen, and E. Stenhagen, *Arkiv Kemi*, **18**, 393 (1961).

TABLE I
PARTIAL MASS SPECTRA OF SAMPLES OF THE *p*-PHTHALIMIDOPHENACYL ESTER OF 4,8-DIMETHYLNONANOIC ACID

	Relative ion abundance[a]			
m/e	I	II	III	IV
323 (ion 2)	100	100 (100)	100	100
324	22	22 (24)	23	23
336	23	23 (21)	26	50
337 (2 + 14)	42	28 (22)	21	15
350	7	7 (4)	6	
351 (2 + 28)	7	7 (3)	2.5	
364	11	12 (9)	14	23
378	6.5	7 (4)	7	3
420 (M − 29)	13	13 (5.5)	16	8.5
447	5	5 (2.5)	5	
448	7	7 (3.5)	8.5	7
449 (M)	16	16 (2.5)	20	5
450	6	6 (2)	6	11

[a] Compounds I, II, and III are samples of ester from fraction IV-2-C-2, crystallized once, twice, and thrice, respectively. Compound IV is the ester of synthetic 4,8-dimethylnonanoic acid. Spectra of I, II (first number), and III were recorded on a CEC Model 21-103C, while the spectra of II (second number) and IV were recorded on this instrument after modification (*cf.* Experimental Section). Spectra on the modified instrument differ only in the lower intensity at higher mass numbers.

A reasonable mechanism has been proposed.[13] If there is a methyl substituent at the α or β positions, loss of the α and β carbons gives an ion of mass M − 43; so the presence of a significant ion of *m/e* 420 (M − 29) in the spectrum under consideration and the complete absence of the 406 ion support the deduction from the nmr spectrum that the α and β positions are unsubstituted. There is a less abundant ion in methyl esters at M − 43, ascribed to loss of the α, β and γ carbons plus an additional hydrogen, when there is no substituent on any of these carbons. In the present spectrum, there is a very minor ion at 392 (M − 57), consistent with presence of a γ-methyl; however, a much better indication of this substituent depends on the relative intensities of the ions of *m/e* 336, 350, and 364. Preferred fragmentation at the branch, as depicted in **3**, gives the characteristic high-low-high pattern which becomes more emphatic in Table I as purification progresses. Thus, the chain methyl is located at the 4 position, as required by the isoprenoid structure.



3

The significant ion at M + 1, characteristic of nitrogen-containing acid derivatives such as nitriles and amides,[4,14] has been included in Table I. As is true for the data in Table I, the relative intensity of this ion tends to vary with conditions such as vapor pressure of the sample in the spectrometer. Presumably, the significant ion at *m/e* 324 also results from hydrogen capture by the 323 ion.

(13) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1964, p 15.

(14) F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).

For comparison with the isolated sample, 4,8-dimethylnonanoic acid was synthesized from citronellol, *via* hydrogenation and chain extension by the cyanide route. Synthetic methyl 4,8-dimethylnonanoate had the same retention time in glpc as fraction IV-2-C-2, on two different partitioning agents. The nmr spectrum of the synthetic ester differed from that of the isolated ester only in having sharper resonance lines, with lower valleys between the peaks in the methyl region. The *p*-phthalimidophenacyl esters of the isolated and synthetic acids showed no depression in melting point on mixing, and the mass spectra (Table I) were the same except for the ions resulting from the impurity in the isolated ester.

In order to facilitate precise location of the ester of the C_{10} isoprenoid acid in glpc, this acid was synthesized by oxidation of dihydrocitronellol (tetrahydrogeraniol). The methyl 3,7-dimethyloctanoate proved to have a retention time on NPGS slightly shorter than that of methyl nonanoate. Highest concentration of methyl nonanoate occurred in the naphthenate fraction which had bp 95–100° (11.5 mm). Glpc of this fraction on NPGS, collection of fractions contiguous to methyl nonanoate, removal of the normal ester by urea adduction, and rechromatography on silicone (*cf.* Experimental Section) revealed about eight peaks, one of which had a retention time identical with that of methyl 3,7-dimethyloctanoate. The nmr spectrum of this fraction proved to be quite different from that of the synthetic ester, and the mass spectrum showed the presence of at least three major components (*m/e* 172, 184, and 186). Thus, it may be stated that if the C_{10} isoprenoid acid is present at all in the naphthenic acids under investigation its concentration is so minute that it could not be detected.

Experimental Section

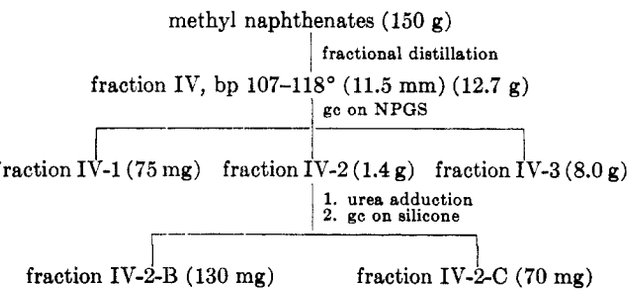
Physical Measurements.—Melting points were determined with a calibrated thermometer in a Büchi Schmelzpunktbestimmungsapparat. Microanalyses were by the Microanalytical Division, Department of Chemistry, University of California. Glpc was carried out with an Aerograph A-90-P under conditions specified in the individual cases. The nmr spectra were determined on a Varian Model A-60 spectrometer, using 15 mg of ester in 0.4 ml of carbon tetrachloride with TMS added as internal reference standard. Ultraviolet spectra were observed on a Beckman DK-2A ratio recording spectrometer, and infrared spectra were recorded on a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Mass spectra were determined by Miss Sherri Firth on a CEC Model 21-103C mass spectrometer, with the inlet heated to about 180° and with the ionizing voltage at 70 ev. Some of the spectra (including those specified in Table I) were determined after this instrument had been equipped with an ion multiplier and otherwise modified to give unit resolution to about 800. After modification, there was discrimination in favor of ions in certain regions of low mass number; hence a decrease in ion intensities occurred at high mass numbers. There were also greater variations in absolute intensities from one spectrum to another, but the ratios of ion intensities remained comparable.

Separation of Methyl 4,8-Dimethylnonanoate.—The distilled ester fractions were those obtained as described in an earlier publication.[2] Tracings for the gas chromatographic separations are found in the thesis of Khodair;[11] material distribution in a typical separation was as shown in Chart I.

The final chromatography of fraction IV-2-C on NPGS gave 60–70% recovery of fraction IV-2-C-2.

Further gas–liquid partition chromatography of fraction IV-2-B, and mass spectra of fractions IV-2-B′-2 and IV-2-B″-1 are reported in the thesis of Khodair.[11] Also reported is the mass

CHART I



spectrum of the *p*-phthalimidophenacyl ester of the acid obtained by saponification of fraction IV-2-B'-2.

Search for Methyl 3,7-Dimethyloctanoate.—Distillation fraction II, bp 95–100° (11.5 mm), was chromatographed on a 20 ft × 3/8 in. column, 10% NPGS partitioning agent at 140°, helium flow rate 180 cc/min. The tracing showed 11 peaks, with retention times of 17.9 and 18.8 min for peaks 4 and 5. Retention time for synthetic methyl 3,7-dimethyl octanoate under the same conditions was 18.4 min. Peak 5, the most prominent in the tracing, proved to be due largely to methyl nonanoate; therefore the collected fraction 5 was adducted with urea in hexane containing methanol, and the unadducted material was chromatographed on a 10 ft × 3/8 in. column, silicone SE-30 partitioning agent at 155°, helium flow rate 150 cc/min. The tracing contained two major bands, of which the first had a retention time of 17.5 min, the same retention time as shown by methyl 3,7-dimethyloctanoate under these conditions. The nmr spectrum of collected fraction II-5-A proved quite different from that of methyl 3,7-dimethyloctanoate, and the mass spectrum of this fraction exhibited molecular ions at *m/e* 172, 184, and 186. Chromatography of fraction II-4 under the same conditions used for fraction II-5 gave a tracing with about 85% of the area under a band of retention time 15.8 min, and only a slight shoulder at a retention time of 17.5 min.

The glpc tracings cited in this section are depicted graphically in the thesis of Khodair.[11]

4,8-Dimethylnonanoic Acid.—Commercial citronellol was distilled through a 2-ft simple Podbielniak column, and the material of bp 100–102° (6–6.5 mm) was used for hydrogenation; 22 g of citronellol, 250 mg of commercial platinum oxide catalyst, and 50 ml of 95% ethanol were subjected to an initial pressure of 45 psi. The time for complete hydrogenation was 2 hr. Distillation of the product through the 2-ft column yielded 17.9 g (80%) of dihydrocitronellol, bp 106–107° (10 mm) [lit.[15] bp 108–109° (10 mm)]. Glpc of this product on a 10-ft silicone column indicated a homogeneous product, with no peak observed at the retention time of the starting material.

Dihydrocitronellol was converted to the bromide in 62% yield using hydrobromic and sulfuric acids, and the cyanide was formed in dimethyl sulfoxide. For this purpose, 11.5 g of the bromide was added during 30 min to a stirred solution of 3 g of sodium cyanide in 15 ml of technical DMSO, as the temperature was maintained at 60–65°. After an additional 15 min at 90–92°, the cooled reaction mixture was worked up by addition of water and extraction with ether. The yield of nitrile was 7.1 g (82%), bp 106–107° (6 mm) [lit.[16] bp 113–114° (15 mm)]. Glpc indicated a single compound, and infrared absorption was observed at 4.47 μ (nitrile stretching vibrations).

The nitrile was hydrolyzed by heating 3.4 g under reflux for 3 hr in 30 ml of an equivolume solution of glacial acetic acid, concentrated sulfuric acid, and water. The reaction was worked up by dilution with water and extraction with ether. Distillation through the 2-ft column yielded 2.3 g of 4,8-dimethylnonanoic acid of bp 146–147° (17 mm) [lit.[16] bp 156–157° (15 mm)]. Glpc indicated about 2% nitrile in this product. The nitrile was readily removed by ether extraction of an alkaline solution of the acid.

Methyl 4,8-dimethylnonanoate was prepared by acid catalyzed esterification of the acid. In the infrared, absorption occurred at 8.55 (skeletal vibration of the terminal isopropyl group), 7.25, 7.30 doublet (CH deformation vibrations in isopropyl), 13.6 μ [weak, methylene vibration in $-(CH_2)_3-$]. Glpc of this ester and the isolated ester gave identical retention times on two partitioning agents: 20 ft × 3/8 in. 10% NPGS column at 155°, helium flow rate 180 cc/min, retention time 21.5 min; 10 ft × 3/8 in. silicone SE-30 column at 148°, helium flow rate 200 cc/min, retention time 33.5 min.

***p*-Phthalimidophenacyl Ester of 4,8-Dimethylnonanoic Acid.**—A 44.5 mg sample of fraction IV-2-C-2 was hydrolyzed by heating under reflux for 1 hr with 1.5 ml of 15% potassium hydroxide in 3 ml of methanol. The acid isolated after saponification was heated for 5 min at 90° with 56.8 mg of dicyclohexylethylamine (DICE) and 77.5 mg of *p*-phthalimidophenacyl bromide in solution in a mixture of 8 ml of acetone and 2 ml of dimethylformamide. The product was precipitated from the cooled reaction mixture with water and crystallized from aqueous acetone (80% acetone by volume) to yield white crystals of mp 109.5–111.5°. A second crystallization raised the melting point to 110.5–112°. After two additional crystallizations, the melting point of 114.5–115.5° was determined (to conserve material) only in admixture with the synthetic sample.

Synthetic 4,8-dimethylnonanoic acid was converted into the derivative by the method described above, mp 114.5–115.5°.

Anal. Calcd for $C_{27}H_{31}O_5N$: C, 72.3; H, 6.9; N, 3.2. Found: C, 72.8; H, 7.1; N, 3.3.

Methyl 3,7-Dimethyloctanoate.—A 680-mg sample of dihydrocitronellol was oxidized with 2 g of potassium permanganate in presence of 100 mg of sodium bicarbonate, in solution in 20 ml of acetone. After the mixture had been heated under reflux for 1.5 hr, solvent was evaporated and the residue was acidified with 6 *N* sulfuric acid. The mixture was shaken with 10 ml of hexane, then the manganese dioxide was removed by filtration and washed with several portions of hexane. Acid isolated from the hexane extracts by way of extraction into 15% aqueous potassium hydroxide amounted to 120 mg. The ester formed by acid-catalyzed esterification with methanol contained about 5% of an unidentified compound which was removed by glpc. The purified ester gave an nmr spectrum in agreement with expectation, the fragmentation pattern in mass spectrometry expected for the structure and a molecular ion of 186 [lit.[17] boiling point of the acid is 93–95° (0.6–0.7 mm)].

Registry No.—4,8-Dimethylnonanoic acid, 7540-70-7; *p*-phthalimidophenacyl ester of 4,8-dimethylnonanoic acid, 13758-79-7; methyl 4,8-dimethylnonanoate, 13758-80-0.

(15) P.-H. Yeh, *Perfumery Essent. Oil Record*, **52**, 697 (1961).

(16) N. Polgar and R. Robinson, *J. Chem. Soc.*, 3941 (1945).

(17) C. Herschmann, *Helv. Chim. Acta*, **32**, 2537 (1949).