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Tobacco Ionones: Dehydration of α-Ionol

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A number of ionone-related compounds are important tobacco flavor and aroma constituents. The acid-catalyzed dehydration and subsequent rearrangements of 1,3,3-trimethyl-2-(3-hydroxybutenyl)-cyclohexene (α-ionol), an ionone derivative, have been investigated. When subjected to treatment with mild acid, α-ionol yielded megastigma-4,7(E),9-triene as the major product and 2,2,6,7-tetramethylbicyclo[4.3.0]nona-7,9-diene and 3-(2,6,6-trimethyl-2-cyclohexenyl)-2-*trans*-propenal as other products. It was found that megastigma-4,7(E),9-triene yielded the 2,2,6,7-tetramethylbicyclo[4.3.0]nona-7,9-diene constituent by an unusual ring-closure reaction. Further, 3-(2,6,6-trimethyl-2-cyclohexenyl)-2-*trans*-propenal, a C-12 oxygenated compound which displayed a strong floral-musty fragrance and had not been reported in the literature previously, could be formed by aerial oxidation of megastigma-4,7-(E),9-triene.

Numerous research findings during the past several years which dealt with the flavoring isoprenoids in tobacco and smoke condensate have strongly suggested that many of those isoprenoids may have derived from the carotenoid metabolites or their degradation products (Stedman, 1968; Roberts and Rohde, 1972; Demole and Berthet, 1972; Kimland et al., 1973; Tso, 1974). While biochemical degradation processes of such constituents are possible in burley tobacco leaf during senescence and curing, many other secondary degradation reactions such as further oxidation-reduction, rearrangement, and possibly dehydration may occur. The ionones, which possess unique flavoring properties, have been isolated from tobacco and other plants (Demole and Berthet, 1972; Kimland et al., 1972; Schumacher and Vestal, 1974; Enzell, 1977; Davis, 1977). It has been reported that β-ionone and its related compounds were formed from the carotenoid precursors (e.g., β-carotene) by chemical transformation such as photooxygenation reactions (Isoe et al., 1969, 1972). Other structurally related tobacco constituents which have been reported as flavoring components of burley tobacco were megastigma-4,7(E),9-trien-3-one (Figure 1, I), megastigma-4,6(Z),8(Z)-trien-3-one (Figure 1, II), megastigma-4,6-(Z),8(E)-trien-3-one (Figure 1, III), megastigma-4,6(E),8-(E)-trien-3-one (Figure 1, IV), and megastigma-4,6(E),8-(E)-trien-3-one megastigma-4,6(E)8(E)-trien-3-one (Figure 1, V) (Roberts and Rohde, 1972; Demole and Enggist, 1974). It has been suggested that these compounds were derived from the dehydration of (9R)-9-hydroxy-4,7(E)-megastigmadien-3-one (3-oxo-α-ionol, Figure 1, VI) (Aasen et al., 1973, 1974). The objective of the present investigation was to examine the dehydration and rearrangement products of α-ionol in an effort to determine if it would yield megastigmatrienes.

METHODS

Chemicals. α-Ionone (Figure 2, VII) was obtained from Aldrich Chemical Co., Milwaukee, WI, and purified by distillation using a spinning band column. α-Ionol was synthesized from this purified product by sodium borohydride reduction (Corey et al., 1972). Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Spectra. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer. Proton NMR spectra were obtained in CDCl₃ solution with a Varian T60A spectrometer and carbon-13 spectra with a Varian CFT-20 spectrometer. UV spectral data were collected with a Shimadzu Model MPS-50L spectrophotometer. Mass spectra were obtained with a Finnigan Model 3300 GC/MS spectrometer operating at 70 eV.

Dehydration Reaction. This reaction was accomplished by treating α-ionol (5.0 g) with 5% *p*-toluenesulfonic acid in refluxing benzene (60 mL) for 30 min. The products were separated on a silicic acid column by serial elution using hexane and hexane-ether (9:1). The analytical samples were purified by using a preparative gas chromatograph (Varian Model 37111 equipped with a 12-port valve and a thermal conductivity detector) and a stainless steel column (12 × 1/8 in. i.d.) packed with 5% XE-60. The operating conditions were as follows: injector at 200 °C, detector at 210 °C, and temperature programming the column oven after a 5-min isothermal hold at 95 °C to 190 °C at 3 °C/min.

RESULTS AND DISCUSSION

The reaction of 1,3,3-trimethyl-2-(3-hydroxybutenyl)-cyclohexene (α-ionol, Figure 2, VIII) with 5% *p*-toluenesulfonic acid in refluxing benzene yielded a mixture of three compounds, megastigma-4,7(E),9-triene (Figure 2,

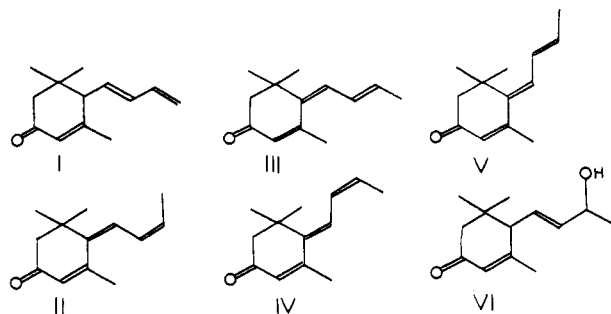Department of Agronomy, University of Kentucky, Lexington, Kentucky 40546.

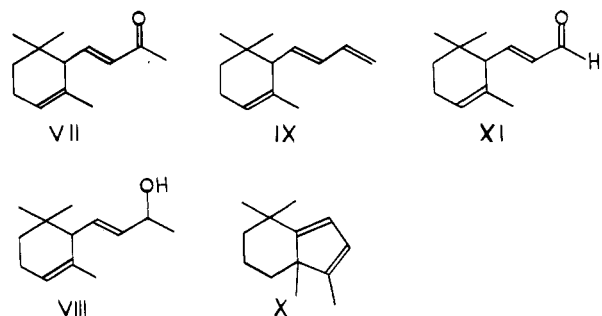**Figure 1.** Geometric isomers of megastigmatrienones and precursor 3-oxo-α-ionol from tobacco.

Figure 2. α-Ionone, α-ionol, and dehydration products.

Figure 3. Carbon-13 NMR spectrum of megastigma-4,7(E),9-triene.

Figure 4. Carbon-13 NMR spectrum of the olefinic region of megastigma-4,7(E),9-triene.

IX), 2,2,6,7-tetramethylbicyclo[4.3.0]nona-7,9-diene (Figure 2, X), and 3-(2,6,6-trimethyl-2-cyclohexenyl)-2-*trans*-propenal (Figure 2, XI), in a total yield of 75%. The molar ratio of compounds IX, X, and XI was determined to be 62:21:5 after separation by column chromatography (silicic acid). The GLC retention times of IX, X, and XI were 17.4, 18.6, and 24.8 min, respectively.

The structural assignments were made for these compounds on the basis of the following data. Compound IX, the principal component of this dehydration, had the elemental composition of $C_{13}H_{20}$. The mass spectrum had the following prominent ions: m/e (relative intensity) 176 (M^+, 7), 105 (100), 120 (92), 91 (51), 77 (24), 107 (21), 156 (4), 133 (4). The infrared spectrum displayed absorption bands at 1365 and 1380 cm^{-1} indicative of a *gem*-dimethyl group, a band at 965 cm^{-1} suggestive of a trans-disubstituted olefin, and a band at 896 cm^{-1} indicative of the terminal vinyl. The UV spectrum had an absorption maximum at λ 231 nm which was consistent with a conjugated system. The 60-MHz proton NMR spectrum ($CDCl_3$, Me_4Si) exhibited a six-proton doublet at δ 0.90 and 0.95 which was indicative of the *gem*-dimethyl group and a methine proton which occurred at δ 2.15 (1 H, $J = 10.0$ Hz). The methylene signals were observed at both δ 1.20 and 1.95 (4 H, multiplets). A vinylic methyl signal was found at δ 1.65 (3 H, singlet). The remainder of the olefinic signals (5 H) appeared as complex multiplets in the region δ 4.95–6.55. On the basis of the appearance of only two different methyl signals, all other possible structures of any exocyclic double-band isomers were eliminated.

Due to the complexity of the olefinic region of the proton spectrum, more conclusive evidence for the assignment of the olefin geometry was necessary. Thus, carbon-13 NMR techniques were employed. The chemical shifts of all the 13 signals exhibited by the carbon NMR were assignable based on the number of lines observed on the off-resonance proton-decoupled analysis. The ^{13}C NMR data (recorded in ppm, Me_4Si; Figure 3) were as follows: C-1, 32.4 (s); C-2, 23.1 (t); C-3, 31.7 (t); C-4, 120.4 (d); C-5, 134.1 (s); C-6, 54.5 (d); C-7, 137.3 (d); C-8, 135.9 (d); C-9, 132.4 (d); C-10, 114.8 (t); C-11, 22.8 (q); C-12 or C-13, 27.0 or 27.6 (both q). The
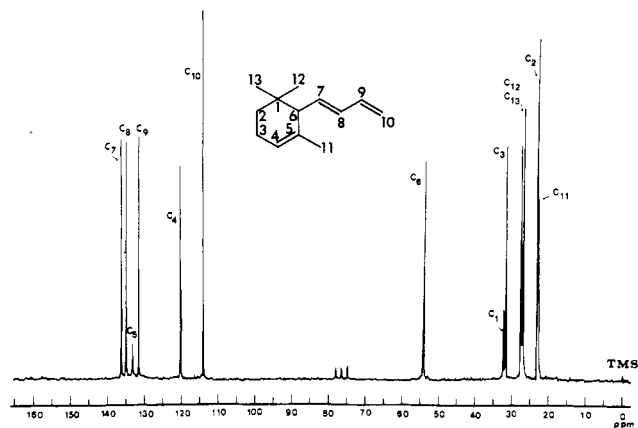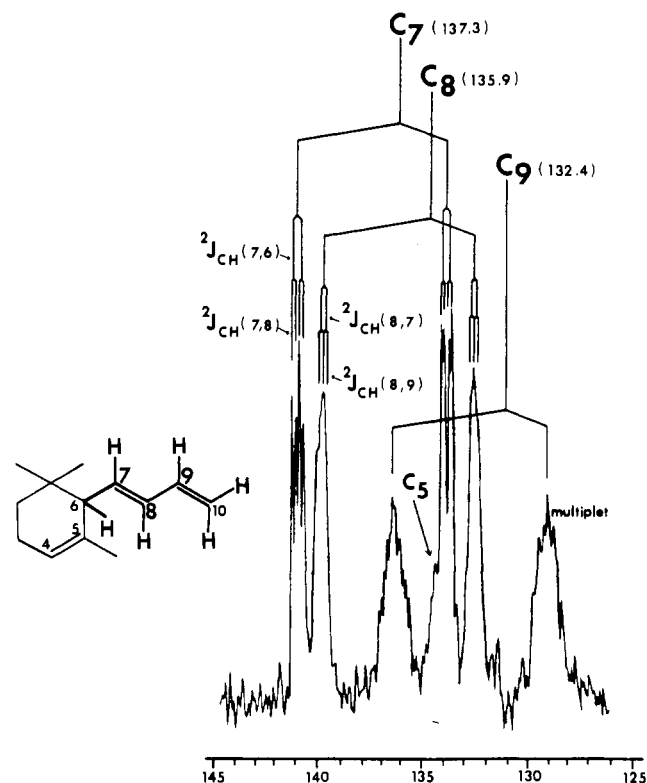
points which should be emphasized are the following: (1) a methine carbon (54.5 ppm from Me_4Si) was observed; (2) six carbon signals were observed in the olefinic region with C-10 being the most upfield signal (114.8 ppm) and exhibiting a clear triplet on the off-resonance spectrum which was in good agreement with the designation of a terminal carbon of this type; (3) assignments for C-4 and C-5 were straightforward with C-5 being the quaternary carbon further downfield in the spectrum; (4) assignment of the remainder of the olefinic carbons required a study of the long-range two-bonded carbon–hydrogen coupling patterns (Figure 4). For each of these signals (C-7, C-8, and C-9), a large directly bonded $^1J_{C-H}$ (54 Hz) was observed. The geometry of C-9 indicated that there were three $^2J_{C-H}$ coupling constants, and the overlapping of these different coupling patterns indicated a multiplet. C-8, being in a symmetrical environment, had two fairly identical $^2J_{C-H}$ long-range coupling constants [$^2J_{C-H(8,7),(8,9)}$ = 5.2 Hz] and $^2J_{C-H(7,8)}$ = 2.2 Hz was observed for C-7. The carbon NMR analyses provided a complete assignment for
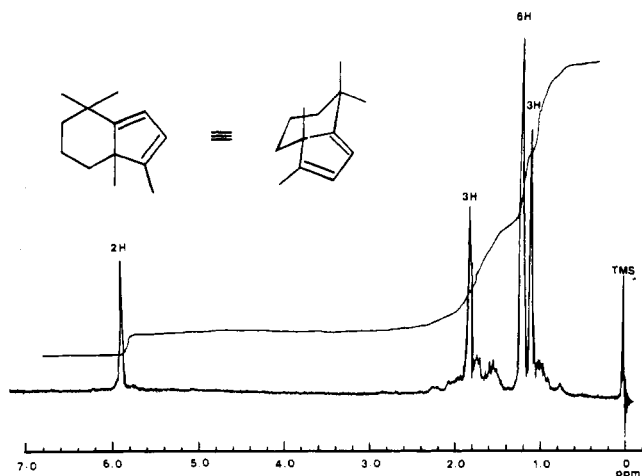
Figure 5. Proton NMR spectrum of 2,2,6,7-tetramethyl-bicyclo[4.3.0]nona-7,9-diene.

each of the carbons and strongly supported the designated structure of IX. Compound IX had a sweet floral aroma. An alternate synthesis with a good yield of this compound was obtained by directly heating the starting alcohol in $KHSO_4$ at 150 °C for 1.0 h.

Compound X had an empirical formula of $C_{13}H_{20}$ deduced from carbon–hydrogen analysis and mass spectral data. Compound X was purified with preparative GLC and was identified by using the following spectral data: MS m/e (relative intensity) 176 (M^+, 5), 105 (100), 119 (98), 91 (95), 77 (77), 79 (60), 120 (49), 133 (37), 107 (34), 121 (33), 106 (32), 115 (19), 117 (18), 161 (16). The infrared spectrum showed bands at 1365 cm^{-1} (*gem*-dimethyl) and 829 cm^{-1} (trisubstituted olefin). The UV absorption at λ 257 nm supported a conjugated diene. The proton NMR (Figure 5) of this sample exhibited a methyl signal at δ 1.08 and the *gem*-dimethyl signal occurred at δ 1.22 (6 H, singlet). The vinylic methyl appeared at δ 1.95 (3 H, broad singlet). Surprisingly, the two remaining olefinic protons occurred as a sharp singlet at δ 5.85. On the basis of these spectral data, a fused cyclopentadiene was suggested. The olefinic signal at δ 5.85 appeared to be rather unusual for the two-ring protons; therefore, elucidation was required. A Dreiding model of this molecule was constructed which showed that the fused cyclohexane ring was more in the stable chair conformation. The stereochemistry of the olefinic protons with respect to the remainder of the six-membered ring as well as the methyl protons was similar in this chair conformation. The molecular distances between the respective methyl groups were approximately the same. Since this type of rearrangment product is not usually encountered in a normal dehydration, a further structural elucidation of this molecule was needed. The carbon NMR was found to be the only analytical tool to solve this vital problem. The carbon NMR spectrum exhibited 13 signals and was found to be consistent with the structure of X. In addition, a theoretical calculation of the chemical shifts of each carbon was found to be in good agreement with the observed chemical shift data. The carbon NMR spectral data (in ppm) including the off-resonance proton-decoupled results (Figure 6) were as follows: C-1, 35.3 (s); C-2, 43.6 (t); C-3, 19.8 (t); C-4, 36.7 (t); C-5, 53.3 (s); C-6, 161.7 (s); C-7, 121.5 (d); C-8, 122.6 (d); C-9, 153.8 (s); C-10 or C-11, 25.6 (q) or 31.1 (q); C-12, 12.2 (q); C-13, 19.9 (q). Also, compound X could be produced by directly stirring IX in the presence of a trace amount of acid.

Another compound, XI, which may be considered as a new flavor component based on our laboratory evaluation,
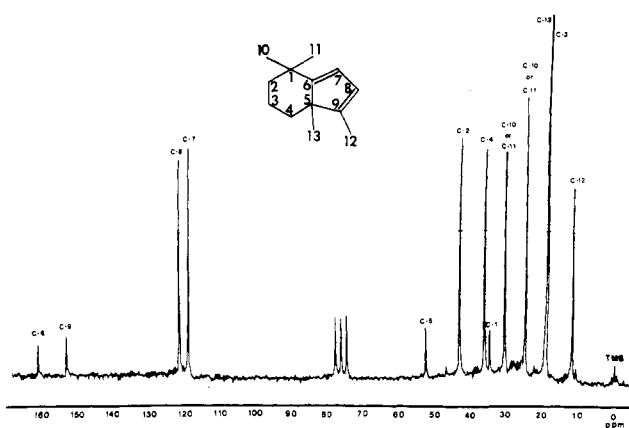

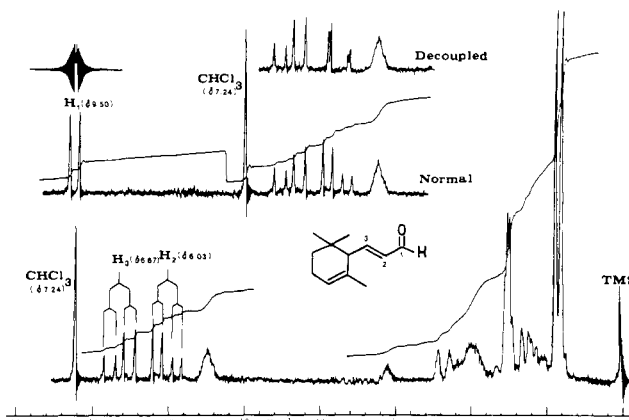**Figure 6.** Carbon-13 NMR spectrum of 2,2,6,7-tetramethyl-bicyclo[4.3.0]nona-7,9-diene.

Figure 7. Proton NMR spectrum of 3-(2,6,6-trimethyl-2-cyclo-hexyl)-2-*trans*-propenal.

was derived from α-ionol. This compound (XI) was isolated as one of the secondary reaction products. The structure of this compound was easily determined from its mass spectra data: MS m/e (relative intensity) 178 (M^+, 32), 107 (100), 93 (98), 122 (97), 79 (81), 91 (51), 95 (46), 123 (32), 121 (26), 163 (23), 105 (22), 92 (16), 120 (13), 135 (10). The composition of this compound was established as $C_{12}H_{18}O$ by elemental analysis and mass spectrometry. The UV spectrum displayed an absorption maximum at λ 230 nm, and the infrared spectrum indicated a trans olefin at 970 cm^{-1}. The carbonyl aldehyde was confirmed by IR bands at 1690 and 2720 cm^{-1} and by the preparation of a 2,4-DNP derivative (yellow crystals, mp 116–117 °C). Further structural elucidation of this compound was achieved by a detailed proton NMR decoupling analysis. The proton NMR (Figure 7) of this compound exhibited signals at δ 0.85 and 0.90 (3 H, 3 H, *gem*-dimethyl, singlets) and δ 1.55 (3 H, vinylic methyl, broad singlet). The 1-H doublet (J = 10.0 Hz) at δ 2.35 revealed the presence of a methine proton. Moreover, three olefinic proton (δ 5.50, 6.03, and 6.67) signals corresponded to the vinylic protons, H_2 and H_3. The aldehyde proton appeared at δ 9.50, a doublet with J = 8 Hz. Direct irradiation of this δ 9.50 signal changed the upfield quartet signal at δ 6.03 into a doublet, which permitted the assignment of H_2 (olefinic proton adjacent to the carbonyl). Similarly, when H_3 was irradiated, the signal at δ 2.35 sharpened to a singlet. The NMR spectrum of this compound resembles that of α-ionone, and assignment for the olefin geometry was in agreement with that of an α-ionone system. Although the exact mechanism for its formation is not understood, it is possible that this compound was derived by photooxygenation of the triene IX. Photo-

oxygenation of a conjugated diene, solanone, was found by Johnson and Nicholson (1965) to yield norsolanone. In a separate experiment compound IX was readily converted to XI by UV photolysis. Compound X was found to form readily under these conditions.

The compounds synthesized in these studies showed an important finding concerning the dehydration of α-ionol. Isomerization of IX to form several double-bond isomers analogous to megastigmatrienones (Figure 1) was not found in this study. The formation of X most likely involved a carbonium ion intermediate derived from megastigmatriene. Presently, we are examining other related systems to determine the exact mechanism.

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Statistical Evaluation of Thermally Modified Sulfur as a Coating Agent for Urea Granules

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The recently developed technology of using sulfur as an effective coating material for fertilizers to provide controlled release of the plant nutrients represents a potentially large-scale commercial use of the element. Because sulfur is needed in only small amounts as a plant nutrient, ways to reduce the total coating weight in production of slow-release fertilizers are of interest. This report evaluates the effect of heat treatment as a method to modify the properties of commercial-grade sulfur. Particular interest is focused on how these thermally induced changes in the sulfur may affect the dissolution rates of sulfur-coated urea (SCU) granules.

The National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, AL, has for several years been developing controlled-release fertilizers by coating water-soluble substrates with multiple layers of sulfur. Most of this work has been concentrated on the sulfur-coated urea (SCU) process (Young, 1974). Numerous greenhouse and field tests have shown this material to be a superior source of nitrogen for certain row crops and turf grasses. This product also has some physical advantages over conventional fertilizers in handling and resistance to caking under humid conditions. However, the cost of the sulfur application and the diluting effect the extra sulfur has on the overall nutrient value of the product must be considered its main disadvantages. Means to reduce the sulfur requirements to give a product with desirable release characteristics would therefore be of interest.

Experiments have shown that nitrogen is released rapidly from individual granules once the coating fails and water gets access to the substrate. Therefore, it seems likely that it should be possible to control the N release not only by the thickness of the sulfur coat but also to some degree by improvement of the mechanical strength of the sulfur. The data presented in this paper show that when commercial-grade sulfur is heated above 200 °C, a redistribution of the sulfur allotropes occurs and that a significantly higher portion of these allotropes remains in the polymeric state when the sulfur is cooled to room temperature. Earlier work (Dale and Ludwig, 1965) has shown that a high level of polymeric sulfur increased the tensile strength of sulfur. The data from this study show how such thermally induced changes in the properties of sulfur will affect the release of nitrogen from urea granules coated with this modified sulfur.

EXPERIMENTAL SECTION

The sulfur used in these experiments was commercial grade, dark colored, Frasch-process sulfur supplied to us by Texasgulf, Inc. Organic carbon represents the major impurity in Frasch sulfur, ranging in concentration from

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