mmol) of ethyl formate was refluxed for 12 hr. All volatiles were removed at reduced pressure, the residual oil was dissolved in methylene chloride, washed with dilute hydrochloric acid, then water, and the organic phase was dried ($MgSO_4$). The solvent was removed and the residual oil was distilled, giving 1.39 g (58%) of formamide **2**: bp 121–122° (0.6 mm); $n^{25}D$ 1.5433; ir (neat) 1675 (amide C=O) and 3290 cm^{-1} (amide NH); nmr ($CDCl_3$) δ (TMS) 8.15 (s, 1, HCON), 7.13 (m, 3, ArH), 6.75 (m, 1, NH), 5.23 (m, 1, J = 16.5, 7.5 Hz, CH), 1.87 (m, 2, J = 7.5 Hz, $-CH_2-$), and 0.93 ppm (t, 3, J = 7.5 Hz, $-CH_3$); mass spectrum (70 eV) m/e (rel intensity) 169 (30), 140 (100), 113 (36), 97 (7), 85 (25).

Anal. Calcd for $C_8H_{11}NOS$: C, 56.77; H, 6.55; N, 8.28. Found: C, 56.60; H, 6.43; N, 8.44.

Addition of deuterium oxide and a trace of trifluoroacetic acid to the nmr solution ($CDCl_3$) resulted in the complete loss of the peak at δ 6.75 due to the amide proton and the collapse of the methine AB quartet at δ 5.23 to a triplet, J = 7.5 Hz.

Registry No.—**1**, 13679-75-9; **2**, 39207-57-4; **3**, 39204-58-5; **3** picrate, 39204-59-6; 1-(2-thienyl)-1-aminopropane, 6315-55-5; formamide, 75-12-7; ethyl formate, 109-94-4.

Preparation and Purification of Tetrasodium *meso*-Tetra(*p*-sulfophenyl)porphine. An Easy Procedure[1]

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Tetraphenylporphine sulfonate was first reported by Winkelman, who studied localization of this compound in tumors. He found that it could be localized with a higher concentration ratio in animal tumors than in other tissues.[3,4] It was later found that Winkelman's sample is, in fact, a mixture of various isomers.[5] The sodium salt of *meso*-tetra(*o*-sulfophenyl)porphine was recently prepared in low yield by condensing pyrrole and benzaldehyde sulfonic acid (sodium salt) in *n*- or *tert*-butyl alcohol in the presence of sodium acetate.[6] *meso*-Tetra(*p*-sulfophenyl)porphine was prepared by heating *meso*-tetraphenylporphine and concentrated sulfuric acid on a steam bath for 4 hr. The diacid was precipitated by adding the requisite amount of water. The tetraammonium salt was precipitated by dissolving the diacid in methanolic ammonia and then adding acetone. Further purification of the tetraammonium salt was carried out by a cumbersome procedure involving six successive reprecipitations from a methanolic solution with acetone. The tetraammonium salt of *meso*-tetra(*p*-sulfophenyl)-porphine was further converted to the tetrasodium salt by treating the former with sodium methoxide.[4] We wish to report an easy preparation and purification procedure for the tetrasodium *meso*-tetra(*p*-sulfophenyl)porphine (60% yield).

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Experimental Section

Finely powdered *meso*-tetraphenylporphine (2 g)[7] was mixed with 50 ml of concentrated sulfuric acid. The mixture was heated on a steam bath for 4–5 hr. After cooling to room temperature, the solution was filtered through a sintered glass frit and the filtrate was diluted carefully to 1. The dilute solution was heated and a sludge of lime was added slowly with stirring until the solution changed to a permanent purple color. Calcium sulfate was filtered off and washed with a minimum quantity of hot water, which was then combined with the filtrate. Crushed Dry Ice was added to the filtrate and was filtered. The filtrate was concentrated to a small volume (about 100 ml) and the pH of the final warm solution was regulated at 8–10 by adding the required quantity of concentrated sodium carbonate solution. Calcium carbonate was removed by filtration and washed with water, which was then combined with the filtrate. Hot ethanol (90%) in small quantities was periodically added to the filtrate, which was further concentrated on a steam bath. The saturated solution was cooled at room temperature and crystals of tetrasodium *meso*-tetra(*p*-sulfophenyl)porphine (I) were obtained. They were filtered off and washed with a minimum quantity of cold 90% ethanol. Finally the material was dried at 100° for 1 hr. The water content in compound I was determined by heating it under vacuum at 140° for 15 hr. I has an empirical formula of $C_{44}H_{50}N_4O_{24}S_4Na_4$ with 12 water molecules. *Anal.*[8] Calcd for $C_{44}H_{26}N_4O_{12}S_4Na_4 \cdot 12H_2O$: N, 4.50; S, 10.29. Found: N, 4.54; S, 10.55. The compound is very soluble in water. The visible spectrum of I (H_2O) shows five peaks at 413 (soret), 506 (I), 543 (II), 570 (III), and 634 (IV) nm (rel intensity I > II > III > IV). The ir spectrum of I (KBr) shows four strong bands at 1226, 1194, 1134, and 1046 cm^{-1} due to sulfonic acid (salt) absorption[9] in addition to free porphyrin vibrations. The ^1H nmr (T-60 Varian Associates) of I (D_2O) shows pyrrole protons at δ 7.51 and two doublets due to protons of phenyl groups centered at δ 6.85 and 7.85 with a coupling constant of 8 Hz.[4] The ratio of peak areas of pyrrole protons and phenyl protons is 1:2. This excludes the possibility of substitution of the pyrrole protons and supports the substitution of the phenyl protons by four sulfonate groups. Furthermore, the presence of the two doublets at δ 6.85 and 7.85 in the ^1H nmr of I shows clearly that four sulfonate groups are substituted only at para positions of the phenyl groups.

Registry No.—Tetrasodium *meso*-tetra(*p*-sulfophenyl)porphine, 39050-26-5; *meso*-tetraphenylporphine, 917-23-7.

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The Rearrangement of α-Ethynyl Alcohols to Unsaturated Carbonyl Compounds (The Rupe Reaction)

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The identity of the products from, and the mechanism of, the Rupe reaction has been debated in the

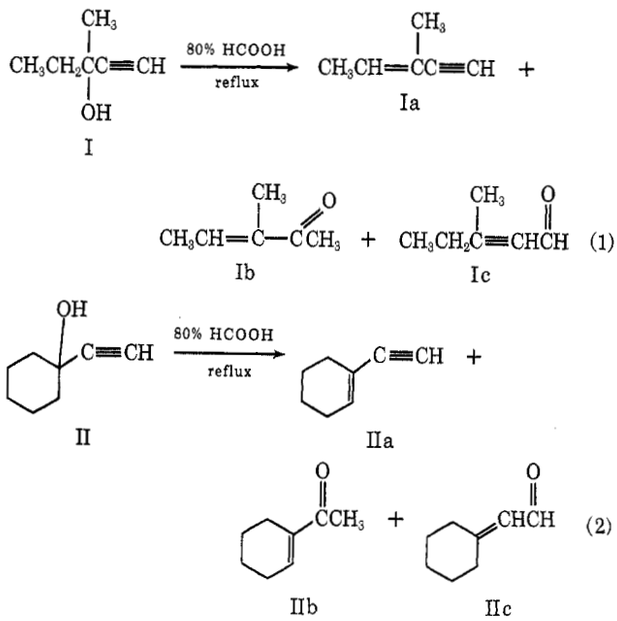
(1) Abstracted in part from the M.S. thesis of A. D. Anderson, Central Washington State College, Aug 1967. The Research Corporation provided funds that allowed Miss Anderson's work.

literature since Hans Rupe first reported that α-ethynyl carbinols can be rearranged to carbonyl products when refluxed with formic acid.[2] Rupe believed that the carbonyl products were α,β-unsaturated aldehydes. More recent authors have reported that the major carbonyl products were α,β-unsaturated ketones.[3] Some authors report formation of both aldehydes and ketones, while others report only ketones.[4,5] Several others report formation of hydrocarbon products the structures of which have been determined to be vinylacetylenes.[6,7] Surprisingly, several authors have proposed mechanisms for the reaction despite the fact that consistent agreement as to the structures and relative proportions of products has never been reached and that few other mechanistic studies have been performed.[8-10] The work described in this paper was prompted by a need to understand the reason for the discrepancies and an interest in gaining other mechanistic data.

Results and Discussion

Two typical α-ethynylcarbinols were chosen for study. The carbinols were 3-methyl-1-pentyn-3-ol (I) and 1-ethynyl-1-cyclohexanol (II). Each of the carbinols was subjected to normal Rupe reaction conditions.[2] Normal conditions involve refluxing the carbinols with an excess of formic acid for periods of from 2 to 8 hr. In the studies reported in the literature to date, the organic products have been isolated by classical work-up and identification procedures. These have involved isolation of the organic products by organic solvent extraction and distillation followed by preparation of various derivatives and/or formation of other organic compounds. In our study the organic products were separated from the reaction mixture by organic solvent extraction and then each major organic product was detected and isolated by gas–liquid partition chromatography (glpc). The structure of each isolated product was then determined by use of ir, uv, and nmr and by use of classical techniques.

Carbinols I and II produce several organic products, but in each case three of the products accounted for greater than 85% of the total initially formed organic material. In our study, as has been established before, some of the initially formed products undergo subsequent acid-catalyzed polymerization to compounds of not much interest.[8] Consequently, the yield of initially formed products normally varies from 40 to 70% depending on the structure of the starting carbinol. Over the years interest has focused on only three of the several organic products of the reaction, and these we have found to constitute at least 85% of the initially formed products of reaction of carbinols I and II. Equations 1 and 2 show the



primary reactions that were found to take place and that will be discussed further.

Table I presents a list of the relative percentages of the primary products of interest and carbinol reactant following a normal Rupe reaction.

TABLE I

Compd	Reaction time, hr (approx)	Reaction temp, °C	% vinylacetylene	% ketone	% aldehyde
I	2	85–90	20	60	13
II	2	85–90	2	63	4

During the study to obtain the data in Table I it was found that the relative percentage of aldehyde formed in the reaction was higher if product analysis was done early in the course of the reaction. As a consequence, experiments were carried out allowing a time-dependent product analysis. In this study it was found that, when a 10:1 ratio of acid to carbinol was employed at reflux temperatures, the reaction rate was too fast to allow analysis. As a result, a modified procedure was adopted. The modification involved treating the carbinol with formic acid at a 1:5 ratio at reflux temperatures rather than a 1:10 ratio. This modification produced nearly identical product distribution, but at a slower reaction rate.

A time-dependent product analysis study was then carried out using a 5:1 ratio of formic acid to carbinol at reflux and several other temperatures. Table II is a summary of the relative percentages of the principal organic products that were determined at several times in the course of the reaction at two different temperatures.

The results of the experiments described in this paper suggest that the reason for the past controversy over the nature and distribution of carbonyl products formed in the Rupe reaction was due to lack of control of experimental conditions, as has been implied by Parham.[9] As noted earlier in this paper, early workers apparently simply mixed reagents, brought

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TABLE II

Compd	Reaction time, hr	Reaction temp, °C	% reaction[a]	% vinylacetylene	% ketone	% aldehyde
I	1	85–90	60	26	51	16
	2	85–90	66	21	60	13
	4	85–90	76	19	70	7
	8	85–90	88	13	83	5
	0.25	55–60	17	5	1	91
	1	55–60	20	7	2	90
	4.5	55–60	25	25	3	72
II	1	85–90	51	4	83	13
	2	85–90	84	2	93	4
	4	85–90	89	2	95	2
	8	85–90	95	1	96	1
	0.25	60–70	14	17	9	75
	1.5	60–70	27	40	14	47

[a] Per cent reaction based on per cent unreacted alcohol.

the reaction mixture to reflux temperatures, and heated it for indefinite periods of time. Product identity, isolation, and composition was done using classical techniques, which probably has produced some of the uncertainty in the distribution of the carbonyl products produced. As a consequence, the mechanisms based on product analysis that have been proposed for the Rupe reaction are subject to question. Some other mechanistic studies have, however, been reported. Ansell, for example, has shown that the vinylacetylenes produced in the reaction undergo an acid-catalyzed hydration reaction, but at rates much slower than ketone formation.[8] We have found this to also be the case in our study. Vinylacetylenes Ia and Ib were found to undergo no hydration reaction under the conditions of this study. This work obviates several reports that the vinylacetylenes are required intermediates, although minor amounts of ketone may have been formed by this reaction in other reported work. In the same report, Ansell also verified that the α,β-unsaturated aldehydes undergo self-condensation reactions and that the vinylacetylenes undergo oxidation reactions. We found this to also be the case in our study. When mixtures of the three principal organic products were subjected to Rupe conditions, there were no changes in the relative proportions of the starting materials. However, considerable polymeric products were formed.

The numerous competing side reactions of the products produced, therefore, greatly complicate a detailed kinetic study and are no doubt the cause of production of substantial amounts of the colored, high molecular weight organic products that always accompany the reaction. Work has been initiated in our laboratory to develop appropriate Lewis acid catalysts which we have found produce the same principal organic products but apparently do not result in the numerous side reactions of the principal organic products. Thus, we hope in the near future to report a detailed kinetic study and also the results of appropriate labeling studies.

Experimental Section

Materials and Equipment.—The starting carbinols, 3-methyl-1-pentyn-3-ol (I) and 1-ethynyl-1-cyclohexanol (II), were prepared according to a modified method of Campbell, Campbell, and Eby.[11] Metallic sodium (11.5 g) was added slowly and with constant stirring to 500 ml of liquid ammonia which was being perfused with acetylene. Following sodium addition either 31 g of 2-butanone or 49 g of cyclohexanone was slowly added through a dropping funnel. The solvent, liquid ammonia, was allowed to evaporate and the resulting solid was hydrolyzed with water. The organic material was extracted with ether, washed, dried, and purified by vacuum distillation. This procedure afforded 30 g (61%) of carbinol I: bp 77–80° (150 mm); 99% pure by glpc, R_v 312 ml; nmr (neat) δ_{TMS} 2.5 (s, 1, OH), 2.4 (s, 1, C≡CH), 1.1 (t, 3, CH_2CH_3, J = 7 Hz), 1.6 (m, 5, CCH_3, CH_2CH_3); ir (neat) 3.2 (OH), 6.8, 7.3, 7.5, 7.7, 7.8, 8.5, 8.8, 9.6, 10.0, 10.8 μ (OH). It also gave 25 g (40%) of II: bp 76–78° (17 mm); 99% pure by glpc, R_v 345 ml; nmr (CCl_4) δ_{TMS} 3.2 (s, 1, OH), 2.5 (s, 1, C≡CH), 1.70 (m, 10, ring CH_2); ir (CCl_4) 2.9 (OH), 3.4 (CH), 6.9, 7.3, 7.8, 7.9, 8.9 (OH), 10.8 μ.

Spectra were recorded on a Perkin-Elmer 137B prism ir spectrophotometer, a Perkin-Elmer Hitachi 139 uv-visible spectrophotometer, and a Varian HA60IL nmr spectrometer. Gas–liquid partition chromatography was carried out with a Perkin-Elmer 811 equipped with a 10 ft × 0.125 in. aluminum column packed with a 20% silicone DC200 on 70/80 Anakrom. Operation conditions for carbinol I were injector, 200°; column, 110°; detector, 160°; He flow rate, 25 ml/min. For II they were injector, 200°; column, 130°; detector, 200°; He flow rate 25 ml/min. The glpc data was standardized by the internal normalization method that is applicable for hydrogen flame detectors.[12]

3-Methyl-3-penten-2-yne (Ia).—The vinylacetylene Ia detected as a product from treatment of carbinol I was prepared according to the method of Newman, *et al.*[13] Thionyl chloride (11.8 g) in dry ether (7.5 ml) was added dropwise with vigorous stirring to 9.8 g of carbinol I (dried over molecular sieves 5A) in 18 ml of dry pyridine (dried over BaO) in 20 ml of dry ether. The drop rate and heating were set to maintain gentle reflux. After refluxing for 5 hr, cold water was added and then cold, dilute HCl. The vinylacetylene Ia, 4 g (50% yield), was recovered by distillation: bp 70–72° (760 mm);[14] glpc R_v 45 ml; ir (neat) 3.05 (C≡CH), 3.4 (CH), 4.8 (C≡C), 6.1 (C=C), 7.0, 7.7, 11.0, 12.0, 16.0 μ.

1-Ethynyl-1-cyclohexene (IIa).—The vinylacetylene IIa detected as a product from formic acid treatment of carbinol II was prepared according to the method described above except that 12.4 g of starting carbinol was used. Following vacuum distillation 5.8 g (55% yield) of vinylacetylene IIa was recovered: bp 42–43° (13 mm);[15] glpc R_v 100 ml; ir (neat) 3.3 (C≡CH), 3.4 (CH), 4.75 (C≡C), 6.95 (C=C), 7.70, 11.0, 11.9, 12.0, 12.6, 15.8, 18.8, 19.3 μ.

3-Methyl-3-penten-2-one.—The α,β-unsaturated ketone Ib detected as a product from formic acid treatment of carbinol I was isolated and purified following a Rupe reaction. The physical and spectral properties of the compound were obtained and compared to those of authentic material obtained from Alpha Chemical Co. Ketone Ib was isolated and purified *via* glpc (99% pure, R_v 250 ml); bp 62–65° (50 mm); ir (neat) 3.3 (CH), 5.9 (C=O), 5.95 (C=C), 6.9, 7.0, 7.6, 8.5, 8.7, 9.2, 9.7, 10.4, 12.0, 13.9 μ; nmr (CCl_4) δ_{TMS} 6.65 (q, 1, =CH, J = 4 Hz), 2.18 (s, 3, CCH_3), 1.7 (m, 6, C=CH_3); λ_{max}^{EtOH} 228 nm (ϵ 12,800) [lit.[4] λ_{max}^{EtOH} 230 nm (ϵ 12,600)]; negative to Schiff reagent.

1-Acetyl-1-cyclohexane.—The α,β-unsaturated ketone IIb detected as a product from formic acid treatment of carbinol II was isolated and purified following a Rupe reaction. The physical and spectral properties of the compound were obtained and compared to those of authentic material obtained from Alpha Chemical Co. Ketone IIb was isolated and purified *via* glpc (99% pure, R_v 300 ml): bp 111–114° (50 mm); ir (neat) 3.3 (CH), 5.9 (C=O), 6.05 (C=C), 6.9, 7.2, 7.4, 7.8, 8.0, 8.08, 8.8, 9.2, 9.3, 10.2, 10.8, 11.0, 11.7, 11.8, 12.5 μ; nmr (CCl_4) δ_{TMS} 6.73 (m, 1, =CH), 2.12 (s, over m, 7), 1.69 (m, 4); λ_{max}^{EtOH} 232 nm (ϵ 14,000) [lit.[5] λ_{max}^{EtOH} 233 nm (ϵ 12,500)]; negative to Schiff reagent.

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3-Methyl-2-pentenal.—The α,β-unsaturated aldehyde Ic detected as a product from formic acid treatment of carbinol I was isolated and purified following a Rupe reaction. The physical and spectral properties of the compound were obtained and used to establish the structure of the aldehyde. Aldehyde Ic was isolated and purified *via* glpc (95% pure, R_v 300 ml): ir (neat) 3.4 (CH), 5.8 (C=O), 5.9 (C=C), 6.8, 7.2, 8.4, 8.6, 8.9, 9.4, 9.6, 9.8, 10.7, 11.5, 12.3 μ; nmr (CCl_4) δ_{TMS} 9.4 (m, 1), 6.8 (s, 5), 6.1 (m, 1), 2.1 (t, 3); positive to Schiff reagent instantaneously.

Cyclohexlideneacetaldehyde.—The cyclic α,β-unsaturated aldehyde IIc detected as a product from formic acid treatment of carbinol II was isolated and purified following a Rupe reaction. The physical and spectral properties of the compound were obtained and used to establish the structure of the aldehyde. Aldehyde IIc was isolated and purified *via* glpc (95% pure, R_v 450 ml): bp 114–117° (50 mm); λ_{max}^{EtOH} 235 nm (ϵ 14,500) [lit.[5] λ_{max}^{EtOH} 235 nm (ϵ 14,400)]; positive to Schiff reagent instantaneously.

Rupe Reaction Conditions.—A 1:5 or a 1:10 molar ratio of carbinol to 85% formic acid were mixed and heated at selected temperatures for each time period ranging from 15 min to 8 hr. The reaction mixture was cooled in an ice bath and neutralized with cold 5% sodium hydroxide until the organic layer was completely separated and the aqueous layer was washed twice with small portions of hexane. The combined organic fractions were combined, washed twice with small portions of water, and dried over anhydrous sodium sulfate. Aliquot portions of each reaction mixture were then subjected to glpc analysis.

Registry No.—I, 77-75-8; Ia, 1574-33-0; Ib, 565-62-8; Ic, 3592-19-6; II, 78-27-3; IIa, 931-49-7; IIb, 932-66-1; IIc, 1713-63-9; 2-butanone, 78-93-3; cyclohexanone, 108-94-1; acetylene, 74-86-2.

The [3,3]-Sigmatropic Rearrangement of Allylic Dialkylthiocarbamates

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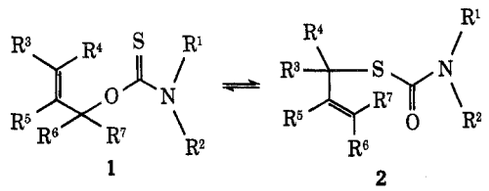
In the course of work on the synthesis of juvenile hormone analogs by way of [3,2]-sigmatropic rearrangements of sulfonium ylides,[1] a general route to hindered allylic thiols and sulfides was needed. It was clear from the work of Newman and Karnes[2] that the dialkylthiocarbamate linkage was more stable when joined through the sulfur than when joined through the oxygen. These workers reported[2] that O-aryl dialkylthiocarbamates could be converted to S-aryl dialkylthiocarbamates when heated at 130–335°, the temperature depending upon the ring substituents. It seemed that the added stability of the sulfur linkage could provide the driving force for a [3,3]-sigmatropic rearrangement when an O-allylic dialkylthiocarbamate was employed.

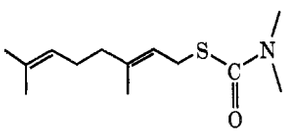
[3,3]-Sigmatropic rearrangements have been reviewed,[3] and more recent examples have been reported.[4,5] The same skeletal sequence of atoms as the thiocarbamates of this report has been observed with thionocarbonates,[6] and more recently with two allylic xanthates of a carbohydrate series.[7] Although both aryl[2] and alkyl[8] dialkylthiocarbamates have been pyrolyzed, allyl dialkylthiocarbamates are known primarily in the patent literature, and a limited amount of chemistry has been reported on them.

We wish to report the successful conversion of a series of O-allyl dialkylthiocarbamates to S-allyl dialkylthiocarbamates in which the allyl group is rearranged, as required by an electrocyclic mechanism. This transformation is illustrated by structures **1** and **2**, and Table I shows some of the compounds which



1 **2**

have been employed in this reaction. The temperature required for the reaction depends principally on the substituents on the allylic carbon to which the oxygen is originally attached. When this carbon is primary, the temperature required for 90% reaction in 20 min is 130–140°. The corresponding temperature for secondary carbamates is around 100–110°, while tertiary derivatives such as **1b**, **1l**, and **1m** cannot be isolated, but rearrange at room temperature or below to the S-allyl derivatives **2b**, **2l**, and **2m**. A competing reaction is noted if the temperature rise is not controlled adequately. For example, if **1a** is heated at greater than 150°, dissociation apparently occurs, as evidenced by the formation of **3** in small amounts.



3

That the driving force for this rearrangement is strong is seen by the rearrangement of **1c**, in which conjugation of the double bond with the aromatic ring is destroyed. The rate of conversion of **1c** to **2c** is about the same as the rate for the unsubstituted **1e** to **2e**.

The rearrangements were monitored by ir, tlc, or nmr. The O-allyl derivatives showed strong bands at 1530 and 1190 cm^{-1}, and pyrolysis resulted in the diminishing of these bands and enhancement of the carbonyl band at about 1660 cm^{-1} for the S-allyl product. On silica gel tlc, the O-allyl derivative always had a higher rate of flow than the S-allyl derivative. Allyl isomerization produced changes in the nmr patterns, and protons α to oxygen and sulfur were in the predictable positions. In general, the dimethylamino group occurred as two peaks in the O-allyl compounds, but as a sharp singlet for the S-allyl isomers.

Hydrolysis of **2a** with sodium hydroxide in aqueous methanol did not give linalylthiol **5** as expected, but

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