somewhat more negative half-wave potentials were obtained. The values are, in fact, indicative of considerable oxidizing power on the part of diazonium cations. The electrode reaction studied here apparently involves the reversible addition of an electron to the diazonium cation to produce a diazonium radical, eq 1, which may either be reduced further, reacts, or more often decomposes with the release of N_2 to produce a phenyl radical. The existence of the phenyl diazonium radical, $C_6H_5N_2\cdot$, is attested to by the composition of the tar $(C_6H_5N_2)_n$ found by Kochi.[5] It is also supported by the fact that phenylhydrazine is the normal product of polarographic reduction of diazonium compounds.[7] The ready decomposition of these diazonium radicals, when further reduction does not take place, to phenyl radicals will be the subject of the next paper in this series.

Registry No.—Tetrabutylammonium perchlorate, 1927-70-2; sulfolane, 77-79-2.

The Synthesis of Bilobanone

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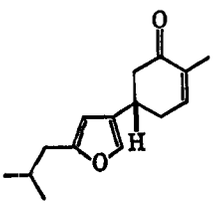
Oxidation of (+)-carvone with selenium dioxide in alcohol solution gave the optically active aldehyde **5**, the optically inactive tertiary alcohol **7**, and dehydrocarvacrol (**6**). The mechanism of oxidation is discussed. Condensation of the aldehyde **5** with the Grignard reagent from 3-methyl-1-butyne produced the secondary alcohol **16**. Oxotropic rearrangement to the primary alcohol **20** followed by mercuric ion catalyzed cyclization completed the synthesis of bilobanone (**1**). Two minor products, **22** and **23**, are formed concurrently and their origin is discussed.

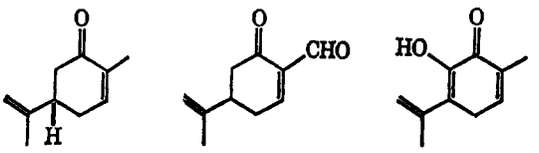
Bilobanone, a constituent of the heartwood of *Ginko biloba* L., is a sesquiterpene with structure **1**.[1] It became of interest to evaluate bilobanone (**1**) as a potential raw material in perfumery and in this paper we describe its synthesis.



1

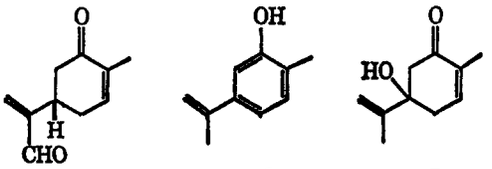
(+)-Carvone was an obvious starting material and selenium dioxide appeared to be a suitable reagent for introducing a functional group into the isopropenyl side chain. This oxidizing agent attacks the most nucleophilic double bond in polyolefins[2,3] and the rules of Guillemonat[4] predict the alcohol **13** to be the major product of oxidation. Our enthusiasm for this approach was temporarily dampened by reading a paper on the oxidation of carvone (**2**) with selenium dioxide to a mixture of the aldehyde **3** and the diosphenol **4**.[5] The structural arguments presented, however, were far from convincing and we decided to reinvestigate the reaction.

In our hands this oxidation gave a product mixture of which approximately 20% could be distilled under a high vacuum. Extraction of the volatile portion



2 **3** **4**

with aqueous sodium hydroxide followed by distillation of the nonacidic portion gave an optically active substance, mp 25–26° (6% yield), whose spectral properties (see Experimental Section) demand structure **5**. The base-soluble material consisted of essentially pure dehydrocarvacrol (**6**). Analysis of the volatile portion of a crude oxidation mixture by gas chromatography *prior* to extraction with aqueous sodium hydroxide revealed the presence of approximately 10% aldehyde **5**, only 8% phenol **6**, and 70% optically inactive hydroxy ketone **7**. Hence, the major volatile product formed in the oxidation of carvone (**2**) with selenium dioxide is not the primary alcohol **13** nor the corresponding aldehyde **5** but, contrary to the "rules",[4] the tertiary alcohol **7** which was indeed transformed to the phenol **6** by brief exposure to sodium hydroxide.



5 **6** **7**

The formation of the three products can be rationalized in terms of a mechanism proposed by Wiberg and Nielsen.[6] Addition of the conjugate acid of selenous acid to the isopropenyl group of carvone (**2**)

(1) H. Irie, H. Kimura, N. Otani, K. Ueda, and S. Uyeo, *Chem. Comm.*, 678 (1967); H. Kimura, H. Irie, K. Ueda, and S. Uyeo, *Yakugaku Zasshi*, **88**, 562 (1968).

(2) R. Delaby and E. Dupin, *Bull. Soc. Chim. Fr.*, **5**, 931 (1938).

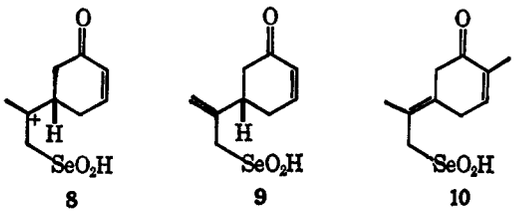
(3) G. Büchi and H. Wüest, *Helv. Chim. Acta*, **50**, 2440 (1967).

(4) A. Guillemonat, *Ann. Chim.* (Paris), **11**, 143 (1939).

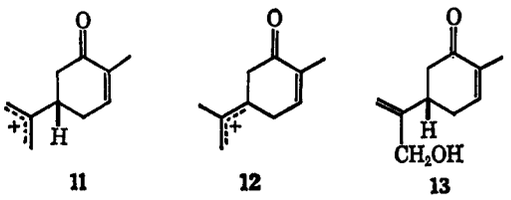
(5) K. K. Chakravarti and S. C. Bhattacharyya, *Perfum. Essent. Oil Rec.*, **46**, 341 (1955).

(6) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).

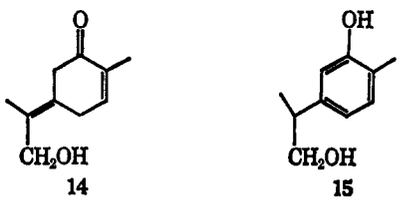
would give a carbonium ion **8** which by proton loss could proceed to the two allyl seleninic acids, **9** and **10**. SN1-type decomposition of **9** to the allyl carbonium ion **11**, followed by combination with water and further oxidation, would lead to the aldehyde **5**. The analogously formed allylic ion **12** could again combine with water to give the relatively stable alcohol **7** actually isolated and the hypothetical primary alcohol **14** which is expected to isomerize to the phenol **15**. Selenium dioxide is known to oxidize phenols[7] to a multitude of higher molecular weight products and the absence of **15** among the reaction products is therefore not surprising. Proton loss within the allylic ion **12**, followed by tautomerization, would produce dehydrocarvacrol (**6**), of which for reasons just mentioned only very minor amounts survive the conditions of the reaction.



8 **9** **10**



11 **12** **13**

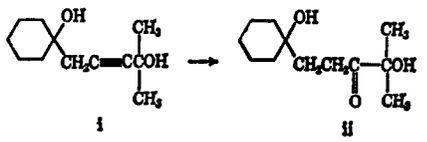


14 **15**

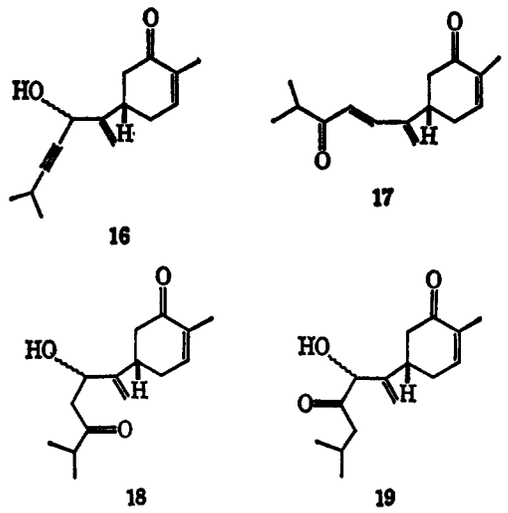
When the aldehyde **5** was condensed with 1 equiv of the Grignard reagent prepared from 3-methyl-1-butyne and ethylmagnesium bromide, the secondary alcohol **16** was obtained in 53% yield. Efforts to convert the latter into bilobanone (**1**) in one operation met with failure. When alcohol **16** was subjected to the action of dilute aqueous sulfuric acid in the presence of mercuric sulfate the trienedione **17** was produced in 33% yield. It probably results from dehydration of the initially formed β-hydroxy ketone **18**. We doubt that hydration of the unsymmetrical acetylene **16** is unidirectional and the many other more polar substances formed could well originate from the isomeric α-hydroxy ketone **19**.[8]

(7) N. Rabjohn, *Org. Reactions*, **5**, 331 (1949).

(8) The hydration of disubstituted acetylenes containing an α-hydroxy grouping is reported to yield β-hydroxy ketones and the corresponding α,β-unsaturated ketones,[9] but the yields are far from quantitative. An interesting "exception" is provided by the diol i which is converted into the ketone ii in 82% yield.[10] We attribute this structural specificity to neighboring-group participation by the β-hydroxy group in the transition state for hydration. This mechanistic principle was first recognized and put to preparative use in the hydration of acetylenic ketones.[11]

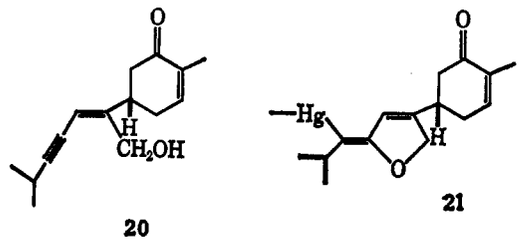


i ii



16 **17** **18** **19**

To prepare an acetylene which might undergo the desired unidirectional transformation, we studied the oxotropic rearrangement[12,13] of the secondary alcohol **16**. In the presence of aqueous mineral acid it was slowly transformed in 72% yield to the crystalline isomer **20**, mp 58–60°. The nuclear magnetic resonance (nmr) spectrum (see Experimental Section) was found to be in perfect agreement with the structure assigned and the ultraviolet (uv) spectrum features a maximum at 234 mμ (ε 20,700) attributable to superposition of two maxima caused by vinylacetylene and α,β-unsaturated ketone groupings. The geometry of the side-chain double bond was not established but the *trans* isomer shown below should represent the more stable situation. As anticipated mercuric sulfate promoted cyclization of the primary alcohol **20** gave the furan **1** directly[14] presumably *via* the intermediate **21** (*cf.* ref 11).



20 **21**

Infrared and nmr spectra of the synthetic furan were essentially identical with those of natural bilobanone (**1**) and the semicarbazones were identical as judged by comparison of ir spectra, melting points, and mixture melting point.[15] Natural bilobanone had an uv absorption maximum at 224 mμ (ε 12,000) in ethanol while our synthetic material had maximal absorption at 223 mμ (ε 13,600) in ethanol. Comparison with carvone (**2**), λ_{max} 235 mμ in ethanol, shows that the furan ring in bilobanone (**1**) has an effect on π–π* transition of the α,β-unsaturated ketone

(9) E. D. Venus-Danilova and S. N. Danilow, *J. Gen. Chem. USSR*, **2**, 645 (1932).

(10) A. Mondon, *Ann.*, **585**, 43 (1954).

(11) G. Stork and R. Borch, *J. Amer. Chem. Soc.*, **86**, 935, 936 (1964).

(12) E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 261 (1943).

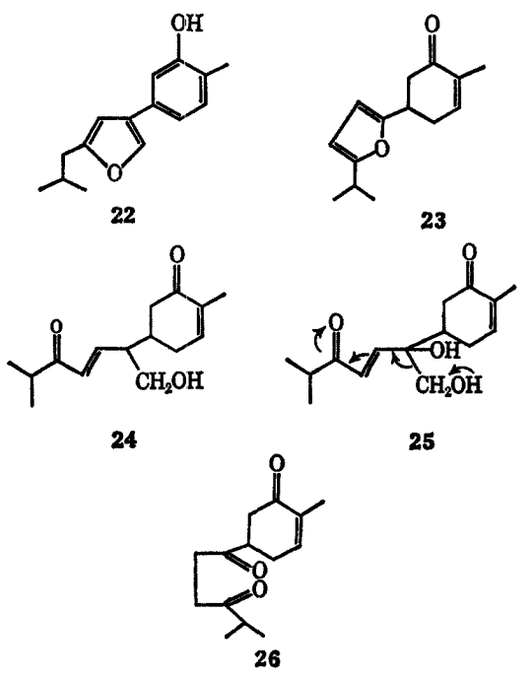
(13) E. A. Braude, *Quart. Rev.*, **4**, 404 (1950).

(14) I. M. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1586 (1947).

(15) We are much indebted to Professor S. Uyeo, Kyoto University, for this information and for a sample of natural bilobanone.

function.[16] The optical rotations of natural, $[\alpha]_D$ +42° (ethanol),[15] and synthetic, $[\alpha]_D$ +32° (ethanol), bilobanone unfortunately were not in good agreement and this situation might be attributed to partial racemization in the course of synthesis. Synthetic bilobanone was essentially odorless.

In conclusion we would like to discuss the structures and origin of two minor products formed in the mercuric salt catalyzed cyclization of the primary alcohol **20**. They are the phenol **22**, probably produced from bilobanone (**1**) by further oxidation with mercuric sulfate[17] and the C_{14} compound **23**. Nothing factual is known about the formation of the latter substance and we only tentatively suggest that it originates from the "wrong" diketone **24** which could have been oxidized further to the diol **25**. Retroaldol cleavage (**25**, arrows) followed by dehydration of the resulting γ diketone **26** would complete the change to the furan **23**.



Experimental Section

Microanalyses were performed by Dr. S. M. Nagy and associates of the Massachusetts Institute of Technology microchemical laboratory. Melting points and boiling points are uncorrected. Vapor phase chromatographic (vpc) analyses were performed on a F & M 720 instrument, using silicon rubber gum SE-30 and Carbowax 20M columns. The following spectrometers and solvents were used: nmr, Varian A-60 (CCl_4, TMS as internal standard); ir, Perkin-Elmer Model 237 ($CHCl_3$); uv, Cary Model 14 (EtOH); optical rotation, Zeiss polarimeter (EtOH); mass spectra (ms), Hitachi Perkin-Elmer RMU-60. Silicic acid "Mallinckrodt" 100 mesh was used for column chromatography.

Selenium Dioxide Oxidation of (+)-Carvone (2). A.—A stirred solution of 85 g (0.57 mol) of (+)-carvone, $[\alpha]_D$ +55°, in 300 ml of 95% ethanol was heated to reflux. Selenium dioxide (80 g, 0.72 mol) was then added in portions over a period of 45 min. After an additional 30 min of stirring the dark red solution was decanted from precipitated selenium and the solvent was removed *in vacuo*. The residue was distilled to give 18.5 g of an oil, bp 130–140° (0.4 mm), which was taken up in 100 ml of ether–pentane (1:1). The solution was extracted with three 35-ml portions of 1 *N* NaOH, washed to neutrality, dried (Na_2SO_4), and evaporated. Distillation of the remaining oil (10 g) through a short Vigreux column yielded 6.3 g (6.7%) of 85% pure aldehyde **5**, bp 80–82° (0.07 mm). An analytical sample was obtained by chromatography over silicic acid, using 25% AcOEt in hexane as eluent. It had mp 25–26°; $[\alpha]_D$ +76° (*c* 13.34); uv 219 mμ (ϵ 14,200), 234 (9600); ir 2700, 1690, 1670, 910 cm^{-1}; nmr 1.77 (d, 3, J = 1.5 Hz), 2.0–3.6 (m, 5), 6.21 (s, 1), 6.42 (s, 1), 6.8 (broad, 1), 9.65 (s, 1) ppm.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.10; H, 7.33.

The combined alkaline extracts from the treatment described above were acidified with 1 *N* H_2SO_4 and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. Distillation of the residue afforded 3.4 g of phenol **6**: bp 65° (0.1 mm) [lit.[18] bp 132° (14 mm)]; $n^{24}D$ 1.5608 (lit.[18] $n^{20}D$ 1.5587); ir 3590, 3380, 1880, 1790, 1660, 1620, 1580, 905, 830 cm^{-1}; nmr 2.05 (s, 3), 2.25 (s, 3), 5.03 (s broad, 1), 5.29 (s broad, 1), 5.80 (s, 1) (disappears on exchange with D_2O), 6.88 (s broad, 1), AB system centered at 7.08 (2 H) ppm.

B.—A mixture of 18 g (0.12 mol) of (+)-carvone, 6.6 g (0.06 mol) of selenium dioxide, and 20 ml of 95% EtOH was stirred and refluxed for 2 hr. The solution was decanted, evaporated, and distilled to give 2.4 g of recovered carvone [bp 55–75° (0.3 mm)] and 6.9 g of a mixture [bp 100–108° (0.3 mm)] consisting of approximately 70% hydroxy ketone **7**, 10% aldehyde **5**, and 8% phenol **6** (vpc analysis). Pure hydroxy ketone **7** was obtained by chromatography over silicic acid, using 30% AcOEt in hexane as eluent. It had bp 79–80° (0.2 mm); $[\alpha]_D$ 0°; uv 236 mμ (ϵ 7800); ir 3580, 3430, 1670, 915 cm^{-1}; nmr 2.8 (m, 6), 2.2–2.9 (m, 4), 3.96 (s, 1) (disappears on exchange with D_2O), 4.91 (s broad, 1), 5.04 (s broad, 1), 6.7 (broad, 1) ppm.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.35; H, 8.22.

Alcohol 16.—A solution of 10.9 g (0.16 mol) of 3-methyl-1-butyne (commercial product from Farchan Research Laboratories, Willoughby, Ohio) in 40 ml of dry tetrahydrofuran was added dropwise at 5–10° to ethylmagnesium bromide, prepared from 3.65 g (0.15 g-atom) of magnesium and 17.4 g (0.16 mol) of ethyl bromide in 125 ml of tetrahydrofuran. Stirring was continued at room temperature until ethane evolution had ceased (~1 hr). This reagent was then added at 5° over a period of 1 hr to a stirred solution of 21.3 g (0.13 mol) of aldehyde **5** in 100 ml of tetrahydrofuran. The entire procedure was carried out under nitrogen. After 2-hr stirring at room temperature, the mixture was decomposed with cold saturated NH_4Cl solution and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. Distillation of the residue yielded 15.9 g (53%) of alcohol **16**, bp 120–122° (0.05 mm). An analytical sample was obtained by chromatography on silicic acid, using 20% AcOEt in hexane as eluent. It had $[\alpha]_D$ +15° (*c* 12.25); uv 237 mμ (ϵ 10,100); ir 3580, 3410, 2230, 1670, 925, 910 cm^{-1}; nmr 1.18 (d, 6, J = 6.5 Hz), 1.76 (s broad, 3), 2.0–3.3 (m, 6), 3.8 (broad, 1) (disappears on exchange with D_2O), 4.8 (broad, 1), 4.97 (s, 1), 5.36 (s, 1), 6.76 (broad, 1) ppm.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.67; H, 8.83.

Ketone 17.—A stirred mixture of 800 mg of alcohol **16**, 15 ml of 0.1 *N* H_2SO_4, and 100 mg of $HgSO_4$ was heated to reflux for 45 min under nitrogen. It was then extracted with ether, and the organic layer was washed with 5% $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated. The remaining oil was chromatographed on 25 g of silicic acid. A mixture of hexane and 20% AcOEt eluted 266 mg (33%) of ketone **17**: bp ~110° (0.1 mm); $[\alpha]_D$ −33° (*c* 6.55); uv 243 mμ (ϵ 15,000), 267 (17,400); ir 1670, 1620, 1600, 920, 905 cm^{-1}; nmr 1.10 (d, 6, J = 6.5 Hz), 1.75 (s broad, 3), 2.0–3.5 (m, 6), 5.42 (s, 1), 5.56 (s, 1), 6.38 (d, 1, J = 16 Hz), 6.73 (broad, 1), 7.18 (d, 1, J = 16 Hz) ppm.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.68; H, 8.81.

Alcohol 20.—A solution of 4.80 g of alcohol **16** in 70 ml of monoglyme and 50 ml of 2 *N* H_2SO_4 was refluxed under nitrogen for 5 hr. The cooled mixture was diluted with water and extracted twice with ether. The combined extracts were subsequently washed with water, 5% $NaHCO_3$, and water, dried

(16) Similar long-range effects were discussed by E. M. Kosower and D. C. Remy, *Tetrahedron*, **5**, 281 (1959), and by V. Georgian, *Chem. Ind.* (London), 930 (1954); 1480 (1957).

(17) *Cf.* the high temperature oxidation of cyclohexanone to phenylacetate with mercuric acetate: W. Treibs and H. Bast, *Ann.*, **561**, 165 (1949).

(18) W. Treibs, G. Lucius, H. Kogler, and H. Breslauer, *ibid.*, **581**, 59 (1953).

(Na_2SO_4), and evaporated. The remaining oil was chromatographed on 180 g of silicic acid. A mixture of hexane and AcOEt (3:1) eluted 0.86 g of recovered alcohol **16** and 2.84 g (72%, based on recovered starting material) of alcohol **20**, mp 54–56°. A sample was recrystallized from benzene–hexane to give colorless needles: mp 58–60°; $[\alpha]D$ −124° (*c* 1.82); uv 234 mμ (ε 20,700); ir 3600, 3440, 2200, 1670 cm^{-1}; nmr 1.16 (d, 6, J = 6.5 Hz), 1.76 (s broad, 3), 2.0–3.5 (m, 6), 4.08 (s, 3) (1 H disappears on exchange with D_2O), 5.55 (m, 1), 6.8 (broad, 1) ppm.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.72; H, 8.79.

Bilobanone (1).—A mixture of 2.63 g of alcohol **20**, 50 ml of monoglyme, 40 ml of water, 0.5 ml of 0.1 N H_2SO_4, and 500 mg of $HgSO_4$ was stirred and refluxed under nitrogen for 8 hr. Working up as described above gave a yellow oil which was transferred to a distillation flask. Upon heating in a 150° oil bath for 5 min (2 mm), followed by distillation at 120° (0.1 mm), 1.60 g of a mixture of products was obtained. Vpc analysis indicated the presence of approximately 56% bilobanone (**1**), 23% starting material **20**, 3% ketone **23**, and 8% phenol **22**. For separation on a preparative scale the mixture was chromatographed on 60 g of silicic acid. Elution with hexane and 1% AcOEt gave 950 mg of bilobanone, containing *ca.* 5% of ketone **23**. Further purification was achieved by vpc collection, followed by distillation. Pure bilobanone (**1**) had bp 102° (0.05 mm); $[\alpha]D$ +32° (*c* 4.85); uv 224 mμ (ε 13,600); ir 1670, 1610, 1550 cm^{-1}; nmr 0.94 (d, 6, J = 6.5 Hz), 1.75 (d, 3, J = 2 Hz), 2.8–3.3 (m, 8), 5.88 (s, 1), 6.67 (broad, 1), 7.08 (s, 1) ppm; ms 232 (parent peak), 148 (base peak). Synthetic and natural bilobanone were indistinguishable on two different vapor phase chromatographic columns and had identical R_f values on thin layer chromatography.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.64; H, 8.78.

The semicarbazone had mp 143–145° pure and admixed with an authentic sample.

Ketone 23.—This substance obtained from above vpc collection had ir absorptions at 1670, 1600, 1550 cm^{-1}; uv 229 mμ (ε 19,800); nmr 1.22 (d, 6, J = 6.5 Hz), 1.75 (d, 3, J = 2 Hz), 2.2–3.5 (m, 6), AB system centered at 5.78 (2 H), 6.63 (broad, 1) ppm; ms 218 (parent peak), 121 (base peak).

Phenol 22.—This compound (135 mg) was eluted with 5% AcOEt in hexane from the chromatogram described above: ir 3590, 3320, 1630, 1610, 1570 (broad), 870 cm^{-1}; uv 210 mμ (ε 41,300), 255 (8200), 292 (3600); nmr 0.92 (d, 6, J = 6.5 Hz), 1.94 (m, 1), 2.20 (s, 3), 2.46 (d, 2, J = 6.5 Hz), 5.23 (broad, 1) (disappears on exchange with D_2O), 6.10 (s, 1), 6.72 (s broad, 1), AB system centered at 6.94 (2 H, signals at 6.89 and 6.75 further split into doublets, J = 1.5 Hz), 7.39 (s, 1) ppm; ms 230 (parent peak), 187 (base peak). This substance is exceptionally air sensitive and its solutions in organic solvents turn green rapidly.

Registry No.—**1**, 17015-33-7; **5**, 19191-07-2; **7**, 19202-67-6; **16**, 19191-08-3; **17**, 19191-09-4; **20**, 19202-68-7; **22**, 19185-78-5; **23**, 19185-79-6.

Acknowledgment.—The authors wish to thank Firmenich et Cie, Geneva, for generous financial support.

Synthesis of 2-Thiabicyclo[2.2.1]heptane Derivatives[1a-c]

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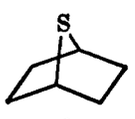
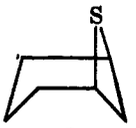
Received July 24, 1968

The addition of thiophosgene to cyclopentadiene provided 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene (**5**) which was converted into the more stable sulfone **7** by oxidation with *m*-chloroperbenzoic acid. Catalytic hydrogenation of the dichloro sulfone **7** resulted in the formation of the saturated monochloro sulfone **13** which was subsequently reduced to the parent sulfide **12** with lithium aluminum hydride. Reduction of sulfone **7** with chromous ion in aqueous acetone followed by lithium aluminum hydride provided 2-thiabicyclo[2.2.1]hept-5-ene (**10**). The alcohol, *exo*-5-hydroxy-2-thiabicyclo[2.2.1]heptane, was prepared by a multistep sequence from 4-hydroxycyclopentene.

The preparation of conformationally rigid molecules which include heteroatoms in the skeleton is of value for a variety of reasons including stereochemical studies and studies of intramolecular interactions.[2,3] Polycyclic compounds provide examples of conformationally fixed systems; however, only a few such simple compounds which incorporate sulfur in the skeleton are known. The most recent examples are certain caged ketosulfides synthesized by Paquette and Wise.[3] Thiabicycloheptanes would be of interest for stereochemical studies, but only a few such compounds (*e.g.*, **1** and **2**) are known.[4]



1



2

We wish to report convenient syntheses of 2-thiabicyclo[2.2.1]heptane (**12**) and 2-thiabicyclo[2.2.1]-hept-5-ene (**10**) and certain of their derivatives *via* the reaction sequences outline in Scheme I. The Diels–Alder reaction between cyclopentadiene and thiophosgene, first reported by Middleton,[5] was found to proceed readily to furnish dichlorosulfide **5** in very good yield. This compound is quite unstable; it decomposes to a black tar unless stored at Dry Ice temperatures and solvolyzes rapidly in hydroxylic solvents. The extreme reactivity of **5** places severe restrictions on the conditions which can be employed to effect synthetic transformations on the molecule; *i.e.*, moderate temperatures and nonhydroxylic solvents must be

(1) (a) Part XIII in the series Chemistry of Sulfoxides and Related Compounds. (b) Part XII: C. R. Johnson and J. J. Rigau, *J. Org. Chem.*, **33**, 4340 (1968). (c) We gratefully acknowledge support of this work by the National Science Foundation (GP 5944). (d) Alfred P. Sloan Reasearch Fellow, 1965–1968.

(2) For reviews of this subject, see N. J. Leonard, *Rec. Chem. Prog.*, **17**, 24 (1956); and L. N. Ferguson and J. C. Nadi, *J. Chem. Educ.*, **42**, 529 (1965).

(3) L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, **89**, 6659 (1967).

(4) (a) S. F Birch, R. A. Dean and N. J. Hunter, *J. Org. Chem.*, **23**, 1026 (1958); (b) E. J. Corey and E. Block, *ibid.*, **31**, 1663 (1966).

(5) W. J. Middleton, *ibid.*, **30**, 1390 (1965).