C, 80.26; H, 8.72; N, 11.02. Found: C, 80.03; H, 8.83; N, 11.08.

1-Methyl-4-*tert*-butylimidazole: R_f (1:1 EtOH/$CHCl_3$) 0.40; IR (neat) cm^{-1} 2980, 2180, 1560, 920, 730; NMR (partial) δ [7.39 (s, minor isomer), 7.35 (major isomer), 1 H], [6.76 (s, minor isomer), 6.60 (s, major isomer), 1 H], [4.03 (s, minor isomer), 3.98 (s, major isomer), 3 H], 1.44 (s, 9 H); mass spectrum, *m/e* (relative abundance) 138 (M^+, 10), 137 (22), 123 (30), 88 (65), 84 (100); calcd for $C_8H_{14}N_2$ 138.1157, found 138.1145.

1-Benzyl-2,4-dimethylimidazole:[17] R_f (Et_2O) 0.14; IR (neat) cm^{-1} 2910, 1670, 1510, 1410, 1200, 1140, 730, 710; NMR (partial) δ [6.69 (s, minor isomer), 6.51 (s, major isomer), 1 H], 4.95 (s, 2 H), 2.28 (s, 3 H), 2.16 (d, 3 H, J = 0.5 Hz); mass spectrum, *m/e* (relative abundance) 186 (M^+, 89), 92 (10), 91 (100), 65 (12).

1-[(*p*-Benzyloxy)phenethyl]-2,4-dimethylimidazole: R_f (Et_2O) 0.03; IR (neat) cm^{-1} 2920, 1610, 1510, 1240, 750; NMR δ [6.65 (s, minor isomer), 6.52 (s, major isomer), 1 H], 5.02 (s, 2 H), 3.57 (t, 2 H, J = 6 Hz), 2.90 (t, 2 H, J = 6 Hz), 2.18 (s, 3 H), 2.07 (s, 3 H); mass spectrum, *m/e* (relative abundance) 306 (M^+, 10), 131 (20), 107 (12), 91 (26); calcd for $C_{20}H_{22}N_2O$ 306.1732, found 306.1726.

1-Benzyl-2-methyl-4-phenylimidazole: R_f (Et_2O) 0.32; IR (neat) cm^{-1} 3060, 1600, 1420, 1180, 750, 690; NMR (partial) δ 7.11 (s, 1 H), 5.05 (s, 2 H), 2.38 (s, 3 H); mass spectrum, *m/e* (relative abundance) 248 (M^+, 85), 157 (5), 92 (14), 91 (100), 89 (10); calcd for $C_{17}H_{16}N_2$ 248.1314, found 248.1309.

Photooxidation of 1-Benzyl-2,4-dimethylimidazole. Preparation of *N*-acetylalanine-*N*-benzylamide. A solution of the imidazole (26.5 mg, 0.142 mmol) in 4 mL of dry THF containing 30 μL (0.20 mmol) of DBU and ca. 2 mg of hematoporphyrin is fitted with a gas dispersion tube through which dry oxygen is continuously passed.[25] The solution is cooled in an ice bath and irradiated externally with a 275-W sunlamp for 30 min while maintaining the reaction temperature (ca. 1–5 °C). Following consumption of the starting material as monitored by TLC, the mixture was concentrated in vacuo, diluted with 15 mL of distilled EtOAc, and transferred to a hydrogenation vessel (Parr apparatus) containing palladium on charcoal as catalyst. Hydrogenation at 19 psi for 15 min followed by rotary evaporation of the solvent and filtration through silica gel (5% EtOAc/Et_2O) afforded 22.7 mg of the desired diamide (83% yield based on 87% purity of the starting imidazole), identical by TLC, IR, NMR, and MS with an authentic sample prepared from alanine via standard amino acid chemistry.

The intermediate dehydrodiamide could also be isolated and displayed the following properties: R_f (1:1 Et_2O/EtOAc) 0.50; IR (neat) cm^{-1} 3450, 1750, 1650, 1630, 1500, 1380, 1270, 1030, 740, 700; NMR δ 7.32 (s, 5 H), 6.41 (d, 1 H, J = 1 Hz), 5.25 (m, 1 H), 4.47 (d, 2 H, J = 5 Hz), 2.09 (s, 3 H); mass spectrum, *m/e* (relative abundance) 218 (M^+, 9), 200 (3), 175 (7), 131 (6), 130 (6), 106 (100), 91 (55), 79 (6).

N-Acetyl-N'-formyl-N'-benzyl-1,1-ethylenediamine (19): R_f (1:1 Et_2O/EtOAc) 0.53; IR (neat) cm^{-1} 2990, 1750, 1690, 1500, 1380, 1280, 1230, 1020; NMR δ 9.01 (s, 1 H), 7.21 (s, 5 H), 4.82 (s, 2 H), 4.35 (m, 2 H), 2.05 (s, 3 H); mass spectrum, *m/e* (relative abundance) 218 (M^+, 12), 200 (3), 176 (8), 175 (10), 149 (5), 131(7), 130 (6), 106 (100), 91 (64); calcd for $C_{12}H_{14}N_2O_2$ 218.1055, found 218.1057.

Acknowledgment. Financial support provided by the National Institutes of Health (Grant GM 28128), Merck Sharp and Dohme, and the American Cancer Society (Grant JFRA #37 to B.H.L) is gratefully acknowledged. We thank Drs. P. Boshoff and H. Webb for recording the mass spectra and Johnson Loh for expert technical assistance. NMR spectra at 300 MHz were made possible by a departmental grant from the National Science Foundation (Grant CHE-80 18438).

Registry No. **5** (R = H; R_1 = Me; R_2 = Pr), 86921-32-6; **5** (R = H; R_1 = Me; R_2 = *i*-Pr), 37455-52-0; **5** (R = H; R_1 = Me; R_2 = Bu), 29680-52-2; **5** (R = H; R_1 = Me; R_2 = *i*-Bu), 86921-33-7; **5** (R = R_1 = H; R_2 = *i*-Bu), 61893-08-1; **5** (R = H; R_1 = Me; R_2 = *t*-Bu), 42252-94-8; **5** (R = R_1 = H; R_2 = *t*-Bu), 21149-98-4; **5** (R = H; R_1, R_2 = Me), 930-62-1; **5** (R = H; R_1 = Me; R_2 = Ph), 13739-48-5; **5** (R = Bu; R_1 = Me; R_2 = Pr), 86921-34-8; **5** (R = $PhCH{=}CHCH_2$; R_1 = Me; R_2 = *i*-Pr), 86921-35-9; **5** (R = *i*-Pr; R_1 = Me; R_2 = Bu), 86921-36-0; **5** (R = $PhCH_2CH_2$; R_1 = Me; R_2 = Bu), 86921-37-1; **5** (R = *p*-$ClCH_2OC_6H_4CH_2CH_2$; R_1 = Me; R_2 = *i*-Bu), 86921-38-2; **5** (R = $CH_2CH{=}CH_2$; R_1 = Me; R_2 = *i*-Bu), 86921-39-3; **5** (R = $CH_2CH{=}CH_2$; R_1 = H; R_2 = *i*-Bu), 86921-40-6; **5** (R = $PhCH_2$; R_1 = Me; R_2 = *t*-Bu), 86921-41-7; **5** (R = *p*-$PhCH_2OC_6H_4CH_2CH_2$; R_1 = Me; R_2 = *t*-Bu), 86921-42-8; **5** (R = R_1 = Me; R_2 = *t*-Bu), 86921-43-9; **5** (R = $PhCH{=}CHCH_2$; R_1 = Me; R_2 = *t*-Bu), 86921-44-0; **5** (R = Me; R_1 = H; R_2 = *t*-Bu), 86921-45-1; **5** (R = $PhCH_2$; R_1 = R_2 = Me), 52726-31-5; **5** (R = *p*-$PhCH_2OC_6H_4CH_2CH_2$, R_1 = R_2 = Me), 86921-46-2; **5** (R = $PhCH_2$; R_1 = Me; R_2 = Ph), 86921-47-3; **15**, 86921-49-5; **16**, 86921-48-4; **19**, 86921-50-8; BuBr, 109-65-9; $PhCH{=}CHCH_2Cl$, 2687-12-9; $(CH_3)_2CHI$, 75-30-9; $PhCH_2CH_2Br$, 103-63-9; *p*-$PhCH_2OC_6H_4CH_2CH_2OTs$, 86587-62-4; $CH_2{=}CHCH_2Br$, 106-95-6; $PhCH_2Br$, 100-39-0; CH_3I, 74-88-4; $HOCH_2COCH_2CH_2CH_3$, 64502-89-2; $HOCH_2COCH(CH_3)_2$, 36960-22-2; $HOCH_2CO(CH_2)_3CH_3$, 73397-68-9; $HOCH_2COCH_2CH(CH_3)_2$, 68113-55-3; $AcOCH_2COC(CH_3)_3$, 38559-25-0; $AcOCH_2COCH_3$, 592-20-1; $AcOCH_2COPh$, 7250-94-4; CH_3CHO, 75-07-0; CHO, 50-00-0.

(25) For a description of the apparatus used, see: Foote, C. S.; Vickers, R. S. *Boll. Chim. Farm.* **1970**, *109*, 599.

Ene-Ene-Retroene Conversion of (-)-β-Pinene to (+)-β-Selinene

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(-)-β-Pinene undergoes an ene reaction with acryloyl chloride at 70 °C to afford 6,6-dimethylbicyclo[3.1.1]-hept-2-ene-2-butanoyl chloride (**2**) in better than 80% yield. Cyclization of **2** to 10,10-dimethyltricyclo-[7.1.1.$0^{2,7}$]undec-2(7)-en-6-one (**4**) by way of an intramolecular ene reaction involving a ketene intermediate occurs on heating with tributylamine at 150 °C. Unsaturated ketone **4** undergoes a clean retroene reaction to yield (+)-7-(2-propenyl)-Δ^9-decal-1-one (**11**) on brief heating at 265 °C. Lithium dimethylcuprate addition to **11** yields a mixture of four isomeric 7-(2-propenyl)-10-methyl-1-decalones (**15**–**18**) where the isomers having the desired cis relationship between the angular methyl and the 2-propenyl groups comprise ca. 75% of the product. Treatment of the ketone mixture with methylenetriphenylphosphorane completes the synthesis of (+)-β-selinene.

We have observed that acryloyl chloride undergoes an ene reaction[1,2] with β-pinene (**1**) under relatively mild conditions to yield adduct (**2**) in high yield (Scheme I). Herein we report the use of **2** in a stereoselective synthesis

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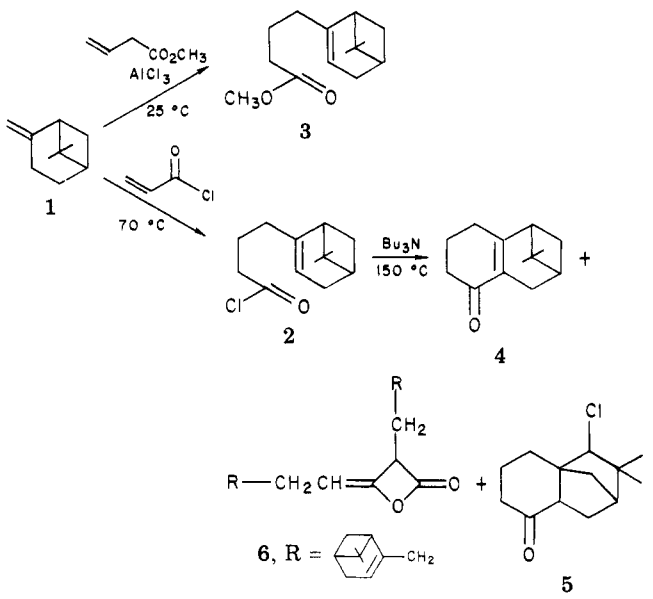
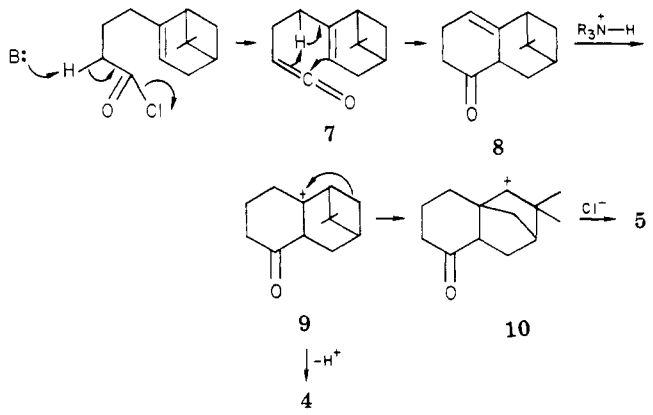
Scheme I



Scheme II

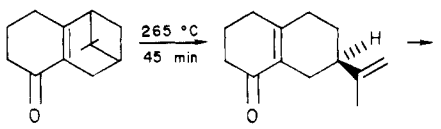


of β-selinene (**19**), a member of the eudesmane class[3] of sesquiterpenes. Acid chloride **2** is formed in 84% yield when acryloyl chloride is heated with β-pinene in a sealed tube at 70 °C for 48 h. Alternatively, **2** may be prepared, in somewhat lower yield, by simply refluxing acryloyl chloride and β-pinene for 48 h. Acid chloride **2** was characterized by conversion to the known methyl ester **3**[2] by using methanol and pyridine.

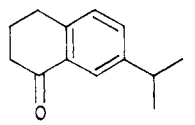
Heating **2** with tri-*n*-butylamine at 150 °C for 48 h yields, following distillation, a mixture of tricyclic ketone **4**[4] (55% yield) and chloro ketone **5** (5% yield). Purification of the distillation residue by column chromatography yielded a viscous, oily substance thought to be dimer **6** on the basis of its chemical and spectral properties (see Experimental Section).

The mechanism of the cyclization of acid chloride **2** to **4** is envisioned as involving the ketene intermediate **7** which undergoes an intramolecular ene reaction[5] to form nonconjugated ketone **8** (Scheme II). Further action of tributylamine or tributylamine hydrochloride results in the isomerization of ketone **8** to the conjugated tricyclic ketone **4**. The ion **9**, formed by protonation of **8**, may lose a proton to give **4**, or it may undergo a Wagner–Meerwein rearrangement to ion **10** followed by capture of chloride ion to form chloro ketone **5**. Dimer **6** is viewed as resulting from a head to head dimerization of ketene **7**.

Ketones **4** and **5** may be separated by column chromatography. However, it was found more convenient to take the ketone mixture on to the next step and purify at that point. The ketone mixture was pyrolyzed at *265 °C for 45 min* to yield, following chromatography, bicyclic ketone **11** (94% yield) and unchanged chloro ketone **5** (eq 1).

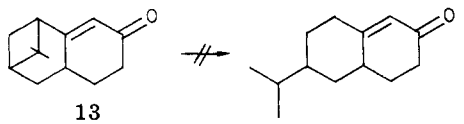


4 **11**



12 (1)

Prolonged heating of **4** produced a complex mixture of aromatic materials from which tetralone **12** could be isolated via its semicarbazone derivative.[6] By way of comparison, Thomas[7] et al. have found that the related tricyclic ketone **13** does not undergo fragmentation to give the analogous bicyclic ketone **14** (eq 2). Instead, a complex



13 **14** (2)

mixture of compounds is formed from which several radical recombination products may be isolated. The facile fragmentation of tricyclic ketone **4** to form bicyclic ketone **11** is probably due to the fact that the hydrogen on one of the methyl groups of **4** lies directly over the carbon–carbon double bond which makes **4** ideally disposed to undergo a retroene fragmentation. On the other hand, tricyclic ketone **13** cannot achieve the proper transition state to undergo the retroene reaction and instead fragments by an alternate pathway.

Bicyclic ketone **11** may also be formed in one step by heating β-pinene and acryloyl chloride in a sealed tube at 150 °C for 48 h or by heating ene adduct **2** at 150 °C for several hours. However, the yield of ketone **11** from either of these procedures is low, and it is contaminated by large

(1) The ene reactions of acrolein, acrylonitrile, and methyl acrylate with olefins typically require high temperature and proceed in relatively low yield. Alder, K.; Pascher, F.; Schmitz, A. *Chem. Ber.* **1943**, *76*, 27. Kruk, C.; Velyers, J. C.; de Boer, T. J. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 139. Albisetti, C. J.; Fisher, N. G.; Hogsed, M. J.; Joyce, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 2637. Alder, K.; Von Brachel, H. *Justus* Liebigs *Ann. Chem.* **1962**, *651*, 141.

(2) For examples of the Lewis catalyzed ene reaction see: Snider, B. B. *J. Org. Chem.* **1974**, *39*, 255.

(3) For references to the isolation and syntheses of eudesmanes see: MacKenzie, B. D.; Angelo, M. M.; Wolinsky, J. *J. Org. Chem.* **1979**, *44*, 4042.

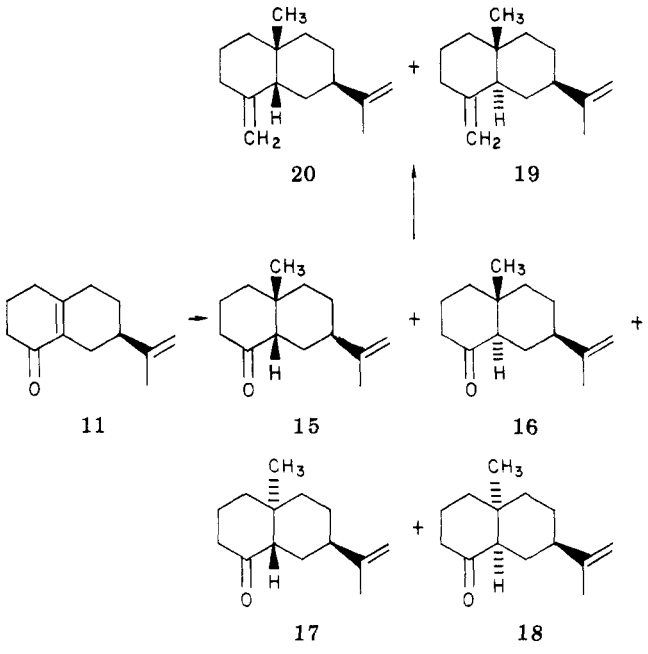
(4) Krieger, H.; Yrjanheikki, E.; Huhtala, P. *Finn. Chem. Lett.* **1978**, 219.

(5) (a) Erman, W. F.; Treptow, R. S.; Bakuzis, P., Wenkert, E. *J. Am. Chem. Soc.* **1971**, *93*, 657. See this reference for the thermal conversion of chrysanthenone to piperitenone possibly via a ketene intermediate. (b) For a review of the intramolecular ene reaction see: Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. (c) Alternate pathways for the formation of **4** and **5** visualize a two-step process involving ionic or biradical intermediates or an acid-catalyzed (tributylamine hydrochloride) cyclization of **7** involving an acyl cation and direct formation of cation **9**. It should be noted that ketone **4** is not converted to chloro ketone **5** under the conditions of the cyclization.

(6) Adachi, K. *Nippon Kagaku Zasshi* **1971**, *92*, 654.

(7) Bessiere, Y.; Barthelemy, M.; Thomas, A. F.; Pickenhagen, W.; Starkemann, C. *Nouv. J. Chim.* **1978**, *2*, 365.

Scheme III

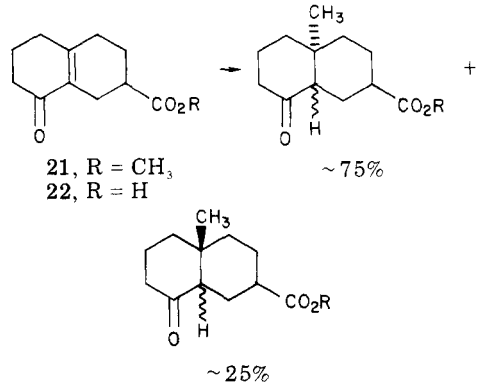


amounts of chloro ketone **5**, bornyl chloride, and fenchyl chloride. We believe that the mechanism of this reaction is essentially the same as that previously proposed: β-pinene (**1**) and acryloyl chloride react at 150 °C to form ene adduct **2** which further reacts to give tricyclic ketone **4**. The fragmentation of ketone **4** at 150 °C instead of 265 °C may be due to acid catalysis (HCl) of the retroene step.

With compound **11** in hand, we turned next to the final steps in the elaboration of the eudesmane skeleton. The angular methyl group was introduced via lithium dimethylcuprate addition. This reaction gave a mixture of four isomeric ketones, **15–18** (Scheme III), which could be separated by column chromatography. Isomers **15** and **16**, with the angular methyl group cis to the isopropenyl group, were obtained in 35% and 40% yields, respectively, whereas the trans isomers **17** and **18** were obtained in 12% and 13% yields, respectively. Thus, the majority (75%) of the products resulting from the cuprate addition to **11** contained the angular methyl group cis to the isopropenyl group as found in β-selinene (**19**). The structural assignments of these compounds were based on equilibration data and the useful generalization that trans-fused 10-methyl-1-decalones show NMR shifts for the angular methyl group which are typically in the 0.75–0.95-ppm range, while cis-fused 10-methyl-1-decalones show NMR shifts for the angular methyl which are typically in the 1.05–1.25-ppm range.[8]

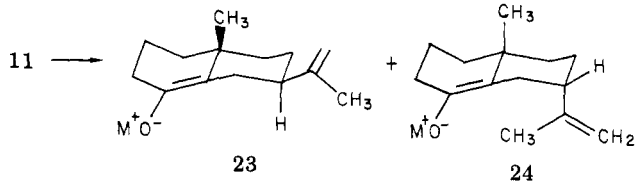
The results of this cuprate addition to ketone **11** contrast sharply with those reported by Carlson[9] and Huffman,[10] who employed ester **21**[9] or carboxylic acid **22**[10] (eq 3). In the latter cases the major products (75%) from cuprate addition are those with the angular methyl group trans to the ester or the acid group.

We believe our results are in accord with the bulk of the literature on cuprate additions to conjugated enones.[11] There seems to be a stereoelectronic preference for axial attack of the cuprate reagent leading to enolates **23** and **24** (eq 4). Enolate **23** would be expected to predominate

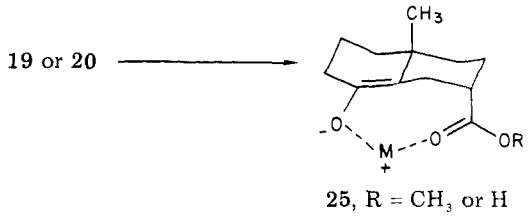


(3)

on the basis of its greater thermodynamic stability (isopropenyl equatorial). Our results seem to bear this out.



(4)



(5)

The Carlson and Huffman results may be explained if one assumes that the transition-state energy of enolate **25** is lowered by chelation of the ester or acid functions and the enolate with a metallic ion (copper or lithium; eq 5).

An attempt was made to equilibrate the isomeric ketones **15–18** by treating them with methanolic sodium methoxide at room temperature for 24 h. Under these conditions ketone **15** equilibrated to a 9:1 mixture of ketones **16** and **15** as determined by integration of the methyl signals in the NMR. Ketone **16** likewise equilibrated to a 9:1 mixture of **16** and **15**. However, pure ketone **17** failed to equilibrate after 96 h. Finally, ketone **18** was observed to equilibrate to a 4:1 mixture of ketones **17** and **18** after 24 h. Equilibrium was apparently not reached in this case after 24 h.

The mixture of ketones **15–18** was treated with methylenetriphenylphosphorane in refluxing Me_2SO as previously described.[3] Examination of the NMR of the reaction mixture, following the removal of nonreacted starting materials by column chromatography, suggested not only the presence of β-selinene (**19**) but also its C-5 epimer **20**.[12] Unfortunately, efforts to isolate this material by conventional column chromatography or by HPLC were unsuccessful. Preparative gas chromatography likewise was not found useful. GC purified β-selinene showed an optical rotation of +49.2° which is in reasonably good agreement with the value reported for natural β-selinene.[13,14] The NMR and IR spectrum of **19** was identical with that of an authentic sample.[3]

(8) Marshall, J. A.; Hochstetler, A. R. *J. Org. Chem.* **1966**, *31*, 1020.
(9) Carlson, R. G.; Zey, E. G. *J. Org. Chem.* **1972**, *37*, 2468.
(10) Huffman, J. W.; Mole, M. L. *J. Org. Chem.* **1972**, *37*, 13.
(11) Posner, G. H. *Org. React.* **1972**, *19*, 1.
(12) Naya, Y.; Prestwich, G. D.; Spanton, S. G. *Tetrahedron Lett.* **1982**, *23*, 3047. These authors claim 5β,7β,10β-selinene is present in termite soldiers but in too small a quantity to properly characterize.
(13) Ganter, C.; Keller-Wojtkiewicz, B. *Helv. Chim. Acta* **1971**, *54*, 183.
(14) Pliva, J.; Horak, M.; Herout, V.; Sorm, F. "Die Terpene", Akademie-Verlag: West Berlin, 1960: Part I, p 582.

Experimental Section

All melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Associates A-60 spectrometer at 60 MHz or on a Perkin-Elmer Model R-32 spectrometer at 90 MHz. Infrared spectra were obtained with a Perkin-Elmer Infracord, Model 137-B. Ultraviolet spectra were recorded on a Cary 15 spectrophotometer. Mass spectra were provided by Purdue University Mass Spectral Service. Optical rotation measurements were taken on a Rudolph Research Autopol III polarimeter. Microanalyses were performed by Dr. C. S. Yeh and associates.

6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-butanoyl Chloride (2). A mixture of 7.8 g (0.086 mol) of acryloyl chloride, 46.9 g (0.344 mol) of (−)-β-pinene [$[\alpha]^{23}_D$ −20.7° (neat)], and 1 mg of hydroquinone was heated at 70–72 °C under nitrogen for 48 h. The excess β-pinene (now containing ca. 10–15% α-pinene) was distilled under reduced pressure (0.5 mm) at ambient temperature. The residue, acid chloride **2** (13.80 g, 71% yield), was sufficiently pure for use in the next reaction.

Alternately, a sealed Pyrex tube containing acryloyl chloride (7.8 g, 0.086 mol), (−)-β-pinene (46.9, 0.344 mol), and hydroquinone (1 mg) was heated at 70–72 °C for 48 h. Removal of β-pinene as described above afforded 16.42 g (84% yield) of acid chloride **2**: IR (neat) 1818, 1653 cm^{-1}; NMR ($CDCl_3$) δ 0.83 (s, 3, CH_3), 1.07 (s, 1, CH), 1.20 (s, 1, CH), 1.28 (s, 3, CH_3), 1.50–2.49 (m, 8 H), 2.87 (t, 2, CH_2COCl), 5.23 (br s, 1, =CH).

10,10-Dimethyltricyclo[7.1.1.$0^{2,7}$]undec-2(7)-en-6-one (4). To 11.3 g (0.061 mol) of stirred anhydrous tri-*n*-butylamine, heated to 150–152 °C, was added acid chloride **2** (12.61 g, 0.055 mol) dropwise over a period of 12 h under a nitrogen atmosphere. After the addition was complete, the mixture was allowed to stir at 150 °C for an additional 36 h. The reaction mixture was allowed to cool, and 100 mL of ether was added, causing tri-*n*-butylamine hydrochloride to precipitate. The amine salt was removed by filtration and washed throughly with ether. The ether solution was washed with water, 10% sodium hydroxide, and brine and was then dried ($MgSO_4$). Distillation gave a liquid [bp 73–76 °C (0.10 mm)] and a nondistillable viscous residue.

Column chromatography of the distillate (silica gel, 3:2 ether–pentane) afforded 0.62 g (5% yield) of ketone **5**: mp 33–34.5 °C; $[\alpha]^{23}_D$ +11.19° (*c* 5.73, hexane); IR (melt) 1724, 1333, 1163, 1136, 813, 797 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (s, 3, CH_3), 1.07 (s, 3, CH_3), 1.32 (s, 2, CH_2) 1.50–2.63 (m, 10 H), 3.70 (s, 1, CH-Cl); mass spectrum, *m/e* (relative intensity) 228 (1), 226 (2), 191 (7), 136 (13), 135 (14), 91 (16), 79 (20), 77 (20), 67 (11), 65 (15), 55 (37), 53 (27), 51 (22), 43 (30), 42 (37), 41 (44), 39 (100). Anal. Calcd for $C_{13}H_{19}C10$: C, 68.86; H, 8.44; Cl, 15.63. Found: C, 68.83; H, 8.36; Cl, 15.46.

Later chromatography fractions contained 5.72 g (55% yield) of ketone **4**: mp 30.5–33 °C; $[\alpha]^{23}_D$ −98.98° (*c* 4.05, hexane); UV (EtOH) λ_{max} 262 nm (log ε 4.06); IR (melt) 1666, 1626, 1379, 1266, 1190, 917, 877, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.80 (s, 3, CH_3) 1.12 (s, 1, CH), 1.25 (s, 1, CH), 1.33 (s, 3, CH_3) 1.75–2.67 (m, 10 H); mass spectrum, *m/e* (relative intensity) 191 (1), 190 (3), 149 (7), 147 (19), 106 (7), 105 (9), 91 (40), 79 (11), 78 (8), 77 (16), 65 (15), 55 (23), 53 (20), 52 (12), 43 (23), 42 (21), 41 (100), 39 (90). Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 82.01; H, 9.56.

It was found that column chromatography of the ketone mixture at this stage was unnecessary. The distillate mixture was typically carried on to the next step without further purification.

Column chromatography (silica gel, 1:9 ether–pentane) of the viscous residue which remained after distillation of ketones **4** and **5** afforded a compound, tentatively assigned structure **6**, as an amber oil: IR (neat) 1754, 1612, 1136, 787 cm^{-1} NMR ($CDCl_3$) δ 0.85 (s, 6 H, CH_3), 1.27 (s, 6 H, CH_3), 1.52–2.78 (m, 21 H), 4.73 (br s, 1 H, =CH), 5.23 (br s, 2 H, =CH); exact mass, *m/e* 380.269 (calcd for $C_{26}H_{36}O_{29}$ *m/e* 380.272). Saponification of **6** yielded a carboxy ketone which was not characterized.

(+)-7-(2-Propenyl)-Δ^9-decal-1-one (11). To a 50-mL round-bottomed flask, equipped with a magnetic stirring bar, a gas inlet tube, and a reflux condenser, was placed a 11.64-g portion of the crude mixture of ketones **4** and **5** (approximately 90% ketone **4**) obtained as described above. The mixture was heated under argon at 265–268 °C for 45 min. The crude pyrolyzate was cooled and chromatographed on a silica gel column (4:1 pentane–ether), affording 9.9 g (94% yield) of ketone **11**: bp 88–89 °C (0.1 mm); $[\alpha]^{21.5}_D$ +113.57° (*c* 3.73, ethanol); UV (EtOH) λ_{max} 246 nm (log ε 4.04); IR (neat) 16.80, 16.39, 1258, 1197, 885 cm^{-1}; NMR ($CDCl_3$) δ 1.75 (s, 3, CH_3), 1.83–2.97 (m, 13 H), 4.75 (br s, 2 H, $=CH_2$); mass spectrum, *m/e* (relative intensity) 192 (3), 191 (12), 190 (73), 175 (63), 162 (28), 149 (58), 148 (24), 147 (93), 135 (30), 134 (50), 133 (21), 120 (26), 119 (51), 105 (41), 91 (100), 79 (60), 77 (51), 68 (30), 41 (46), 39 (44). Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 81.86; H, 9.80.

Heating the mixture of ketones **4** and **5** at 265 °C for periods of time exceeding 1 h led to the formation of aromatic materials which could be separated from ketone **11** by column chromatography (SiO_2, pentane). Treatment of the aromatic mixture with semicarbazide hydrochloride yielded the semicarbazone of 7-isopropyl-1-tetralone, mp 199–201 °C (lit.[6] mp 200–201 °C). The other aromatic compounds were not characterized. A similar result was observed when carefully purified ketone **11** was pyrolyzed.

7-(2-Propenyl)-10-methyl-1-decalones 15–18. To a cold (−78 °C) slurry of copper(I) iodide (3.35 g, 0.0176 mol) in 100 mL of anhydrous ether was added 19.6 mL (0.035 mol) of a 1.8 M solution of methyllithium. The reaction mixture was warmed to 0 °C, and 3.05 g (0.016 mol) of ketone **11** in 25 mL of anhydrous ether was added with stirring over a 15-min period. The mixture was kept overnight at 0 °C and treated with aqueous ammonium chloride (adjusted to pH 7–8 with ammonium hydroxide). The aqueous layer was separated and extracted with two 25-mL portions of ether. The combined ether extracts were washed with saturated ammonium chloride solution, saturated sodium carbonate solution, and brine. The ethereal extract was dried ($MgSO_4$) and evaporated. Column chromatography of the residue on silica gel (methylene chloride) afforded 2.61 g (79% yield) of an isomeric mixture of ketones distributed as follows. Fractions 1–84 contained 0.91 g of pure isomer **15**: IR (neat) 1724, 1639, 1190, 1075, 885 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (s, 3, CH_3), 1.76 (s, 3, $=CCH_3$), 1.22–4.13 (m, 14 H), 4.73 (br s, 2, $=CH_2$); mass spectrum, *m/e* (relative intensity) 207 (11), 206 (60), 191 (24), 135 (21), 111 (78), 79 (21), 67 (34), 55 (58), 53 (38), 43 (23), 41 (100), 39 (63). Fractions 89–119 contained 0.69 g of a mixture of isomer **16** (82%) and isomer **17** (18%) as determined by NMR integration of the corresponding methyl signals: IR (neat) 1724, 1653, 885 cm^{-1}; NMR ($CDCl_3$) δ 0.78 (s, 3, CH_3, isomer **16**), 1.02 (s, 3, CH_3, isomer **17**), 1.76 (br s, 3, $=CCH_3$), 1.17–2.5 (m, 14 H), 4.73 (br s, 2, $=CH_2$). Fractions 120–195 contained 0.70 g of a mixture of isomer **16** (69%) and isomer **17** (31%) as determined by NMR integration of the corresponding methyl signals: IR (neat) 1724, 1653, 885 cm^{-1}; NMR ($CDCl_3$) δ 0.78 (s, 3, CH_3, isomer 16), 1.02 (s, 3, CH_3, isomer **17**), 1.76 (br s, 3, $=CCH_3$), 1.17–2.5 (m, 14 H), 4.73 (br s, 2, $=CH_2$). Finally fractions 205–251 contained 0.31 g of pure isomer **18**: IR (neat) 1724, 1639, 1242, 1219, 885 cm^{-1}; NMR ($CDCl_3$) δ 0.92 (s, 3, CH_3), 1.73 (s, 3, $=CCH_3$), 1.1–2.6 (m, 14 H) 4.73 (s, 2, $=CH_2$); mass spectrum, *m/e* (relative intensity) 206 (46), 150 (39), 107 (28), 95 (56), 93 (26), 81 (40), 79 (51), 77 (40), 69 (22), 68 (48), 67 (55), 65 (26), 55 (100), 40 (46).

Equilibration of Ketones 15–18. A solution containing 0.15 g (0.73 mmol) of pure ketone **15** in 6 mL of 0.25 M methanolic sodium methoxide was stirred at room temperature for 24 h under nitrogen. The mixture was acidified with 10% hydrochloric acid and an equal volume of water was added. The product was then extracted with ether. The ether extract was washed with water and dried ($MgSO_4$), and the ether was removed by using a rotary evaporator. The residue contained a mixture of **16** and **15** in a 9:1 ratio as determined by NMR integration of the corresponding methyl signals. The mixture of ketones **16** and **17** and pure ketone **18** were equilibrated by using a procedure identical with that described above. Ketone **17** was observed to equilibrate to a 4:1 ratio of ketones **18** and **17** after 24 h while ketone **16** equilibrated to a 9:1 ratio of **16** and **15**. Pure ketone **18** did not equilibrate to ketone **17** even after 96 h.

β-Selinene (19). To a stirred solution of 7 mL of 1.97 M solution of sodium methylsulfinyl carbanion in dimethyl sulfoxide was added a solution of 5.0 g (14 mmol) of methyltriphenylphosphonium bromide in 15 mL of dimethyl sulfoxide. After 5 min, 1.9 g (9 mmol) of the mixture of isomeric ketones **15–18** in 7 mL of dimethyl sulfoxide was added. The solution was stirred at 80 °C under nitrogen for 65 h, cooled, and poured into an equal volume of water. The mixture was extracted with four 10-mL

portions of pentane, and the combined pentane extracts were washed twice with 10 mL of 50% dimethyl sulfoxide/water and three times with 10 mL of water. The pentane extracts were dried ($MgSO_4$), and the pentane was removed. Plug filtration of the residue (silica gel, pentane) afforded 1.3 g of an amber oil which displayed methyl signals at 0.73 and 1.26 ppm in a ratio of ca. 4:1. Preparative GLC of the oil on a 5% SE-52 column at 150 °C yielded 1.03 g of (+)-β-selinene: $[\alpha]^{23}_D$ +49.2° (c 0.234, hexane) (lit. $[\alpha]_D$ +43°[13]; +48°[14]); IR (neat) 1639, 877 cm^{-1}; NMR (CCl_4) 0.71 (s, 3, CH_3), 1.70 (s, 3, $=CCH_3$), 4.41 (s, 1, vinyl H), 4.68 (s, 3, vinyl H).

Registry No. 1, 18172-67-3; **2**, 86954-28-1; **3**, 42913-51-9; **4**, 81600-98-8; **5**, 86954-29-2; **6**, 86954-30-5; **11**, 86954-31-6; **12**, 35338-72-8; **15**, 71616-19-8; **16**, 5003-59-8; **17**, 87036-86-0; **18**, 87036-87-1; **19**, 17066-67-0; **20**, 83434-35-9.

1-Phenyl-*cis*-3a,7a-dihydrophosphindole and Its Properties[1]

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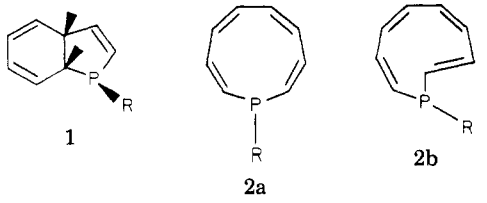
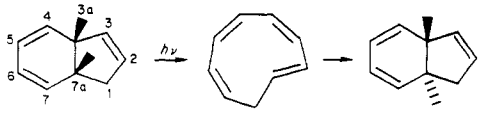
Deoxygenation of the dimer of 1-phenylphosphole oxide gives the diphosphine, whose thermal decomposition provides a useful route to *r*-1-phenyl-*c*-3a,*c*-7a-dihydrophosphindole. In the gas phase in the temperature range 345–370 °C the dihydrophosphindole undergoes partial epimerization about the phosphorus atom. However, in the higher temperature range of 460–490 °C ring cleavage occurs to give the isomeric phenyl-2-styrylphosphines in nearly quantitative yield. Peroxide oxidation of the dihydrophosphindole provides the corresponding oxide, which on thermolysis in the gas phase rearranges to the isomeric 2,3-dihydrophosphindole 1-oxide. Attempts at deoxygenation of the 3a,7a-dihydrophosphindole 1-oxides with trichlorosilane–triethylamine yielded phenyl-*cis*-2-styrylphosphine. Treatment of derivatives of the *cis*-3a,7a-dihydrophosphindoles with base (triethylamine or hydroxide) also effects ring cleavage to give styryl-substituted phosphines.

Although several derivatives of *cis*-3a,7a-dihydrophosphindole **1** have been reported,[2,3] the primary emphasis has been with regard to their usefulness in transformations to the phosphindole system. Other aspects of the chemistry of this class of phosphorus heterocycles have largely been left unexplored. Our attention was attracted to this system during a search[4] for synthetic methods that could provide simple derivatives of the 10-π-electron phosphonin molecule; retrocycloaddition could conceivably provide this ring system (**2a** or **2b**). Such conversions are

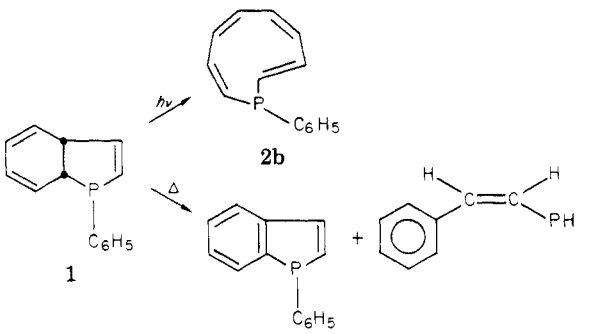


known for their carbocyclic counterpart (dihydroindenes); under photolytic conditions *cis*-3a,7a-dihydroindene was converted to *trans*-3a,7a-dihydroindene,[5] no doubt through the intermediacy of *cis,cis,trans*-cyclononatetraene.



However, under thermolytic conditions, *cis*-3a,7a-dihydroindene provided different products: indene, by a concerted 1,4-elimination of hydrogen followed by a 1,5 hydrogen shift, and allylbenzene, by transfer of a hydrogen atom from C(3a) to C(3) with the rupture of the C(1)–C(7a) bond.[6] Scheme I summarizes the products that could be obtained if similar events occurred for *cis*-3a,7a-dihydrophosphindoles. While photocleavage of the C(3a)–C(7a) bond could provide phosphonin derivatives, a thermal one-step elimination of hydrogen (in analogy to the transformation of cyclopentene to cyclopentadiene[7]) could give the fully unsaturated phosphindole system, and rupture of the P–C(7a) bond could occur to yield secondary phosphines. This paper presents the results of a study of these possibilities.

Scheme I



Synthesis of 3a,7a-Dihydrophosphindole Derivatives

Our route to the 3a,7a-dihydrophosphindole system makes use of the readily available dimers of phosphole oxides.[8,9] Thus dimer **3** (R = C_6H_5) was reduced to the

(1) Supported by Grant CHE-7717876 from the National Science Foundation.
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