Pyrolysis of Some Acetoxynonenes[1]

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ABSTRACT

Current studies on odor thresholds of hydrocarbons autoxidatively derived from fats required the preparation of 1,3- and 2,4-nonadienes. The pyrolysis of 3-acetoxy-1-nonene (I) and 4-acetoxy-2-nonene (II) was investigated as a route to 1,3- and 2,4-nonadienes, respectively. The acetates were pyrolyzed over pyrex helices at 400 C. Distilled pyrolyzates were characterized by mass, UV, IR, and NMR spectroscopy, along with gas chromatography. Since II gave approximately a 50:50 mixture of the 1,3- and 2,4-isomers, an earlier observation was confirmed that allylic esters may rearrange before elimination. Ester I gave about 85% of the 1,3-isomer and 15% of the 2,4. Presumably the 2,4-isomer arises from thermal rearrangement. In pyrolysis, both I and II give conjugated products almost exclusively. UV spectroscopy shows ϵ values in the 24,000 to 28,000 range.

INTRODUCTION

Current studies on odor threshold of hydrocarbons autoxidatively derived from fats required samples of 1,3- and 2,4-nonadienes. In 1963, 1,3-nonadiene was prepared by the Wittig reaction in 34% yield (1). The preparation of 2,4-nonadiene has never been reported.

Certain organic compounds fragment on heating to yield an olefin and other products. Pyrolyses of xanthates and tetraalkylammonium hydroxides are known as the Chugaev and Hofmann elimination reactions, respectively. A third class of compounds to undergo pyrolysis is composed of organic esters, particularly acetates and benzoates. Pyrolysis of esters has been studied extensively from both a mechanistic and synthetic aspect. But only since the advent of gas chromatography has the reaction been well understood. DePuy and King (2) reviewed pyrolysis reactions to 1960.

Although pyrolysis reactions of saturated aliphatic acetates is well known, it has limited synthetic utility because mixtures of olefins are produced. Esters of secondary and tertiary alcohols give mixtures of olefins, whereas esters of primary alcohols give 1-olefins (3).

Rarely has the pyrolysis of unsaturated esters as a route to conjugated dienes been recorded. In 1941, Van Pelt and Wibaut (4) reported that the pyrolysis of 4-acetoxy-2-hexene gave 2,4-hexadiene as the only olefin from the reaction. Later, Greenwood (5) showed that the pyrolysis of 4-acetoxy-2-heptene gave a mixture of 1,3- and 2,4-heptadienes. He was able to isolate an ester fraction from the reaction products, which had undergone isomerization but not elimination. Similar isomerizations have been reported by Marvel and Brace (6) and by Grummitt and Mandell (7).

Although nonconjugated nonadienes have been prepared by ester pyrolysis, no references were found for conjugated nonadienes. Esters containing terminal unsaturation cannot rearrange via classical mechanisms during pyrolysis, and should offer a simple route to conjugated diolefins; however, little work has been done in this area. The report summarizes the first preparation of 1,3- and 2,4-nonadienes by pyrolysis of unsaturated acetates.

MATERIALS AND METHODS

Pyrolysis Equipment

A pyrolysis column was prepared by sealing 14/20 ground glass joints to a 375 x 12 mm Pyrex glass tube. The outside was wrapped with heating wire (10 ft of 1.2 ohms/ft), asbestos and glass tape. Column packing consisted of 1/4 in. Pyrex helices purchased from Scientific Glass Apparatus Co., Bloomfield, New Jersey. A thermocouple was placed at the middle of the tube and was monitored by a MiniMite potentiometer. Heating was accomplished by routing 110 v house current first through an ammeter and then through a large Variac. The pyrolysis column was mounted vertically and held by burette clamps.

Spectroscopic Techniques

UV spectra were recorded on a Cary spectrophotometer. The spectra were taken in spectroquality isooctane over the 200-400 nm range.

IR spectra were obtained in a carbon disul-

Proton	Calculated[a]	Found
α-Methyl	3.0	1.5
α-Methylene	2.0	2.5
Olefinic	4.0	4.0

[a]For 2,4-nonadiene.

fide solution on a Perkin Elmer Model 621 IR spectrophotometer.

NMR spectra were recorded on a Varian Model HA 100 spectrometer. Deuterated chloroform was the solvent and tetramethylsilane (TMS) the internal standard. Chemical shifts were measured as parts per million from TMS.

Mass spectra were taken on a Bendix Time-of-Flight mass spectrometer equipped with a heated inlet and in tandem with a gas chromatograph. The data were normalized and plotted with the aid of an 1130 IBM digital computer.

Alcohols

Non-2-ene-4-ol. n-Amylmagnesium bromide was prepared from 24.3 g of magnesium (1.0 mole) and 151.0 g of 1-bromopentane (1.0 mole). *trans*-2-Butenal (74 g, 1.0 mole) was dissolved in 100 ml of dry ether and added to Grignard reagent at 0 C. The intermediate was decomposed with saturated ammonium chloride, extracted with ether, washed with water until neutral, and dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product distilled under reduced pressure to yield a fraction boiling at 57 C at 0.8 mm Hg. The yield was 80.0 g, 56.5% of theory. Analysis: C, 75.98; H, 12.76. Found: C, 76.88; H, 12.91.

A phthalate ester was prepared according to Airs et al. (8). The derivative was recrystallized from EtOH-CS$_2$ (1:1); mp 80-81 C. Analysis: C, 70.30; H, 7.64. Found: C, 70.58; H, 7.58. The neutral equivalent was 284; theory, 290.

Non-1-ene-3-ol. It was purchased from Aldrich Chemical Co. and was 99+% pure by gas liquid chromatography (GLC).

Authentic 1,3-Nonadiene. This was purchased from Chemical Samples Co. and was 97% pure.

4-Acetoxy-2-nonene. Heating unsaturated alcohols in the presence of acetic anhydride is said to cause rearrangement (9). For this reason mild reaction conditions were chosen for the preparation of acetoxynonenes. The possibility that rearrangement of the acetates occurred during synthesis must be considered. However, NMR spectroscopy showed that no rearrange-

ment occurred during synthesis. Acetic anhydride (18.0 g, 0.18 mole) was added dropwise (at 25 C) to a solution of 25.0 g (0.18 mole) non-2-ene-4-ol and 8 ml of dry pyridine. After the mixture stood for three days at room temperature, the ester was extracted into petroleum ether, washed with dilute hydrochloric acid, and dried over sodium sulfate. Removal of solvent under reduced pressure gave 32.75 g product. GLC indicated the presence of two small unidentified impurities. Analysis: C, 71.67; H, 10.94. Found: C, 71.31; H, 11.39.

3-Acetoxy-1-nonene. To a stirred solution containing 40.0 g (0.281 mole) non-1-ene-3-ol dissolved in 100 ml chloroform, 23.0 g (0.295 mole) pyridine was added. A solution containing acetyl chloride (24.6 g, 10% excess) dissolved in 50 ml chloroform was then added dropwise at 25 C. The crude ester was purified in the manner described for 4-acetoxy-2-nonene. Despite the excess acetyl chloride, capillary GLC on DEGS revealed unreacted alcohol.

The alcohol was removed by passage through alumina as follows: Alumina (Fisher chromatographic grade 80-200 mesh) was packed into a 38 x 1.2 cm glass column fitted with a 500 ml reservoir. The crude ester (54.0 g) was dissolved in 50 ml hexane and poured on top of the column packing. Nitrogen was used to force the ester through the column until the solvent level was just to the edge of the adsorbent. Hexane (500 ml) was added to elute the ester from the column. The solvent was stripped off on a rotating evaporator, and 49 g (90.7%) of ester was recovered. Gas chromatography on a 6 ft x 1/4 in., 3% JXR column showed complete removal of unreacted alcohol. The crude ester was distilled through a 6 in. Vigreux column to give a product boiling at 57-60 C at 0.70 mm Hg. Overall yield was 78%. NMR supported the structures as 3-acetoxy-1-nonene. Analysis: C, 71.67; H, 10.86. Found: C, 70.74; H, 10.80.

Pyrolysis Reactions

Pyrolysis of 4-Acetoxy-2-nonene. 4-Acetoxy-2-nonene (13 g, 0.071 mole) was placed in a dropping funnel fitted with a joint adapted to the pyrolysis column. The ester was allowed to pass dropwise through the column maintained at 400 C. Nitrogen (30 ml/min) was used to sweep the pyrolyzate through the column. The pyrolyzate was collected in a U-trap cooled with dry ice and methyl Cellosolve. The pyrolyzate (10.0 g) was washed with bicarbonate, then with water until neutral, dried over sodium sulfate, and distilled under reduced pressure. A 3.06 g fraction boiling at 61-64 C at 3

mm was collected. Analysis: (Calculated for 2,4-nonadiene) C, 87.00; H, 13.00. Found: C, 87.11; H, 12.99.

Pyrolysis of 3-Acetoxy-1-nonene. 3-Acetoxy-1-nonene (21.14 g, 0.115 mole) was pyrolyzed at 400 C. The pyrolyzate was treated in a manner similar to the pyrolyzate from 4-acetoxy-2-nonene. Distillation of the pyrolyzate (8.67 g) at 10 mm gave 4.13 g of dienes boiling at 83-85 C.

Hydrogenation of Dienes From Pyrolysis of 4-Acetoxy-2-nonene. The pyrolyzate (0.103 g) was hydrogenated in 3 ml of ethanol with 10 mg of 10% palladium catalyst (Matheson, Coleman and Bell). The apparatus consisted of a small, magnetically stirred hydrogenation flask connected to a mercury leveling bulb manometer. The hydrogenation was conducted at room temperature for 1 hr during which the major portion of hydrogen was taken up in 15 min. Hydrogen uptake after 1 hr was 36 ml; theory, 41.8 ml corrected to STP.

RESULTS AND DISCUSSION

The dienes prepared from the pyrolysis of 4-acetoxy-2-nonene were characterized by GLC on squalane and β,β'-oxydipropionitrile. A homologous series of both conjugated and nonconjugated diolefins was chromatographed isothermally on the squalane column at 100 C to aid in identifying pyrolysis products.

Two major peaks were observed plus a smaller peak having a retention time identical to a C_9 nonconjugated diolefin. The first major peak corresponded on the log-log plot to neither a nonconjugated, nor a conjugated C_9 diolefin, nor a higher or lower homolog. Since the elemental analysis suggested a C_9H_{16} formula, a sample was hydrogenated over a palladium catalyst (Materials and Methods). Although the hydrogen uptake was slightly less than theory (36.0 vs. 41.8 ml), it clearly indicated the product's diene nature. GLC of the hydrogenated material (on squalane) gave a peak having a retention time identical to *n*-nonane, and chromatography on squalane as an admixture with *n*-nonane gave a single peak. The foregoing evidence indicated that the pyrolyzate was a mixture of isomeric nonadienes.

Mass spectrometry showed that the pyrolyzate had a molecular weight of 124, identical to that of a C_9 diolefin, but failed to corroborate the structure as 2,4-nonadiene.

The pyrolyzate from 4-acetoxy-2-nonene was analyzed by NMR spectroscopy (Table I). NMR showed four theoretical olefinic protons, a condition which establishes two double bonds in the pyrolyzate. Conclusive proof that the
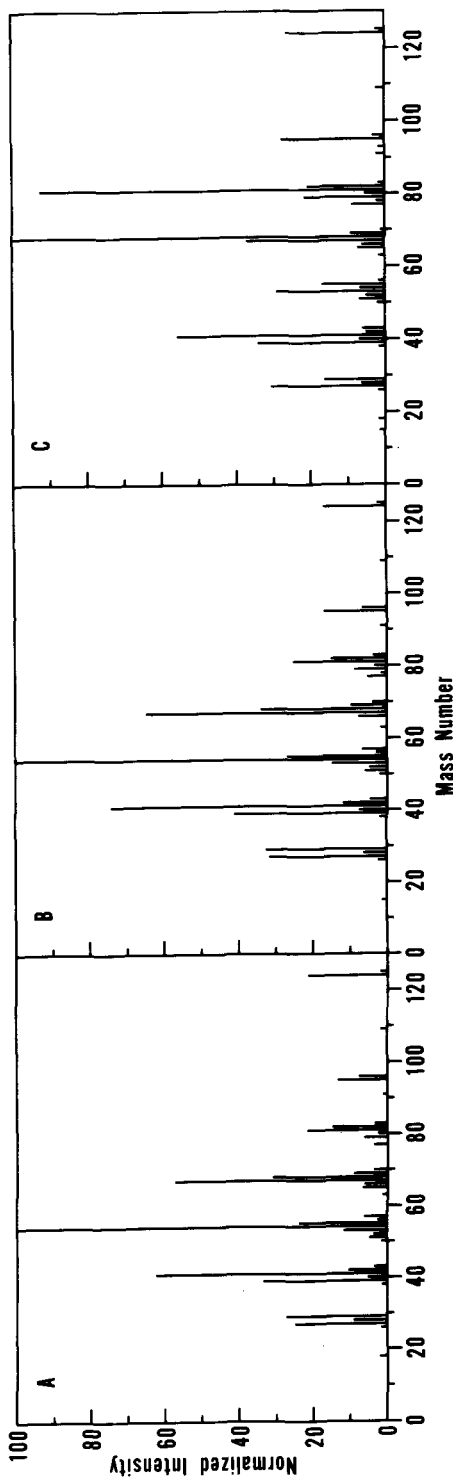

FIG. 1. Mass spectra of nonadiene isomers: (A) Authentic 1,3-nonadiene, (B) fraction 1 isolated from preparative GLC, and (C) fraction 2 isolated from preparative GLC.
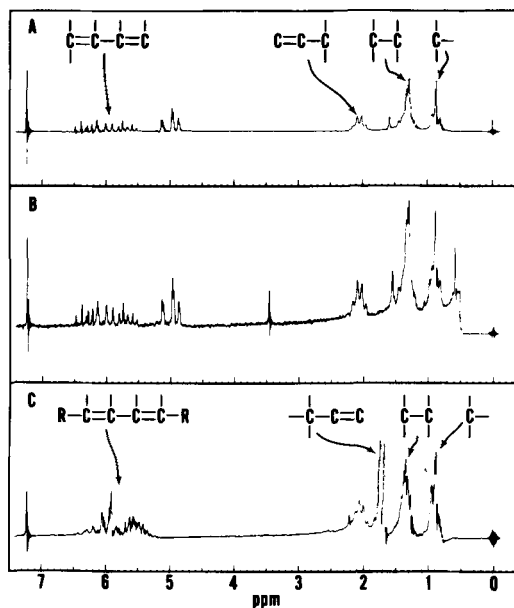
FIG. 2. NMR spectra of nonadiene isomers from pyrolysis of 4-acetoxy-2-nonene: (A) Authentic 1,3-nonadiene, (B) fraction 1 from preparative GLC column, and (C) fraction 2 from preparative GLC column.
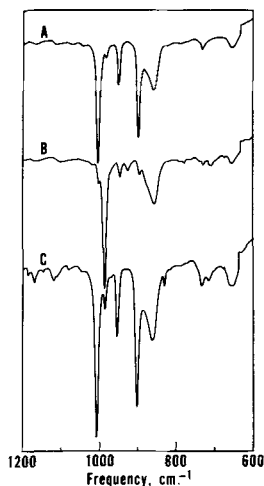

FIG. 3. IR spectra of nonadiene isomers. Solvent carbon disulfide. (A) Fraction 1 from preparative GLC column, 17.7 mg/ml, path length 0.01 cm; (B) fraction 1 from preparative GLC column, 16.0 mg/ml, path length 0.01 cm; and (C) whole pyrolyzate from 3-acetoxy-1-nonene, 21.2 mg/ml, path length 0.021 cm.

pyrolyzate was indeed a mixture of positional isomers is indicated by the number of α-methyl protons. Table I reveals that instead of the three expected (calculated as 2,4-nonadiene) α-methyl protons, only 1.5 were found. Since GLC indicated approximately a 50:50 distribution between the two major components and NMR showed only half the α-methyl protons, further evidence was obtained that the pyrolysis of 4-acetoxy-2-nonene gives a 50:50 mixture of 2,4- and 1,3-nonadienes.

To further characterize the pyrolyzate from the allylic ester, preparative GLC was investigated as a means of separation. Since the boiling point of the pyrolyzate was fairly narrow (61-63 C, 3 mm), it would appear that ordinary distillation could not be used to separate the two isomers. Separations of positional isomeric olefins by spinning band columns, however, have been reported (5). Repeated injections of 100 μl each were made until enough material was collected for analysis by NMR, IR, UV and mass spectroscopy.

Rechromatography (on squalane) of the fractions from preparative GLC showed that purities of about 90% resulted, with each fraction containing about 10% of the other isomer. In addition, GLC of the preparative GLC fractions on squalane showed that the elution order of the components was the same on both the squalane and preparative columns. Purity did, however, permit conclusive identification of the dienes.

The normalized mass spectra of the preparative GLC fractions are reproduced in Figure 1. The spectrum for an authentic sample of 1,3-nonadiene is included for comparison. The mass spectra for the preparative GLC fractions are difficult to interpret because of rearrangement peaks at m/e ratios of 54 and 68. In fraction 1 (Fig. 1, Part B) respective m/e peaks at 27 and 67 indicate cleavage occurred between carbons 2 and 3 and carbons 5 and 6. The base peak at m/e 54 is a rearrangement peak and cannot be explained by a simple carbon-carbon cleavage. Likewise, the base peak m/e 68 in fraction 2 (Fig. 1, Part C) is a rearrangement peak. If Parts A and B of Figure 1 are compared, spectra of the authentic sample of 1,3-nonadiene and fraction 1 from the preparative GLC column are identical.

In his review on mass spectrometry of organic compounds, Beynon (10) points out the difficulty of establishing the structure of simple olefins because of similarity in their mass spectra. It is, therefore, not surprising that the mass spectra of the nonadiene isomers are complex and difficult to interpret.

The NMR spectra of the preparative GLC fractions are reproduced in Figure 2, along with that of an authentic sample of 1,3-nonadiene. When the authentic sample (Part A) and fraction 1 (Part B) from the preparative GLC

column are compared, it is evident that the materials are identical. The doublet at 1.8 ppm in peak 3 (Part C) results from the olefinic methyl proton and confirms the assignment of fraction 2 as the 2,4-nonadiene isomer.

IR spectroscopy also supported the structural assignments of the preparative GLC fractions. Fraction 1 has strong bands at 898 and 1002 cm⁻¹, both characteristic of terminal (vinyl) conjugated polyenes (11) (Fig. 3). Fraction 2 has a strong band at 988 cm⁻¹ indicative of *trans,trans* unsaturation. *Trans,trans* unsaturation could only result from an internal conjugated system.

The pyrolysis products from 3-acetoxy-1-nonene were analyzed by GLC on $\beta\beta'$-oxydipropionitrile. Results indicate an isomer distribution of about 85% 1,3-nonadiene and 15% 2,4-nonadiene. A similar composition was obtained by GLC on squalane.

These studies indicate that pyrolysis of 3-acetoxy-1-nonene and 4-acetoxy-2-nonene gives conjugated products almost exclusively. UV spectroscopic data for the whole pyrolyzate from 4-acetoxy-2-nonene, before and after fractionation by preparative GLC, are given in Table II.

The ϵ_{max} and ϵ values are in the range reported for conjugated aliphatic polyenes (12). Data for peak 1 (1,3-nonadiene) are in good agreement with the data of Butler and Raymond (13). The whole distilled pyrolyzate from 3-acetoxy-1-nonene has a λ_{max} of 226 nm with an ϵ of 26,340 liters mole⁻¹ cm⁻¹.

Attempts to determine the composition of geometric isomers formed in the pyrolysis reactions has been complicated because, to our knowledge, the extinction coefficients for the pure isomers have never been reported. IR spectra (600-1200 cm⁻¹) for the preparative GLC fractions and the pyrolyzate from 3-acetoxy-1-nonene appear in Figure 3. Part A represents fraction 1 from the preparative GLC column. Strong bands at 1002 and 898 cm⁻¹ due to the out-of-plane deformations of the vinyl group and a moderately strong band at 948 cm⁻¹ due to the out-of-plane deformation of the *trans*-disubstituted ethylenic structure, confirm a 1,3-*trans*-nonadiene structure. Part B (fraction 2, preparative GLC column) shows weak bands at 1002 and 898 cm⁻¹ due to the vinyl group resulting from the 10%, 1,3-isomer present as an impurity. A weak band at 945 cm⁻¹ is due to a *trans*-disubstituted ethylenic out-of-plane band, possibly due to the trace of 1,3-*trans*-nonadiene influenced by a 2,4-*trans*, *cis*-nonadiene. Part C (whole distilled pyrolyzate 3-acetoxy-1-nonene) contains strong vinyl absorption bands at 1002 and 898 cm⁻¹ due to

the vinyl group and at 955 cm⁻¹ due to the *trans* unsaturation indicating a 1,3-*trans*-nonadiene and a moderately weak band at 988 cm⁻¹ due to a 2-*trans*-4-*trans*-nonadiene.

The IR data show that the nonadienes from pyrolysis of 4-acetoxy-2-nonene have primarily the 1,*trans*-3 and *trans*-2,*trans*-4 structures, respectively.

These observations are in partial accord with Greenwood (5) who reported that the *trans* isomer was the major component in the 1,3-heptadiene isolated from the pyrolysis of 4-acetoxy-2-heptene. However, Greenwood found that 2,4-heptadiene was composed of a 50:50 mixture of the *trans-trans* and *cis-trans* isomers, whereas our data indicate *trans-trans* predominates.

Conditions promoting the isomerization of olefins under pyrolysis are poorly defined in the literature. Both thermal and chemical effects have been suggested as causes for isomerization of olefins during pyrolysis.

Conditions affecting isomerization during pyrolysis include acetic acid formed in the reaction and carbonization on the helices or reaction tube. Grummitt and Mandell (7) suggested acetic acid might cause isomerization when cyclic acetates are pyrolyzed. Bailey and Rosenburg (14) found that carbonization on helices and the reaction tube promoted isomerization of 1,2-dimethyl-4-cyclohexene and that carbonization occurred when more than 60-70% of the theoretical acetic acid was liberated.

Carbonization can probably be ruled out here because only trace carbon deposits were found on the glass helices or the reaction tube. Under the conditions employed, since about 47% of the theoretical acetic acid was split out, which is below the critical limit found by Bailey and Rosenburg (14), excessive acetic acid is ruled out as a cause for isomerization.

Little information is available on thermal stability of unsaturated materials to pyrolysis conditions. Bailey et al. (14,15) prepared many unusual cyclic olefins via ester pyrolysis reactions without rearrangement. 2,4-Heptadiene is

said not to rearrange at 350 C while some rearrangement (17%) of the 1,3-isomer was observed (5). Froemsdorf et al. (3) found when *cis*-2-butene was subjected to pyrolysis conditions, no conversion to the 1-isomer occurred and no *trans* isomers were formed.

Our data indicate 15% conversion from the 1,3- to the 2,4-isomer, which amount is in good agreement with Greenwood's work (5). Undoubtedly, isomerization of 1,3-nonadiene, formed during pyrolysis of 3-acetoxy-1-nonene, can be attributed to thermal effects.

ACKNOWLEDGMENTS

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