II. The insoluble material was crystallized from acetic acid to give 8 g. of product (46% yield), m.p. 261–262°.

Anal. Calcd. for $C_{19}H_{17}BF_4O$: C, 65.54; H, 4.92. Found: C, 65.5; H, 4.04.

2-Ethyl-4,6-di(4-chlorophenyl)pyrylium Fluoborate.—This material was prepared in a manner analogous to the preceding compound using the same proportion of reactants. From the reaction mixture there was isolated 9 g. of crude product, which gave 8.5 g. of ethyl acetate insoluble material. Recrystallization from acetic acid gave 5 g. (25% yield) of pyrylium salt product, m.p. 245–247° dec.

Anal. Calcd. for $C_{19}H_{15}BCl_2F_4O$: C, 54.17; H, 3.63. Found: C, 54.25; H, 3.56.

The ethyl acetate extract was evaporated to dryness and the residue was recrystallized from ethyl acetate to give a few milligrams of material, m.p. 156–157.5°. Infrared showed it to be analogous to II.

Anal. Calcd. for $C_{11}H_{10}BClF_2O_2$: C, 51.06; H, 3.87. Found: C, 50.92; H, 3.94.

Reaction of Substituted Acetophenones with Acetic Anhydride in the Presence of Boron Trifluoride Etherate.—These materials were prepared by a procedure similar to that employed in the two preceding sections involving 0.1 mole of ketone in 25 ml. of acetic anhydride with 40 g. (0.28 mole) of boron trifluoride etherate. In the case of 4-chloroacetophenone five times these amounts were used. The crude reaction products were washed with ether and extracted with hot ethyl acetate to separate type-I from type-II products. Yields are based on moles of ketone employed. The physical constants and other data are recorded as follows.

4-Hydroxyacetophenone: I (X = 4-OH), m.p. 215–217°, 70% yield; no type-II product observed.

Anal. Calcd. for $C_{18}H_{15}BF_4O_3$: C, 58.70; H, 4.25. Found: C, 58.34; H, 4.33.

3-Nitroacetophenone: no type-I product; II (X = 3-NO_2), m.p. 174–175.5°, 8% yield.

Anal. Calcd. for $C_{10}H_7BF_2NO_4$: C, 47.10; H, 3.16; N, 5.49. Found: C, 47.20; H, 2.87; N, 5.70.

4-Chloroacetophenone: I (X = 4-Cl), m.p. 267–268°, 17% yield.

Anal. Calcd. for $C_{18}H_{13}BCl_2F_4O$: C, 53.64; H, 3.25. Found: C, 53.65; H, 3.26.

II (X = 4-Cl), m.p. 226.5–228°, 9% yield.

Anal. Calcd. for $C_{10}H_7BClF_2O_2$: C, 49.08; H, 3.27. Found: C, 49.23; H, 3.41.

2-Hydroxyacetophenone.—No product analogous to I or II was isolated. There was instead isolated a 52% yield of III, m.p. 142.5–145°.

Anal. Calcd. for $C_8H_7BF_2O_2$: C, 52.17; H, 3.80. Found: C, 51.78; H, 4.19.

Acknowledgment.—Appreciation is expressed to Mr. H. L. Joyce and Mr. C. B. Strow for their aid in obtaining and interpreting the infrared and n.m.r. spectra.

The Nuclear Magnetic Resonance Spectra of *aci*-Nitro Anions

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Received November 18, 1964

The advent of n.m.r. spectroscopy allows the chemist to observe many phenomena that were previously undiscernible except by interpretive methods such as infrared and ultraviolet data, kinetics, characteristic reactions, etc. One of the most interesting fields lies in the area of reactive intermediates. This paper reports the observation of such an intermediate, i.e., the nitronate anion, by n.m.r. spectroscopy.

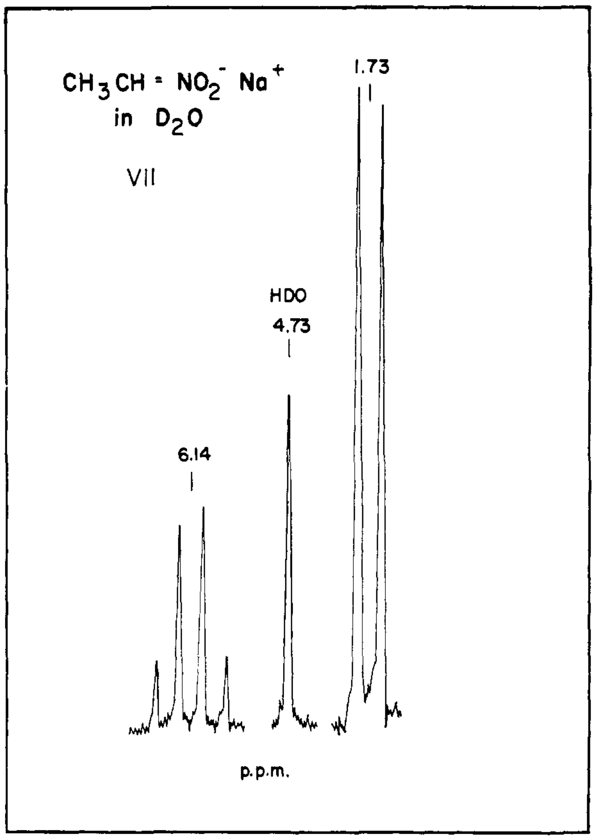
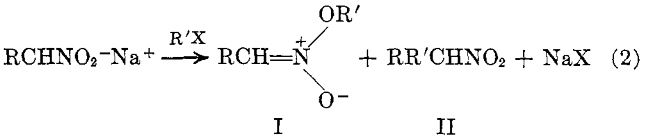


Figure 1.—The 60-Mc. n.m.r. spectrum of the sodium salt of nitroethane (VII) in deuterium oxide at room temperature.

It has been general knowledge for many years that aliphatic nitro compounds dissolve in aqueous base. Using this principle, Holleman[1] (1895), as well as Hantzsch and Schultze[2] (1896), isolated a nitronic acid (eq. 1) by careful acidification of an alkaline solution of the nitro compound. This constituted the first example of the tautomerism of the nitro group.

$$ArCH_2NO_2 \xrightarrow[ROH]{NaOH} ArCHNO_2^-Na^+ \xrightarrow{H_3O^+} ArCHNO_2H \qquad (1)$$

Structural proof for the nitronate anion, as well as for the nitronic acid, has been derived from chemical



$$RCHNO_2^-Na^+ \xrightarrow{R'X} \underset{I}{RCH{=}\overset{+}{N}(OR')O^-} + \underset{II}{RR'CHNO_2} + NaX \qquad (2)$$

evidence. The alkylation[3] of the *aci*-nitro anion provides O-alkylation products (I, a nitronic ester) as well as the C-alkylation products (II). More recently Kornblum and Brown[4] have shown that the *aci*-nitro anion can be completely O-alkylated to the nitronic ester (III).

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[1] A. F. Holleman, *Rec. trav. chim.*, **14**, 121 (1895).

[2] A. Hantzsch and O. W. Schultze, *Ber.*, **29**, 2251 (1896).

[3] A concise review of early alkylation reactions is given by J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183 (1937).

[4] N. Kornblum and R. A. Brown, *J. Am. Chem. Soc.*, **86**, 2681 (1964).

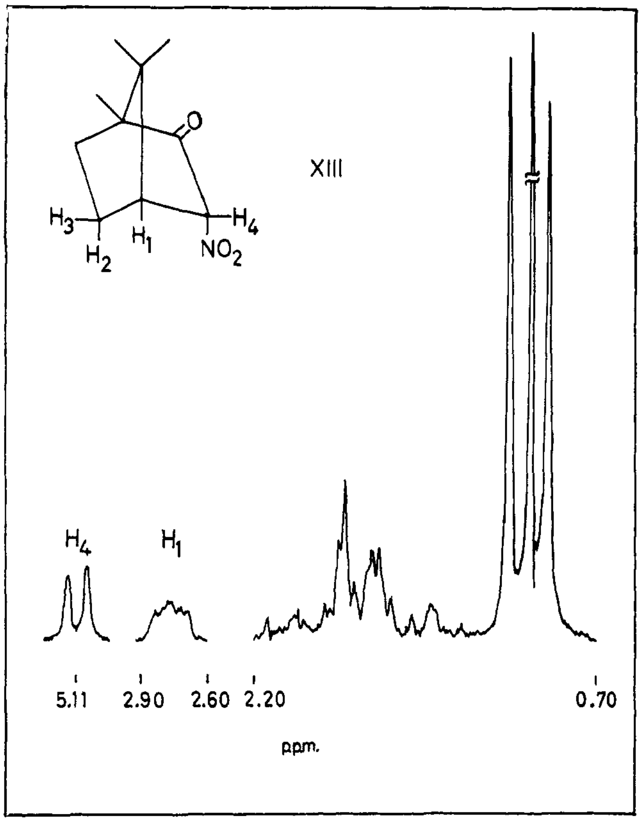


Figure 2.—The 60-Mc. n.m.r. spectrum of α-*d*-nitrocamphor (XIII) in deuterium oxide at room temperature.

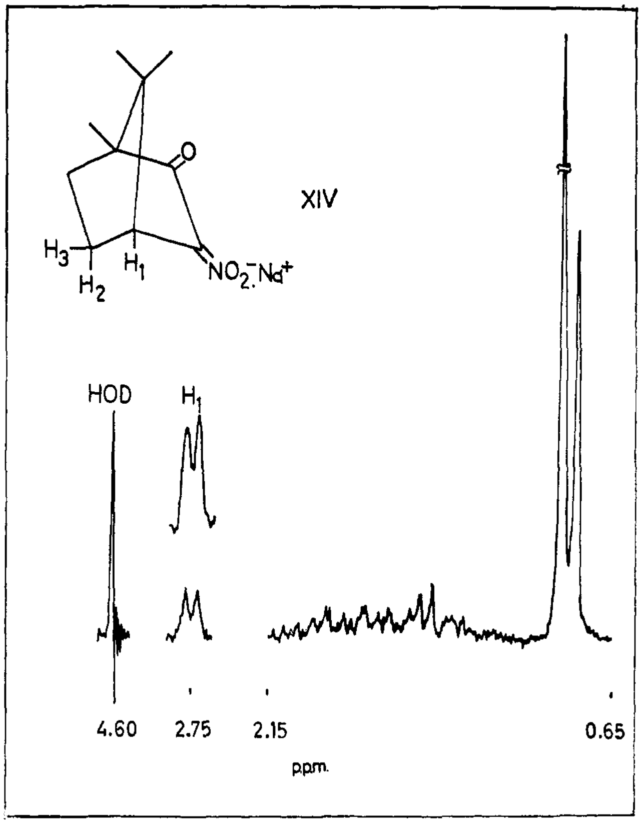
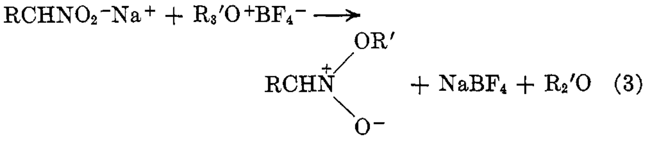


Figure 3.—The 60-Mc. n.m.r. spectrum of the sodium salt of α-*d*-nitrocamphor (XIV) in deuterium oxide at room temperature.



$$RCHNO_2^-Na^+ + R_3'O^+BF_4^- \longrightarrow RCH\overset{+}{N}\begin{matrix} OR' \\ O^- \end{matrix} + NaBF_4 + R_2'O \quad (3)$$

III

The question of the structure of the *aci*-nitro anion was somewhat clouded by the work of Kuhn and Albrecht[5] and later by Shriner and Young[6] when both groups reported the regeneration of an optically active nitro compound, the regeneration being made after proceeding through the anion. Their data indicated that the anion did not completely racemize but to a limited extent retained its stereochemical integrity. This work was neatly disproven by Kornblum, *et al.*,[7] who showed the presence of a small quantity of unaffected, optically active nitrate ester in the pure nitro compound.

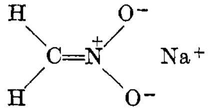
The spectral properties of the alkali metal salts of nitro compounds have been studied very little. Nagakura[8] has shown that nitromethane possesses a weak absorption at 270 mμ in the ultraviolet. Upon increasing the pH, a strong band at 233 mμ was observed and this was attributed to the nitronate anion. Slovetskii, *et al.*,[9] studied the nitronic acid salts in the infrared and found characteristic bands at 1120, 1210, and 1480 cm.$^{-1}$. Feuer, Savides, and Rao,[10] in a more comprehensive study, found similar bands, in addition to another at 734–700 cm.$^{-1}$.

The above physical and chemical data provide support for the commonly written equilibrium (eq. 4) that describes the interaction of a base with a nitro compound. However, it was felt in this laboratory that the

$$R{-}CH_2NO_2 + B^- \rightleftarrows RCHNO_2^- + HB \qquad (4)$$

equilibrium, when using a strong aqueous base, lies far to the right with a large preponderance of the *aci*-nitro form. In order to test this hypothesis, resort was made to proton magnetic resonance spectroscopy.

The sodium derivative of nitromethane (VI), upon dissolution in deuterium oxide at room temperature,



$$\begin{matrix} H \\ \\ H \end{matrix}\!\!>C{=}\overset{+}{N}\!\!<\!\begin{matrix} O^- \\ \\ O^- \end{matrix} \quad Na^+$$

VI

exhibits a single peak at 5.83 p.p.m. The singlet is not persistent, but disappears in about 10 min. owing to deuterium exchange.[11] The large paramagnetic shift (1.55 p.p.m.) of the protons in VI, as compared to nitromethane,[12] indicates a high degree of deshielding characteristic of the olefinic bond.

An apparent anomaly[13] arose when our results with VI were compared to the results of Brownstein,[14] who studied the structure of methazonic acid (O_2NCH_2CH-NOH) and its anions by n.m.r. Brownstein states that

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(5) R. Kuhn and H. Albrecht, *Ber.*, **60**, 1297 (1927).

(6) R. L. Shriner and J. H. Young, *J. Am. Chem. Soc.*, **52**, 3332 (1930).

(7) N. Kornblum, *et al.*, *ibid.*, **69**, 307 (1947).

(8) S. Nagakura, *Mol. Phys.*, **3**, 152 (1960).

(9) V. I. Slovetskii, *et al.*, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 57 (1963).

(10) H. Feuer, C. Savides, and C. N. Rao, *Spectrochim. Acta*, **19**, 431 (1963).

(11) Further work on the kinetics of the deuterium exchange reaction will be reported at a future date.

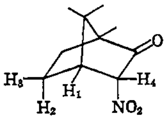
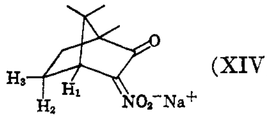
(12) W. Hofman, L. Stefaniak, T. Urbanski, and M. Witanowski, *J. Am. Chem. Soc.*, **86**, 554 (1964).

(13) The authors express their appreciation to the referee for calling attention to the paper by Brownstein.[14]

(14) S. Brownstein, *J. Org. Chem.*, **28**, 2919 (1963).

Table I

P. m. r. Data

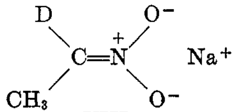
Compd.	Proton or groups of protons	δ values, p.p.m.	Multiplicity	J values, c.p.s.	Integrated peak areas
$CH_2NO_2^-Na^+$ (VI)	CH_2	5.83	1	...	...
$CH_3CHNO_2^-Na^+$ (VII)	CH	6.14	4	6	1
	CH_3	1.73	2		3
$CH_3CH_2CHNO_2^-Na^+$ (XI)	CH	6.03	3	6	1
	CH_2	2.19	5	7.5	2.1
	CH_3	0.96	3	7.5	3.1
$(CH_3)_2CNO_2^-Na^+$ (XII)	CH_3	1.90	1	...	...
 (XIII)[a]	H_1	2.76	?3?	...	1
	H_4	5.11	2	$J_{1,4} = 4.8$	1
 (XIV)[a]	H_1	2.90	2	$J_{1,3} = 3.6$	1
				$J_{1,2} = 0$	...
$HOCH_2CHNO_2^-Na^+$ (XV)	CH	6.27	3	6	...
	CH_2	4.20	3		

[a] α-*d*-Nitrocamphor and α-*d*-nitrocamphor sodium salt were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis., and were used without further purification. [b] Integration of the triplet at 6.27 p.p.m. indicated the presence of 18% of the *aci*-nitro form.

"methazonate anion produced from nitromethane anion in deuterium oxide as solvent, does not contain any deuterium." This statement is not compatible with our observation that VI in D_2O is completely deuterated in approximately 10 min. without any observable, concurrent formation of methazonate anion.

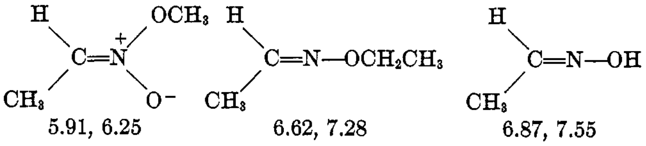
A reasonable explanation of this anomaly is given by Drew, McNesby, and Gordon[15] who found that two literature preparations of VI produced not only VI but also the sodium salt of methazonic acid. It is feasible that Brownstein's preparation of VI contained both salts and when these were dissolved in D_2O, the only spectrum observable by n.m.r., owing to rapid deuterium exchange by VI, was that of the methazonate anion.

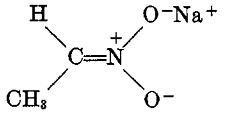
The n.m.r. spectrum of the sodium salt of nitroethane (VII) gave the expected CH_3CH– pattern (see Figure 1). The chemical shifts are revealing, as the methyl doublet (center of group at 1.73 p.p.m., 3 protons) appears in the allylic methyl region,[16] while the vinyl proton appears in the olefinic region[16] as a quartet (center of group at 6.14 p.p.m., $J_{1,2}$ = 6 c.p.s., 1 proton). After approximately 6 hr. at room temperature, a small peak appears in the n.m.r. spectrum at 1.73 p.p.m. This peak represents a small conversion of VII to VIII through deuterium exchange. This reaction[17] is quite slow and after approximately 24 hr. had proceeded to only 80% of completion.[11]



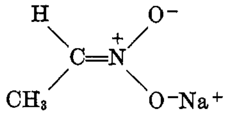
VIII

The chemical shifts of the vinylic protons of these salts are consistent with those observed for the *syn* and *anti* forms of similar structural types.[4] It is of interest that in all compounds studied, the vinyl protons appear as a single quartet and in no instance is there an indication of isomerism such as that indicated by IXa and IXb.



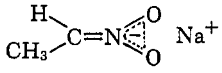


IXa



IXb

This is in contrast to the work of Lustig,[18] who observed two methyl peaks in the n.m.r. spectrum of the sodium salt of acetoxime. The suggestion of Buczkowski and Urbanski,[19] that the sodium salts of nitro paraffins exist as isomers such as IXa and IXb in the solid state, does not appear to hold for aqueous solutions. In actuality, the sodium ion is probably associated with both oxygens, as in X, and the spectrum observed is a time average of both IXa and IXb.



X

The remainder of the salts studied are listed in Table I. The data from compounds XI and XII are readily interpretable in view of that obtained previously. The n.m.r. spectra of the sodium salts can be very useful in the determination of structure of new nitro compounds.[20] Although the following are well-known compounds, this technique is exemplified by comparison of the spectra of α-*d*-nitrocamphor (XIII) and its sodium salt (XIV). Their respective spectra are shown in Figures 2 and 3. It is readily apparent that XIII has

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(15) C. M. Drew, J. R. McNesby, and A. S. Gordon, *J. Am. Chem. Soc.*, **77**, 2622 (1955).

(16) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," International Series Monographs on Organic Chemistry, Vol. V, Pergamon Press Ltd., London, 1959.

(17) The loss in area, compared to the area under the methyl peaks, of the quartet at 6.14 p.p.m. gave an accurate measure of the deuterium exchange reaction.

(18) E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).

(19) Z. Buczkowski and T. Urbanski, *Spectrochim. Acta*, **18**, 1187 (1962).

(20) A paper using this technique has been submitted for publication.

the nitro group in the 3-*endo* position[21] and that $J_{1,4}$ = 4.8 c.p.s. is of the correct magnitude. However, proton H_1 appears as an extremely crude triplet and coupling constants $J_{1,2}$ and $J_{1,3}$ are not obtainable. The sodium salt, XIV, effectively removes H_4 and allows the spectrum to be simplified such that proton H_1 occurs as a doublet with $J_{1,3}$ = 3.6 c.p.s. and $J_{1,2}$ = 0 c.p.s.

$$\underset{\text{XV}}{HOCH_2CH{=}NO_2^-Na^+} \qquad \underset{\text{XVI}}{O_2N{-}CH_2CH_2O^-Na^+}$$

The sodium salt of 2-nitroethanol is a mixture of salts of both possible anions, the *aci*-nitro anion XV and the alkoxy anion XVI. The n.m.r. spectrum of the mixture shows a symmetric triplet centered at 6.27 p.p.m. and another triplet at 4.20 p.p.m. The center peak of the triplet at 4.20 p.p.m. is much larger and represents XVI, while the remainder of the spectrum (see Table I) represents XV.

It is of interest to note that none of the nitro form is present in any of the spectra of the salts except that of XIII. Although the spectrometer is not sensitive beyond 2–3%, it is reasonable that the nitro form is present in only very small amounts.

The observance of the nitronate anion by n.m.r. has practical significance. The base condensation of nitro paraffins with carbonyl compounds in aqueous media can now be observed directly both as to rate of reaction and product formation. It is hoped that further use of this technique will provide a better understanding of these reactions.

Experimental

The n.m.r. spectra were obtained from a Varian A-60 spectrometer using solutions that contained 10–15% of each salt in deuterium oxide. The spectra were calibrated using acetone as an internal standard. The sodium salts of the nitro paraffins were prepared according to known procedures.[3,4] The following preparation of the sodium salt of 1-nitropropane illustrates the procedure used in this study.

An ice-cold solution containing 7.0 g. (0.13 mole) of sodium methoxide in 25 ml. of absolute methanol was added in one portion to an ice-cold solution of 1-nitropropane (12.0 g., 0.13 mole) in absolute methanol (25 ml.). A very small amount of white solid precipitated, and after standing 30 min., ether (100 ml.) was added to precipitate the salt. The white solid was quickly filtered and washed well with anhydrous ether. After drying in a desiccator under high vacuum, the salt weighed 7.6 g. (53%). The infrared spectrum of the salt showed $\lambda_{\max}^{\text{KBr}}$ 2.94, 3.38, 3.47, 6.27, 6.85, 7.30, 8.59, 8.85, 9.61, 10.08, 11.03, and 14.28 μ, while absorption in the ultraviolet occurred at $\lambda_{\max}^{H_2O}$ 232 mμ (ε 9650).

As the procedures for the preparation of the remaining salts were basically identical with the above, only the physical data for each salt are listed below.

Sodium Salt of Nitromethane (VI).—Infrared spectrum (KBr) 2.93, 6.36, 6.93, 7.90, 8.51, 9.74, 10.19, 10.51, and 13.55 μ.

Sodium Salt of Nitroethane (VII).—Infrared spectrum (KBr) 2.95, 3.47, 6.03, 6.22, 7.17, 7.53, 7.86, 8.44, 8.95, 9.55, 11.28, and 13.91 μ; ultraviolet spectrum λ^{H_2O} 228 mμ (ε 9030), 340 (224), and 375 (316).

Sodium Salt of 2-Nitropropane (XII).—Infrared spectrum (KBr) 3.05, 3.42, 6.00, 7.72, 8.63, 10.58, and 12.87 μ; ultraviolet $\lambda_{\max}^{H_2O}$ 222 mμ (ε 10,500).

Sodium Salt of 2-Nitroethanol (XV and XVI).—Infrared spectrum (KBr) 3.10, 3.38, 3.51, 6.40, 7.07, 7.23, 7.57, 8.06, 8.60, 9.22, 9.62, 10.20, 11.52, 12.05, and 13.20 μ.

Sodium Salt of *α-d*-Nitrocamphor (XIV).—Infrared spectrum (KBr) 2.89, 5.93, 6.74, 7.51, 7.68, 7.96, 8.18, 9.07, 10.71, and 11.12 μ; ultraviolet $\lambda_{\max}^{H_2O}$317 mμ (ε 13,100) and 227 mμ (ε 4540).

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[21] R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

Acknowledgment.—The authors wish to thank J. E. McKeon and C. B. Strow, Jr., for their suggestions and helpful discussions.

Volatiles from Oranges. III. The Structure of Sinensal[1]

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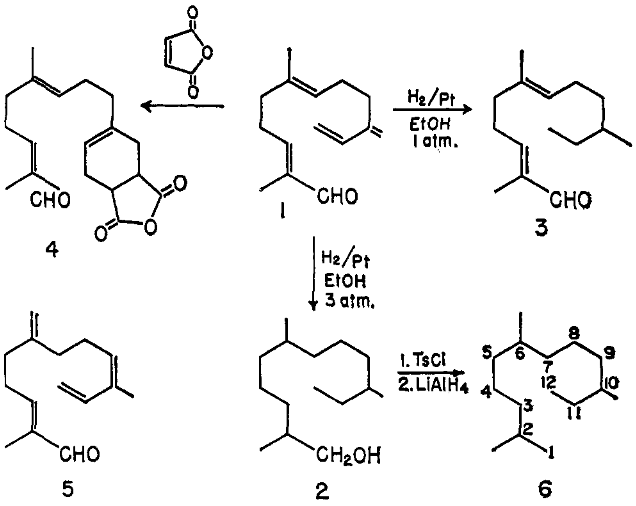
Received November 30, 1964

A new sesquiterpene aldehyde, sinensal ($C_{15}H_{22}O$), has been isolated from orange oil (*Citrus sinensis L.*) and shown to be **1**. Sinensal is a colorless liquid, b.p. ~180° (1 mm.), optically inactive, and has a molecular weight of 218 determined by mass spectrometry. The ultraviolet spectrum shows $\lambda_{\max}^{\text{EtOH}}$ 227 mμ (ε 31,000). Preparation of the 2,4-dinitrophenylhydrazone of sinensal gave a red-orange product with m.p. 87–88°.

Reduction of sinensal with Adams catalyst in ethanol at three atmospheres gave octahydrosinensol (**2**) as an oil. Preparation of the tosylate then reduction with lithium aluminum hydride gave a saturated hydrocarbon with infrared, n.m.r., and mass spectra identical with those of an authentic sample of farnesane (**6**) (see Scheme I).

SCHEME I



An infrared spectrum of sinensal showed peaks at 3.70 and 5.94 μ thus indicating an *α,β*-unsaturated aldehyde.[3] The n.m.r. spectrum (Figure 1) shows a singlet at 9.33 p.p.m. (1H) which confirms an unsaturated aldehyde[4] and also establishes the fact that there are no *α*-protons. This information may also

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[1] Part II: T. H. Schultz, R. Teranishi, W. H. McFadden, P. W. Kilpatrick, and J. Corse, *J. Food Sci.*, **29**, 790 (1964).

[2] One of the laboratories of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 133.

[4] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 62.