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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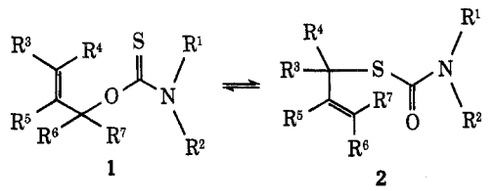
Received February 1, 1973

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.

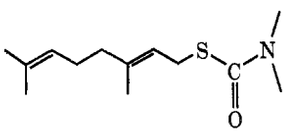
[3,3]-Sigmatropic rearrangements have been reviewed,[3] and more recent examples have been reported.[4,5] The same skeletal sequence of atoms as the thiocarbamates of this report has been observed with thionocarbonates,[6] and more recently with two allylic xanthates of a carbohydrate series.[7] Although 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.



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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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(2) M. S. Newman and H. A. Karnes, *J. Org. Chem.*, **31**, 3980 (1966).
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(4) B. W. Bycroft and W. Landon, *Chem. Commun.*, 168 (1970).
(5) D. St. C. Black and A. M. Wade, *ibid.*, 871 (1970).
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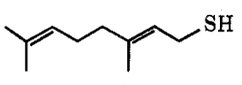
TABLE I[a]

ALLYLIC THIOCARBAMATES 1 AND 2

	R³	R⁴	R⁵	R⁶	R⁷
a	$(CH_3)_2C{=}CHCH_2CH_2$	CH_3	H	H	H
b	H	H	H	CH_3	$(CH_3)_2C{=}CHCH_2CH_2$
c	C_6H_5	H	H	H	H
d	CH_3	H	H	H	H
e	H	H	H	H	H
f	H	H	H	CH_3	H
g	H	H	CH_3	CH_3	H
h	H	H	H	$CH_3CH_2CH_2$	H
i	$CH_3CH_2CH_2$	H	H	H	H
j	$CH_3CH_2CH_2$	H	CH_3CH_2	H	H
k	H	$-(CH_2)_3-$ bridge R⁴ to R⁶	H	$-(CH_2)_3-$ bridge R⁴ to R⁶	H
l	H	H	H	CH_3	CH_3
m	H	H	H	C_6H_5	C_6H_5
n	CH_3	CH_3	H	CH_3	H

[a] $R^1 = R^2 = CH_3$ except for example j, where they form a piperidine ring, and example k, where $R^1 = R^2 = CH_3CH_2$.

instead yielded geranylthiol **4**. Partial hydrolysis showed no linalylthiol present at any time, but only **2a** and geranylthiol. We believe that this result reflects the instability of the hindered thiols in base in favor of the less hindered isomers. Reduction of **2a** with lithium aluminum hydride, however, did give the linalyl isomer **5**, which was isolated without the addition of acid or excess water. The thiocarbamate **2c** could also be reduced with lithium aluminum hydride to the thiol **6**, although, if the mixture was allowed to



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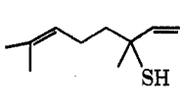

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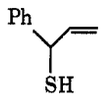

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stand overnight after the addition of water, the product was cinnamylthiol.

This thiocarbamate rearrangement thus provides a route to hindered allylic thiols which are otherwise relatively inaccessible. Displacement of hindered allylic halides or tosylates goes in SN2′ fashion,[9] yielding the less hindered thiols or sulfides. Hindered allylic thiols and even sulfides[1b] are unstable to acid, in which they rearrange to the less hindered isomers.

The linalylthiol obtained from the thiocarbamate has been used in the synthesis of 9-aryl-2,6-nonadienes, which are active[10] as mimics of some of the natural juvenile hormones.[11] The required intermediate sulfides **7** were made by treating the linalylthiol with benzylic halides. Generation of a sulfonium ylide **8** was accomplished using benzyne made from 2-fluorophenylmagnesium bromide. These ylides are not isolable, but undergo the [3,2]-sigmatropic rearrangement previously described[1] to give the sulfide **9**. This sulfide is then reduced with Raney nickel to give the juvenile hormone analog **10**. Thus, the availability of hindered thiols by way of the thiocarbamate rearrangement has made possible the synthesis of biologically active compounds from a previously known ylide rearrangement.

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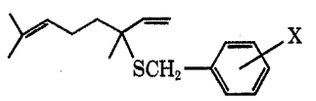

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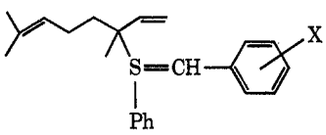

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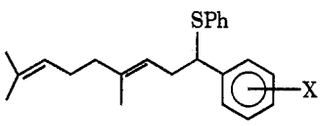

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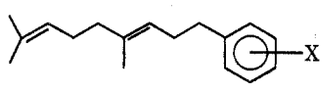

10

Experimental Section

Nmr spectra were measured on a Varian A-60A instrument in $CDCl_3$. Chemical shifts are reported in parts per million from internal TMS, and are followed by parentheses giving multiplicity of signal, coupling constant if applicable, and number of protons. Spin multiplicity is given by s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. All compounds designated by an asterisk after the name showed satisfactory analytical data (±0.3% for C, H, N, and S). Silica gel for chromatographic separations was Davison Chemical grade 62 (60–200 mesh). Diethylthiocarbamoyl chloride was a gift of the Pennsalt Chemicals Corp.

Preparation of O-Allyl Dialkylthiocarbamates.—The O-allyl derivatives were prepared by the published procedure[2] for the corresponding O-aryl compounds, and one example illustrates the process. Sodium hydride (4.8 g, 57% in mineral oil) was washed with absolute ether before 40 ml of DMF was added. Geraniol (15.4 g, 0.1 mol) in DMF (40 ml) was added in portions and the mixture was stirred under nitrogen for 1 hr. The mixture was cooled to 0°, and 12.4 g (0.1 mol) of dimethylthiocarbamoyl chloride was added in DMF (30 ml). The ice bath was removed and the mixture was heated to 60° over 1 hr before cooling and pouring into 1% KOH (400 ml). The aqueous layer was saturated with NaCl and extracted with two 200-ml portions of benzene–hexane. The combined extracts were washed with 100 ml of saturated NaCl and then dried over $MgSO_4$ before the solvents were removed under vacuum. Chromatography over silica gel in benzene–hexane gave a clear oil (17 g), identified as *O*-geranyl dimethylthiocarbamate* (**1a**): nmr δ 5.42 (broad t, J = 7 Hz,

1), 5.05 (m, 1), 4.96 (d, J = 7 Hz, 2), 3.35 (s, 3), 3.10 (s, 3), 2.08 (m, 4), and 1.66 (m, 9).

O-Cinnamyl dimethylthiocarbamate* (**1c**) was obtained as a clear oil: nmr δ 7.30 (m, 5), 6.71 (d, J = 16 Hz, 1), 6.83 (two triplets, J_1 = 16, J_2 = 5 Hz, 1), 5.13 (d, J = 5 Hz, 2), 3.32 (s, 3), and 3.08 (s, 3).

O-(*trans*-2-Butenyl) dimethylthiocarbamate* (**1d**) was obtained as a clear oil: nmr δ 5.71 (m, 2), 4.89 (broad d, J = 4 Hz, 1), 3.33 (s, 3), 3.10 (s, 3), and 1.72 (d, J = 5 Hz, 3).

O-Allyl dimethylthiocarbamate* (**1e**) was obtained as a clear oil: bp 42° (0.1 mm); nmr δ 6.1 (m, 1), 5.33 (broad d, J = 17 Hz, 1), 5.25 (broad d, J = 10 Hz, 1), 5.01 (broad d, J = 6 Hz), 3.37 (s, 3), and 3.17 (s, 3).

O-(1-Methylallyl) dimethylthiocarbamate* (**1f**) was obtained as a clear oil: nmr δ 5.97 (m, 2), 5.22 (m, 2), 3.33 (s, 3), 3.10 (s, 3), and 1.37 (d, J = 6 Hz, 3).

O-(1,2-Dimethylallyl) dimethylthiocarbamate* (**1g**) was isolated as a clear oil: nmr δ 5.98 (q, J = 7 Hz, 1), 5.01 (broad s, 1), 4.90 (broad s, 1), 3.35 (s, 3), 3.12 (s, 3), 1.78 (s, 3), and 1.38 (d, J = 7 Hz, 3).

O-(1-Hexen-3-yl) dimethylthiocarbamate* (**1h**) was eluted from the column as a clear oil: nmr δ 5.96 (m, 2), 5.27 (m, 2), 3.41 (s, 3), 3.20 (s, 3), and 2.0–0.7 (m, 7).

O-(2-Hexenyl) dimethylthiocarbamate* (**1i**) was obtained as a clear oil: nmr δ 5.72 (m, 2), 4.92 (d, J = 5 Hz, 2), 3.34 (s, 3), 3.10 (s, 3), 2.05 (m, 2), 1.4 (m, 2), and 0.9 (t, J = 6 Hz, 3).

O-(2-Ethyl-2-hexenyl) 1-piperidinecarbothioate* (**1j**) was obtained by the above procedure with the substitution of piperidine-*N*-thiocarbonyl chloride for dimethylthiocarbamoyl chloride. This carbamate was isolated as a clear oil: nmr δ 5.47 (broad t, J = 7 Hz, 1), 5.00 and 4.90 (singlets, cis and trans, 2), 3.87 (m, 4), 2.05 (m, 4), and 1.80–0.70 (m, 14).

O-(2-Cyclohexenyl) diethylthiocarbamate* (**1k**) was prepared by the above procedure using diethylthiocarbamoyl chloride, and characterized as a clear oil: nmr δ 5.90 (m, 3), 3.65 (septet, 4), 1.85 (m, 6), and 1.18 (m, 6).

Preparation of S-Allyl Dialkylthiocarbamates—Some S-allyl derivatives are obtained by rearrangement of O-allyl isomers *in situ*, while others are obtained from heating the purified O-allyl derivatives.

Sodium hydride (4.7 g, 57% in mineral oil) was washed with ether before 40 ml of DMF was added. Linalool (15.4 g) in DMF (40 ml) was added in portions, and the mixture was stirred under nitrogen for 1.5 hr. The mixture was cooled to 0°, and dimethylthiocarbamoyl chloride (12.4 g) in DMF (40 ml) was added. The ice bath was removed and the mixture was stirred at room temperature overnight. Work-up as above gave a mixture of 65% *trans*- and 35% *cis*-*S*-(3,7-dimethyl-2,6-octadienyl) dimethylthiocarbamate* (**2b**) (8 g) as a pale yellow oil: bp 110° (0.2 mm); nmr δ 5.2 (m, 2), 3.56 (d, J = 8 Hz, 2), 2.97 (s, 6), 2.07 (m, 4), and 1.66 (m, 9).

In the same manner, 2-methyl-3-buten-2-ol (15 g) yielded *S*-(3-methyl-2-butenyl) dimethylthiocarbamate* (**2l**) (10 g) as a clear oil: bp 74–76° (0.7 mm); nmr δ 5.28 (broad t, J = 8 Hz, 1), 3.55 (d, J = 8 Hz, 2), 2.97 (s, 6), and 1.70 (broad s, 6).

Diphenylethenylcarbinol was converted by the same procedure to *S*-(3,3-diphenyl-2-propenyl) dimethylthiocarbamate* (**2m**), isolated as a thick yellow oil: nmr δ 7.23 (m, 10), 6.23 (t, J = 8 Hz, 1), 3.62 (d, J = 8 Hz, 2), and 2.85 (s, 6).

4-Methyl-3-penten-2-ol was converted by the normal procedure to the *O*-carbamate **1n**, but, after standing at room temperature for several weeks, the product isolated was *S*-(2-methyl-3-penten-2-yl) dimethylthiocarbamate* (**2n**): bp 55–58° (0.2 mm); 90% trans; nmr δ 5.86 (d, J = 15.5 Hz, 1), 5.5 (m, 1), 2.92 (s, 6), 1.67 (d, J = 5 Hz, 3), and 1.56 (s, 6).

O-Geranyl dimethylthiocarbamate (**1a**) was heated without solvent at 140° for 2 hr to give in near-quantitative yield *S*-linalyl dimethylthiocarbamate* (**2a**). Final purification could be achieved by chromatography or distillation: bp 102–103° (0.3 mm); nmr δ ABC pattern 6.07 (A), 5.14 (B), 5.09 (C) (J_{AB} = 17.5, J_{AC} = 10, J_{BC} = 1 Hz), 5.1 (m, 1), 2.94 (s, 6), 1.97 (m, 4), 1.67 (s, 3), and 1.58 (s, 6).

O-Cinnamyl dimethylthiocarbamate (**1c**) heated at 130° for 2 hr gave *S*-(α-vinylbenzyl) dimethylthiocarbamate:* bp 113° (0.2 mm); nmr δ 7.31 (m, 5), 6.7 (m, 1), 5.2 (m, 3), and 2.88 (s, 6).

O-(*trans*-2-Butenyl) dimethylthiocarbamate (**1d**) was heated at 130° for 2 hr to give *S*-(1-buten-3-yl) dimethylthiocarbamate* (**2d**) as a clear oil: bp 55° (0.6 mm); nmr δ 5.98 (m, 1), 5.20 (split d, J = 17.5 Hz, 1), 5.07 (split d, J = 10 Hz, 1), 4.16 (m, 1), 2.98 (s, 6), and 1.54 (d, J = 7 Hz, 3).

O-Allyl dimethylthiocarbamate (**1e**) was heated at 140° for 2 hr to give *S*-allyl dimethylthiocarbamate[12] (**2e**): nmr δ 5.9 (m, 1), 5.2 (m, 2), 3.56 (d, J = 7 Hz, 2), and 2.98 (s, 6).

O-(1-Methylallyl) dimethylthiocarbamate (**1f**) was heated at 126° for 30 min to give *S*-(2-butenyl) dimethylthiocarbamate* (**2f**) (mixture of cis and trans) as a clear oil: nmr δ 5.60 (m, 1), 3.50 (broad d, J = 5 Hz, 2), 2.90 (s, 6), and 1.58 (broad d, J = 5 Hz, 3).

O-(1,2-Dimethylallyl) dimethylthiocarbamate (**1g**) was heated at 112° for 30 min to give *S*-(2-methyl-2-butenyl) dimethylthiocarbamate* (mixture of cis and trans) (**2g**) as a clear oil: nmr δ 5.53 (broad q, J = 6 Hz, 1), 3.57 (broad s, 2), 2.99 (s, 6), 1.66 (s, 3), and 1.57 (d, J = 6 Hz, 3).

O-(1-Hexen-3-yl) dimethylthiocarbamate (**1h**) was heated at 107° for 1.5 hr to give *S*-(2-hexenyl) dimethylthiocarbamate* (**2h**) (mixture of cis and trans) as a clear oil: nmr δ 5.57 (m, 2), 3.52 (broad d, J = 6 Hz, 2), 2.99 (s, 6), 1.98 (m, 2), 1.37 (m, 2), and 0.88 (m, 3).

O-(*trans*-2-Hexenyl) dimethylthiocarbamate (**1i**) was heated at 135° for 2 hr to give *S*-(1-hexen-3-yl) dimethylthiocarbamate (**2i**) as a clear oil: bp 67–68° (0.3 mm); nmr δ 5.9 (m, 1), 5.22 (two doublets, J_1 = 14, J_2 = 2 Hz, 1), 5.00 (two doublets, J_1 = 6, J_2 = 2 Hz, 1), 4.06 (q, J = 7 Hz, 1), 2.96 (s, 6), 1.6 (m, 4), and 0.9 (m, 3).

O-(2-Ethyl-2-hexenyl) 1-piperidinecarbothioate (**1j**) was heated at 130° for 2 hr to give *S*-[1-(1-methylenepropyl)butyl] 1-piperidinecarbothioate* (**2j**): bp 110–115° (0.2 mm); nmr δ 5.00 (broad s, 1), 4.88 (broad s, 1), 4.07 (t, J = 7 Hz, 1), 3.47 (m, 4), 2.16 (q, J = 7 Hz, 2), 1.6 (m, 10), and 1.03 (m, 6).

O-(2-Cyclohexenyl) diethylthiocarbamate (**1k**) was heated at 135° for 1 hr to yield *S*-(2-cyclohexenyl) diethylthiocarbamate* (**2k**) as a clear oil: bp 88–90° (0.2 mm); nmr δ 5.73 (m, 2), 4.17 (m, 1), 3.36 (q, J = 7 Hz, 4), 1.9 (m, 6), and 1.14 (t, J = 7 Hz, 6).

Preparation of Thiols.—The unsuccessful hydrolysis of **1b** with sodium hydroxide is described first, followed by a description of reduction with lithium aluminum hydride to give the desired thiol.

To *S*-linalyl dimethylthiocarbamate (1 g) was added methanol (15 ml), water (4 ml), and NaOH (0.3 g). The solution was stirred and heated under reflux under nitrogen overnight. The methanol was then removed under vacuum and water (15 ml) was added before extracting with ether (3 × 20 ml). The combined ether extracts were dried over $MgSO_4$ and the ether was removed under vacuum to leave a clear oil, which was shown by nmr to be about 60% starting material **1b** and 40% geranylthiol **4**.

To $LiAlH_4$ (3.8 g) in anhydrous ether (300 ml) was added dropwise *S*-linalyl dimethylthiocarbamate (21.1 g) in ether (150 ml) so as to maintain reflux. Stirring was continued while the mixture was heated under reflux for 2 hr. Water (4 ml) was then added, followed by 20% NaOH (3 ml), and water (14 ml). The solid was removed by filtration and washed with ether. The ether solution was dried over $MgSO_4$ and the ether was removed under vacuum to leave a clear oil (9.1 g), identified as linalylthiol **5**: bp 90° (15 mm); nmr δ ABC vinyl pattern 5.98 (A), 5.05 (B), 4.93 (C) (J_{AB} = 17, J_{AC} = 10, J_{BC} = 1 Hz), 2.3–1.5 (m, 4), 1.76 (s, 1), 1.67 (s, 3), 1.60 (s, 3), and 1.47 (s, 3).

S-(α-Vinylbenzyl) dimethylthiocarbamate was reduced in the same manner to give α-vinylbenzyl mercaptan as a clear oil: nmr δ 7.22 (m, 5), 6.11 (m, 1), 5.12 (two doublets, J_1 = 18, J_2 = 1 Hz, 1), 5.01 (two doublets, J_1 = 9, J_2 = 1 Hz, 1), 4.67 (overlapping doublets, $J_1 \cong J_2$ = 6 Hz, 1), and 1.97 (d, J = 6 Hz, 1).

Preparation of Nonadienes.—Given here is just one example of the sequence for synthesis of the nonadienes. Other compounds which have been employed include heterocyclic, cycloalkyl, and naphthyl groups in place of the methylenedioxyphenyl.

Linalyl mercaptan (9.6 g, 56 mmol) was added to a solution made by treating sodium (1.3 g, 56 mg-atoms) with methanol (100 ml). The solution was stirred under nitrogen and cooled to 0°, and piperonyl chloride (9.6 g, 56 mmol) was added in methanol (100 ml). Stirring was continued overnight at room temperature. The methanol was removed under vacuum, water (150 ml) was added, and the mixture was extracted with ether (2 × 100 ml). The ether extracts were combined and dried over $MgSO_4$ and the ether was removed under vacuum to leave a pale yellow oil. Chromatography over silica gel with hexane–benzene gave

(12) H. Tilles, *J. Amer. Chem. Soc.*, **81**, 714 (1959).

a clear oil (10.5 g), identified as linalyl piperonyl sulfide:* nmr δ 6.7 (m, 3), ABC pattern 5.86 (A), 5.08 (B), 4.95 (C) (J_{AB} = 11, J_{AC} = 17, J_{BC} = 1.5 Hz), 5.81 (s, 2), 5.1 (m, 1), 3.47 (s, 2), 2.0 (m, 2), 1.67 (s, 3), 1.59 (s, 3), 1.6 (m, 2), and 1.31 (s, 3).

The Grignard reagent for generating benzyne was made from magnesium (0.6 g, 25 mg-atoms) and 2-bromofluorobenzene (4.0 g, 23 mmol) in dry THF (50 ml). When the Grignard began forming, linalyl piperonyl sulfide was added (6.1 g, 20 mmol) in THF (25 ml). The solution was stirred under nitrogen and heated under reflux for 3 hr before cooling and adding saturated ammonium chloride (65 ml). The layers were separated and the aqueous layer was extracted with ether (75 ml). The combined organic extracts were dried over $MgSO_4$, and the solvent was removed under vacuum to leave a yellow oil. Chromatography over silica gel in hexane–benzene gave a clear oil (5.5 g), identified as 2,6-dimethyl-9-(3,4-methylenedioxyphenyl)-9-phenylthio-2,6-nonadiene: nmr δ 7.2 (m, 5), 6.7 (m, 3), 5.77 (s, 2), 5.1 (m, 2), 4.08 (t, J = 7 Hz, 1), 2.57 (t, J = 7 Hz, 2), 1.9 (m, 4), and 1.5 (m, 9).

2,6-Dimethyl-9-(3,4-methylenedioxyphenyl)-9-phenylthio-2,6-nonadiene (1 g) was stirred at room temperature for 30 min with W-2 Raney nickel[13] (5 ml settled) in ethanol (60 ml). The nickel was removed by filtration and the ethanol was removed under vacuum. The product was dissolved in ether (60 ml) and washed with water before drying over $MgSO_4$. Evaporation of ether and chromatography over silica gel in hexane–benzene gave a clear oil (0.7 g), identified as 2,6-dimethyl-9-(3,4-methylenedioxyphenyl)-2,6-nonadiene.* Glpc shows that the configuration at the central double bond is 70–75% trans and 25–30% cis. This sample is identical with that formed by another method[10] except for the cis:trans ratio: nmr δ 6.66 (s, 3), 5.86 (s, 2), 5.2 (m, 2), 2.4 (m, 4), 2.0 (m, 4), and 1.6 (d, 9).

Registry No.—**1a**, 39707-18-1; **1c**, 39707-19-2; **1d**, 39707-20-5; **1e**, 5513-30-4; **1f**, 39707-22-7; **1g**, 39707-23-8; **1h**, 39707-24-9; **1i**, 39707-25-0; *cis*-**1j**, 39707-26-1; *trans*-**1j**, 39707-27-2; **1k**, 39707-28-3; **2a**, 39707-29-4; *cis*-**2b**, 39707-30-7; *trans*-**2b**, 39707-31-8; **2c**, 39707-32-9; **2d**, 39707-33-0; **2e**, 18283-54-0; *cis*-**2f**, 39707-35-2; *trans*-**2f**, 39707-36-3; *cis*-**2g**, 39707-37-4; *trans*-**2g**, 39707-38-5; *cis*-**2h**, 39707-39-6; *trans*-**2h**, 39707-40-9; **2i**, 39707-41-0; **2j**, 39707-42-1; **2k**, 39707-43-2; **2l**, 39707-44-3; **2m**, 39707-45-4; **2n**, 39707-46-5; **5**, 39707-47-6; α-vinylbenzyl mercaptan, 39707-48-7; linalyl piperonyl sulfide, 39707-49-8; 2,6-dimethyl-9-(3,4-methylenedioxyphenyl)-9-phenylthio-2,6-nonadiene, 39707-50-1; *cis*-2, 6-dimethyl-9-(3,4-methylenedioxyphenyl)-2,6-nonadiene, 39707-51-2; *trans*-2,6-dimethyl-9-(3,4-methylenedioxyphenyl)-2,6-nonadiene, 39707-52-3; piperonyl chloride, 20850-43-5; 2-bromofluorobenzene, 1072-85-1.

Acknowledgment.—We wish to thank Mr. P. L. Unger and associates for spectral measurements and Mr. G. M. Maciak and associates for elemental analyses.

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Studies on the Pinacol Rearrangement

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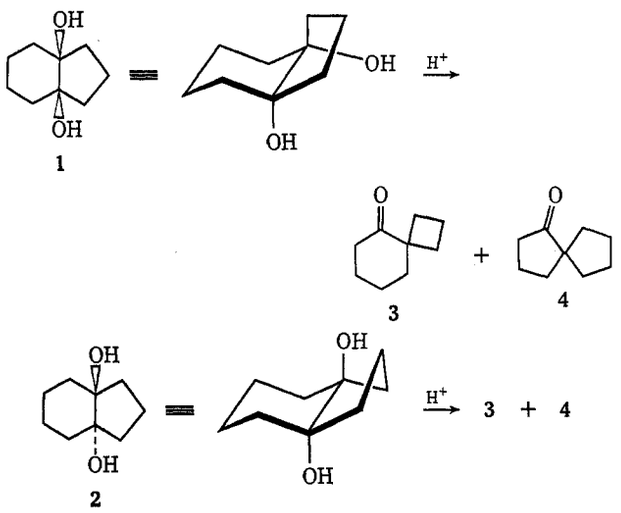
Received October 24, 1972

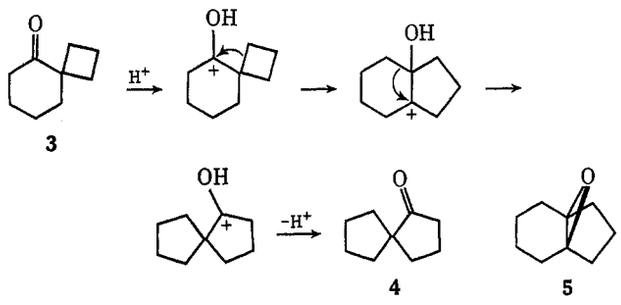
One of the interesting questions regarding the pinacol rearrangement is that concerned with stereochemical requirements. Curtin has demonstrated stereospecificity in semipinacolonic deaminations;[1] however, there exists a paucity of work regarding steric control for the pinacol rearrangement of glycols.[2]

The problem of stereochemistry can be best analyzed with conformationally homogeneous molecules. The *cis*- and *trans*-hydrindan system appeared suitable as a model system in view of the report by Fort that a carbonium ion generated at the ring fusion, under solvolytic conditions, maintained stereochemical integrity.[3]

We were prompted to examine the *cis*- and *trans*-8,9-dihydroxytetrahydroindan in the anticipation that a concerted pinacol rearrangement might be reflected in different product ratios for the two isomers. The glycols **1** and **2** have been previously prepared,[4] as have the spiranones **3**[5] and **4**.[6]



Treatment of either **1** or **2** with concentrated sulfuric acid at 0° for 10 min resulted in *complete* conversion to **4**. The epoxide **5**[3] could not be identified as a



reaction product; and a sample, when subjected to the reaction conditions, was shown to undergo rapid rearrangement to **4**. In testing whether **3** was stable to the reaction conditions, it was observed that **3** → **4**.

At this point the results can be rationalized by (a) glycol interconversion,[7] (b) unfavorable energetics for the formation of **3**, or (c) product instability.[8]

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