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REFERENCES

1. Smouse, T.H., JAOCS 56:747A (1979).
2. Hudson, B.J.F., and S.E.O. Mahgoub, J. Sci. Food Agric. 32:208 (1981).
3. Sonntag, N.O.V., in Bailey's Industrial Oil and Fat Products, Vol. 1, 4th edn., edited by D. Swern, John Wiley and Sons, NY (1979).
4. Stuckey, B.N., in Proceedings of the Symposium on Foods: Lipids and their Oxidation, edited by H.W. Shultz, The AVI Publishing Co., Westport, CT (1962).
5. Bratkowska, I., and H. Niewiadomsk, Acta. Aliment. Pol. 1: 339 (1975).
6. Linow, F., and G. Mieth, Nahrung 20:19 (1976).
7. Bhatia, I.S., N. Kaur and P.S. Svkhija, J. Sci. Food Agric. 29: 747 (1978).
8. Wiedermann, L.H., JAOCS 58:159 (1981).
9. Chapman, G.W., JAOCS 57:299 (1980).
10. Nakayama, Y., K. Saio and M. Kito, Cereal Chem. 58:260 (1981).
11. Nakayama, Y., and M. Kito, Agric. Biol. Chem. 54:2155 (1981).
12. Kanamoto, R., Y. Wada, G. Miyajima and M. Kito, JAOCS 58:1050 (1981).
13. Dittmer, J.C., and R.L. Lester, J. Lipid Res. 5:126 (1964).
14. Yang, S.F., in Methods in Enzymology, Vol. 14, edited by J.M. Lowenstein, Academic Press, NY (1969).
15. Bartlett, G.R., J. Biol. Chem. 234:466 (1959).
16. Terao, J., and S. Matsushita, Agric. Biol. Chem. 45:601 (1981).
17. Asakawa, J., and S. Matsushita, Lipids 15:965 (1980).
18. Carmer, S.G., and M.R. Swanson, J. Am. Statistical Assoc. 68:66 (1973).
19. Watts, B.M., B. Lehmann and F. Goodrich, JAOCS 26:481 (1949).
20. Porter, W.L., in Autoxidation in Food and Biological Systems, edited by M.G. Simic and M. Karel, Plenum Press, NY (1980).
21. Gutfinger, T., and A. Letan, JAOCS 55:856 (1978).
22. Sleeter, R.T., JAOCS 58:239 (1981).
23. Bishov, S.J., and A.S. Henick, J. Food Sci. 40:345 (1975).

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Synthesis of Tetrazole from α, β—Unsaturated Carbonyl Fatty Acid

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ABSTRACT

Methyl 4-oxo-*trans*-2-octadecenoate (II), when treated with excess hydrazoic acid in the presence of BF_3-etherate, produced 66% methyl 5-aza-nonadec-*trans*-2-enoate (4,5-d)-tetrazole (III), 10% methyl 5-aza-nonadec-4-oxo-*trans*-2-enoate (IV) and 7% pentadecamide (V). Individual products were characterized by spectral and elemental methods.

INTRODUCTION

Five-membered diunsaturated heterocyclics with a single carbon and four nitrogen atoms are known as tetrazoles. The method of Schmidt (1) for the synthesis of tetrazole involves rearranging 1 m of ketone with 2 m of hydrazoic acid in the presence of strong acids. Previously, when simple keto fatty acids were treated with hydrazoic acid, only amides were produced (2).

The first example of the formation of tetrazole in the steroidal and triterpenoid field was reported by Barnes et al. (3). But, in the field of fatty chemistry, tetrazoles have not been reported. Tetrazoles have biological as well as nonbiological applications (4,5). Some applications include their use as propellants, dyestuffs, catalysts in polymerizations, intoxicants, sedatives and analgesics (4). They have also been used successfully to produce convulsions in the shock treatment for certain psychoses. These convulsive effects have extended their use as bird-management chemicals (5). With the discovery of these applications of tetrazoles, efforts were made for their synthesis.

EXPERIMENTAL PROCEDURE

The IR spectra were obtained with a Perkin-Elmer 621 spectrophotometer. A Backman DK-2A spectrophotometer was applied for the ultraviolet (UV) spectra. NMR were obtained with a Varian A-60 spectrophotometer. Chemical shifts were reported in relation to tetramethylsilane (TMS) in δ(ppm). The samples were run as 10% solution in $CDCl_3$. The abbreviations "s, m, d, t and br" stand for singlet, multiplet, doublet, triplet and broad. An AEI MS-902 spectrophotometer was used to record the mass spectra. Thin layer chromatography (TLC) plates were coated with silica gel G and developed with a mixture of benzene-ether-acetic acid (70:30:1, v/v). The spots were visualized by charring with a 20% aqueous solution of perchloric acid. The synthesis of (II) from (I) was carried out by the method of Nakayama et al. (6). Compound II has identical spectral and cochromatographic behavior as an authentic sample (7).

Reaction of (II) with Excess of Hydrazoic Acid: (Scheme 1)

The method of Moural and Syhora (8) was used to prepare a hydrazoic acid solution. Methyl 4-oxo-*trans*-2-octadecenoate (II) (2 g) in benzene (10 mL) was added drop by drop over a period of 4 hr to a cooled solution of hydrazoic acid and boron-trifluoride (1.5 ML, freshly distilled). The mixture was stirred for 72 hr and the solvent was removed under reduced pressure. The residue was dissolved in ether, washed with water, sodium bicarbonate (5%), water and dried over anhydrous Na_2SO_4. When the ether had evaporated, a solid (1.87 g) was obtained that was chromatographed over silica gel (40 g) to give three products. Elution with benzene:ether (96:4, v/v) gave (III). Crystallization at 10 C from petroleum ether (60-80 C) gave a yield of 66%, m.p. 52 C. (Found: C, 65.01%; H, 9.6%; N, 15.4%. Calcd. C, 65.1%; H, 9.7%; N, 15.9%.) Further elution with benzene:ether (85:15, v/v) gave (IV). The yield is 10%, m.p. 96 C. (Found: C, 69.6%; H, 10.5%; N, 4.0%. Calcd. C,

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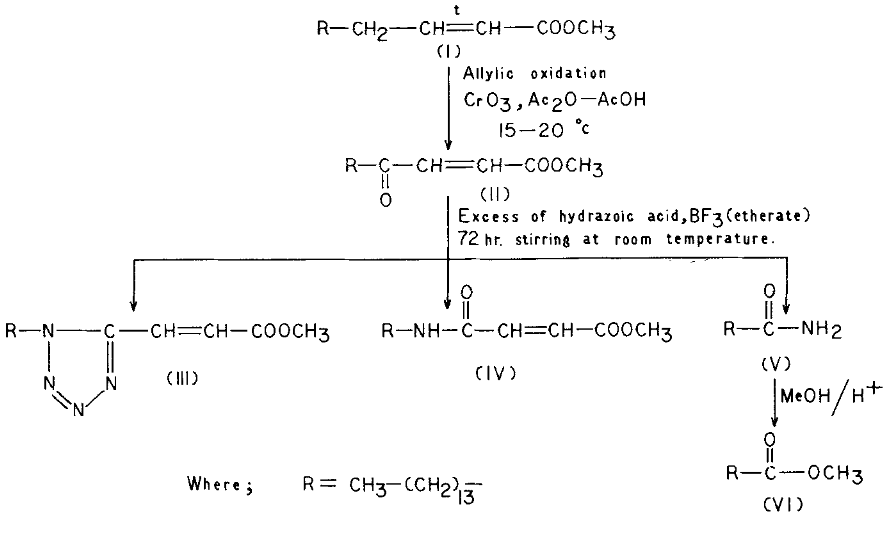

SCHEME 1

70.1%; H, 10.8%; N, 4.3%.) Final elution with benzene: ether (80:20, v/v) gave (V). The yield is 7%, m.p. 100 C. (Found: C, 76.4%; H, 12.7%; N, 5.6%. Calcd. C, 76.6%; H, 12.9%; N, 5.8%.)

RESULTS AND DISCUSSION

Methyl 4-oxo-*trans*-2-octadecenoate (II), when treated with excess of hydrazoic acid in the presence of BF_3-etherate at room temperature for 72 hr, yielded a solid reaction mixture, which on column chromatography was separated into three products.

Compound (III) was shown to be a tetranitrogenous product by its elemental analysis $C_{19}H_{34}O_2N_4$, m.p. 52 C. Its IR spectrum exhibited the bands at 3060w (C=C), 1650 (C=C), 1720 ($-\underline{CO}OCH_3$), 1505, 1460, 1375 (C=N, N=N), 1070, 1030, 1005 (C—O) and 970 cm^{-1} (*trans* olefin). The NMR spectrum of this compound established the structure of tetrazole: δ7.81d (1H, $-C\underline{H}=CH-COOCH_3$, J = 14 Hz), 6.73d (1H, $-CH=C\underline{H}-COOCH_3$, J = 14 Hz). The coupling constant established a *trans* configuration for the double bond, 3.82s (3H, $\overset{O}{\overset{\|}{C}}OC\underline{H}_3$), 2.98t (2H, $C\underline{H}_2-N - C-$, J = 7 Hz), 1.3br,s(chain—$C\underline{H}_2$) and 0.9t (3H, terminal $C\underline{H}_3$). The signal at δ2.98 shows that nitrogen is in between the alkyl chain and the oxo group. If the nitrogen location is reversed (in between oxo and double band) then the signals from $-C\underline{H}_2$ and β-protons would appear in a little higher field (9).

The mass spectrum of methyl 5-aza-nonadec-*trans*-2-enoate, (4,5-d)-tetrazole (III) confirmed the proposed structure: molecular ion peak at m/z 350 (Fig. 1). The fragmentations confirm the location of the tetrazole ring (Fig. 1).

The compound (IV), m.p. 96 C was shown to be mono-

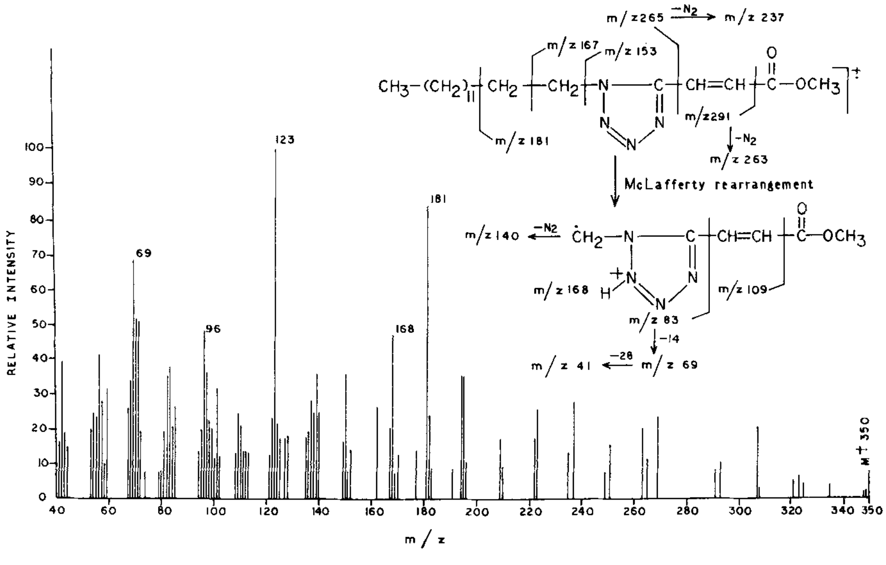

FIG. 1. Methyl 5-azanonadec-*trans*-2-enoate (4,5-d)-tetrazole.

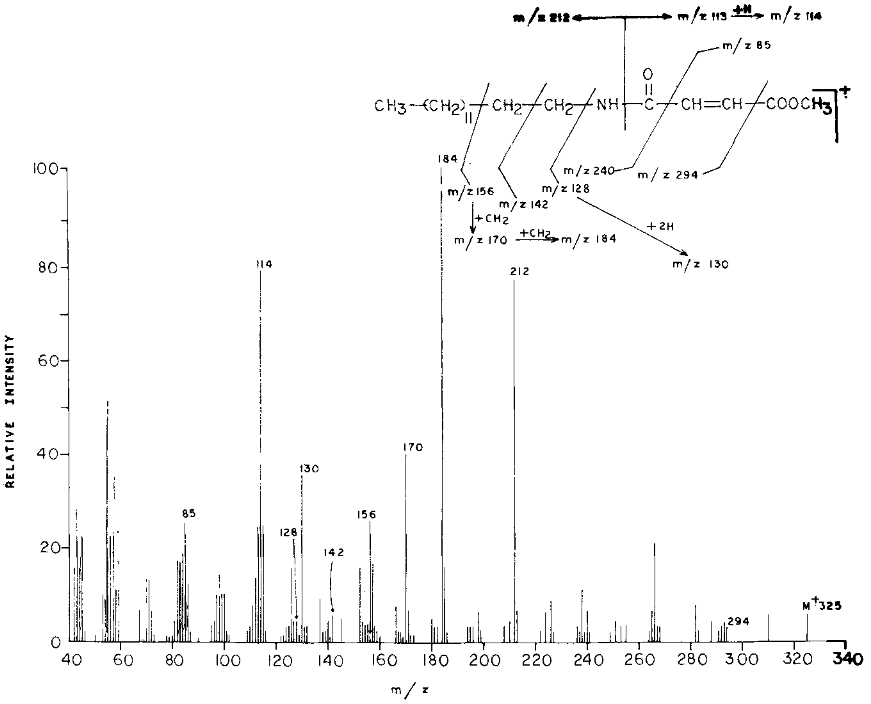

FIG. 2. Methyl 5-azanonadec-4-oxo-*trans*-2-enoate.

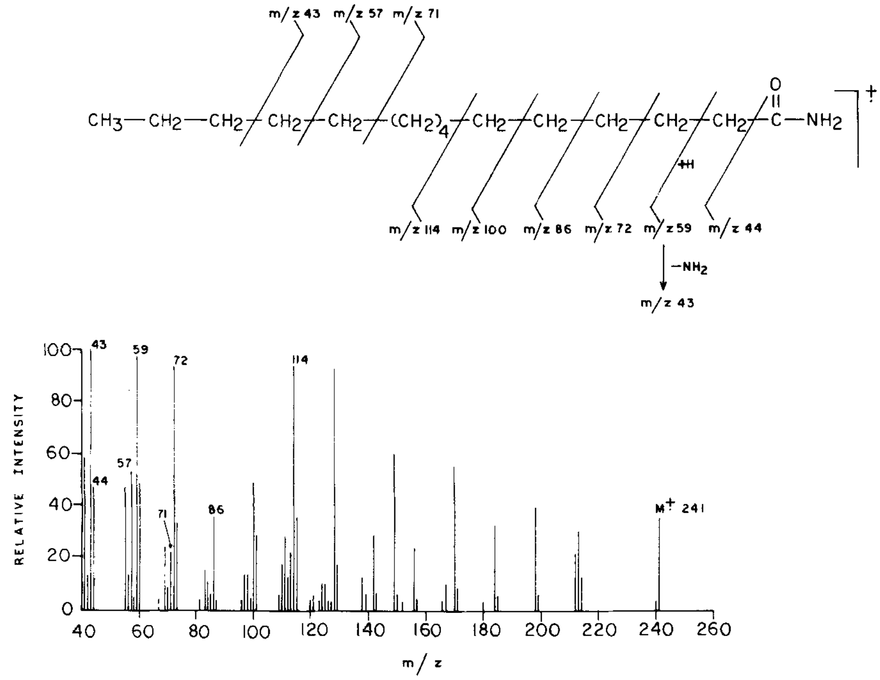

FIG. 3. Pentadecamide.

nitrogenous by its elemental analysis ($C_{19}H_{35}O_3N$). Its IR spectrum exhibited bands at 3310 (NH str.), 3060w (C=C), 1650, 1620 ($\underline{CO}NH$), 1540, 1520 (NH bending), 1705 ($\underline{CO}OCH_3$), 1160, 1030 (C–O) and 990 cm^{-1} (*trans* olefin). The NMR spectrum gave signals at δ6.94d (2H, $-C\underline{H}=C\underline{H}-COOCH_3$, J = 4 Hz), 6.67m (1H, $N\underline{H}$, D_2O exchangeable), 3.82s (3H, $COOC\underline{H}_3$), 3.35m (2H, $-C\underline{H}_2-NHCO$), 1.35br,s (chain $-C\underline{H}_2$) and 0.88t (3H, terminal $C\underline{H}_3$). Mass spectrum of the compound (IV) further confirmed the structure as methyl 5-azanonadec-4-oxo-*trans*-2-enoate (IV). Molecular ion peak is recorded at $M^{+\cdot}$ 325 and various mass fragmentations are postulated (Fig. 2).

The compound (V) was characterized as pentadecamide on the basis of its elemental analysis and spectral studies. The compound obtained as a solid, m.p. 100 C, was analyzed as $C_{15}H_{31}ON$. Its IR spectrum projected bands at 3350, 3180 (NH_2 Str.), 1650, 1620 ($CONH_2$), 1410 (C–N) and 1160 cm^{-1} (NH_2). The NMR spectrum exhibited peaks at δ 5.7m (2H, $-CON\underline{H}_2$), 2.16m (2H, $-C\underline{H}_2-CO-NH_2$), 1.3br,s (chain $-C\underline{H}_2$) and 0.9t (3H, terminal $C\underline{H}_3$). The molecular ion peak is recorded at $M^{+\cdot}$ 241 and different mass fragmentations are consistent (Fig. 3) with the structure given.

Additional evidence for structure (V) was obtained by its conversion to methyl pentadecanoate (VI) with MeOH/H^+. The methyl ester (liquid) was analyzed correctly for

$C_{16}H_{32}O_2$. Its IR spectrum gave bands at 1740 cm^{-1} ($\underline{C}OOCH_3$). The NMR signals are at δ3.6s (3H, $COOC\underline{H}_3$), 2.25m (2H, $-C\underline{H}_2-COOCH_3$), 1.25br,s (chain $-C\underline{H}_2$) and 0.9t (3H, terminal $C\underline{H}_3$).

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REFERENCES

1. Wolft, H., Organic Reactions, Vol. 3, edited by Roger Adams, John Wiley and Sons, Inc., New York, 1947, 307-336.
2. Ahmed, F., S.F. Siddiqi and S.M. Osman, Fette Seifen Anstrich., 1983 (in press).
3. Barnes, C.S., D.H.R. Barton, J.C. Fawcett, and B.R. Thomas, J. Chem. Soc. 2339 (1952).
4. Beckmann, Pharmocology, 2nd Edn., Saunders, Philadelphia, 1961, 318-23.
5. Benson, F.R., Heterocyclic Compounds, Vol. 8, edited by R.C. Elderfield, John Wiley and Sons, Inc., New York, 1967, 1-104.
6. Nakayama, M., S. Shinke, Y. Matsushita, S. Ohira and S. Hayashi, Bull. Chem. Soc., Jpn. 52:184 (1979).
7. Ahmad, M.U., M.S. Ahmad and S.M. Osman, JAOCS, 55:491 (1978).
8. Moural, J. and K. Syhora, Collect. Ozexk. Chem. Commun., 35:2018 (1970).
9. Barluenga, J., F. Azner and R. Liz, J. Chem. Soc. Chem. Comm., 1181 (1981).

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A Study of Dilatation and Acoustic Propagation in Solidifying Fats and Oils: I. Theoretical

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ABSTRACT

A theoretical relationship is presented relating acoustic velocity to dilatation in two-phase systems. The theory is based on studies of seismic propagation by Kuster and Toksöz, who include acoustic propagation in a fluid matrix containing spherical or spheroidal solid inclusions as a special case of their theory. The relationship presented in this paper applies in the long wavelength limit and predicts a linear relationship between acoustic dilatation and volume dilatation in crystallizing liquids, when the acoustic dilatation is much less than unity. I anticipate that this theory may lead to the application of acoustics in the assessment of a wide range of crystallizing systems such as oils.

INTRODUCTION

A number of workers have studied the propagation of ultrasound in liquid oils (1,2,3), in milk (4) and in solidifying coconut oil (5). In addition, ultrasonics have been widely used to study phase transitions in other systems, and a number of workers have applied ultrasonics to the measurement of compressibility and other parameters in a wide variety of biphasic materials (7,8,9). In this paper I will concern myself solely with a two-phase system where the liquid forms the continuous matrix in which the solid phase is suspended. However, the theory on which I base my conclusions is general enough to allow extension to other situations.

THEORY

The treatment in this paper is based on the work of Kuster and Toksöz (7), who in turn developed their treatment of the subject from Ament (10). The problem may be stated as solving the equations of motion for acoustic waves in two-phase media. A number of alternative formulations of the problem exist (9) but that of Kuster and Toksöz is the most convenient for my purpose. Although Kuster and Toksöz's formulation applies to seismic waves in 2-phase media, propagation in a fluid matrix with spherical or spheroidal solid inclusions is included as a special case. In this case, a shear wave cannot be supported and a bulk compressive wave propagates in the liquid matrix. The solid inclusions are assumed to have a mean diameter of much less than one acoustic wavelength. Definitions of the symbols used in the treatment described below are given in Table I.

The starting equations are in Table II. Equations 1-4 are identical to equations 24-26 of Kuster and Toksöz. Note that equation 1 can be obtained by assuming that the effective compressibility of the system is simply the volume average of the compressibilities of the solid and liquid phases and that in equation 2, the ordinary composition rule for densities, equation 5, is modified by the motion of the solid inclusions, relative to the fluid. In addition, v* is the acoustic velocity that is actually measured for the complete system.

The following equations may be derived from equations 1-4 and 6:

$$K = K^*(1 - \epsilon\kappa) \qquad [7]$$

where $\kappa = 1 - K/K'$.

$$\rho^* = \rho(1 + \epsilon R)/(1 - 2\epsilon R) \qquad [8]$$

where $R = (\rho' - \rho)/(\rho + 2\rho')$.

$$\Delta v/v^* = 1 - \sqrt{K\rho^*/K^*\rho} \qquad [9]$$

We call this parameter the acoustic dilatation.

We can substitute for K* and ρ* in equation 9, from equations 7 and 8 to obtain:

$$(1 - \frac{\Delta v}{v^*})^2 = (1 - \epsilon\kappa)(1 + \epsilon R)/(1 - 2\epsilon R) \qquad [10]$$

The above equation can be reduced under the following assumptions. If $\Delta v/v^* \ll 1$ and $\epsilon R \ll 1$ then

$$\epsilon = \frac{\Delta v}{v^*}\, 2/(\kappa - 3R) \qquad [11]$$

The problem of relating ε, the volume fraction of solid, to the dilatation D, as measured in conventional oil dila-