$$2 + H_2O_2, CH_3COOH \rightarrow$$

5

sulfonamide (**5**), identified by the presence of the SO_2 band and epoxide stretching frequencies in the infrared.

Treatment of 5-methylene-2-norbornene with N-sulfinylaniline yielded a single product (**6**). Elemental analysis was indicative of a 1:1 adduct; the infrared spectrum showed the presence of the N–H, S–O, and terminal methylene stretching frequencies. The presence of an *exo*-methylene group in **6** was also confirmed by the nmr spectrum, which may be interpreted as follows: a multiplet signal at 2.65 which integrated for four phenyl protons; a well-defined quartet from 6.05 to 6.65 for two terminal methylene protons; $H_{2,3}$ signal at 7.13; H_4 at 7.60; and H_1, H_6, $H_{7\,syn}$, $H_{7\,anti}$ at 8.11.

p-Methyl-N-sulfinylaniline yielded analogous *exo* adducts with norbornene (adduct **7**) and 5-methylene-2-norbornene (adduct **8**). With norbornadiene only a 1:1 *exo* adduct was isolated (adduct **9**). Reactions of the bicyclic alkenes with 2,6-dimethyl-N-sulfinylaniline were examined since blocking of the *ortho* positions might induce addition across the $N{=}S$ bond with the homoconjugated norbornadiene in a 1,4 fashion. Adduct formation was not observed, however.

Experimental Section

Elemental analyses were by Galbraith Laboratoris Inc., Knoxville, Tenn. All nmr spectra were obtained with a Varian A-60 spectrometer with tetramethylsilane as internal standard; peak assignments were in τ units. Infrared spectra were determined in potassium bromide pellets with a Beckman IR-5. A Wilkens Instrument Autoprep Model A-700 with helium as carrier gas was used for chromatography work.

N-sulfinylaniline and derivatives were prepared from the corresponding amines and thionyl chloride.[3] The bicyclic alkenes were obtained commercially.

Compound **1** was prepared as described previously, mp 229–231° (lit.[4] 230–231°).

Compunds **2** and **3** were prepared by adding N-sulfinylaniline (13.9 g 0.1 mole) dropwise with stirring to norbornadiene (9.2 g 0.1 mole) and refluxing the mixture for 20 min under a dry nitrogen atmosphere. Upon cooling a precipitate was formed which was isolated by filtration. Recrystallization from carbon tetrachloride afforded 9.7 g (42%) of compound **2** as colorless needles, mp 186–187°. Pertinent infrared data are as follows: NH stretching frequency, 3190 cm^{-1}; SO stretching frequency, 1053 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}NOS$: C, 67.50; H, 5.67; N, 6.06; S, 13.86. Found: C, 67.19; H, 5.67; N, 5.88; S, 13.64.

A second solid material was recrystallized from methanol to yield 8.2 g (22%) of compound **3** as colorless needles, mp 306–308°. Infrared stretching frequencies are as follow: NH, 3160 cm^{-1}; SO, 1050 cm^{-1}.

Anal. Calcd for $C_{19}H_{18}N_2O_2S_2$: C, 61.59; H, 4.89; N, 7.56; S, 17.30. Found: C, 61.41; H, 5.01; N, 7.50; S, 17.28.

When the reaction mixture was refluxed for 45 min the yields of **2** and **3** were 7.1 g (31%) and 14.1 g (38%), respectively.

Compound **2** (0.18 g 0.7 mmole) was dissolved in glacial acetic acid (20 ml) and added to 0.027 g of 10% palladium-over-carbon catalyst. The hydrogenation was performed according to the procedure of Pack and co-workers. The reaction mixture was filtered and the filtrate was neutralized with sodium bicarbonate to produce a colorless, crystalline mass. Isolation of the precipitate yielded 0.16 g (88%) of compound **1**, identified by mixture melting point and infrared and nmr spectra.

Compound **5** was obtained by dissolving **2** (2.3 g 0.01 mole) in glacial acetic acid (5 ml) to which was added slowly hydrogen

peroxide (30%, 5 ml). The reaction mixture was allowed to stand for 24 hr, and then poured over cracked ice. The formed precipitate was isolated, yielding 1.7 g (65%) of **5**, mp 122–124°. Pertinent infrared data are as follows: SO_2, 1140 and 1120 cm^{-1}; NH, 3290 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}NO_3S$: C, 59.17; H, 4.98; N, 5.32; S, 12.18. Found: C, 59.30; H, 5.15; N, 5.40; S, 12.18.

Compound **6** was obtained from 5-methylene-2-norbornene and N-sulfinylaniline by the procedure described for **2**. Reflux time was 20 min. Recrystallization of crude product from carbon tetrachloride yielded 37% of **6**, mp 222–224°. Pertinent infrared stretching frequencies are as follows: NH, 3153 cm^{-1}; SO, 1048 cm^{-1}.

Anal. Calcd for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71; S, 13.07. Found: C, 68.26; H, 6.18; N, 5.48; S, 13.06.

Compound **7** was obtained from norbornene and *p*-methyl-N-sulfinylaniline by the procedure described for **2** in 30% yield with a reaction time of 5 hr, mp 235–236° (from ethanol). Pertinent infrared stretching frequencies are as follows: NH, 3220 cm^{-1}; SO 1060 cm^{-1}. Increase of reaction time to 60 hr improved the yield slightly to 34%. Decomposition begins to occur 210–212° (lit.[4] 211–214°).

Compound **8** was obtained from norbornadiene and *p*-methyl-N-sulfinylaniline by the procedure described for **2** in a 36% yield, mp 205–206.5° (from ethanol). Decomposition begins to occur at 170–174°. Pertinent infrared stretching frequencies are as follows: NH, 3220 cm^{-1}; SO, 1060 cm^{-1}; nmr spectrum (in DCCl$_3$) 2.45 (NH), 3.00–3.40 (three-phenyl protons), 3.60 ($H_{5,6}$), 6.90 ($H_{2,3}$), 7.05 (H_1), 7.15 (H_4), 7.75 (methyl protons), 8.00–8.20 ($H_{7\,syn}$), 8.70–8.85 ($H_{7\,anti}$).

Anal. Calcd for $C_{14}H_{15}NOS$; C, 68.54; H, 6.16; N, 5.71; S, 13.07. Found: C, 68.32; H, 6.32; N, 5.42; S, 13.34.

Compound **9** was prepared from 5-methylene-2-norbornene by the procedure described for **2** in 30% yield, mp 218–219° (from ethanol). Decomposition begins to occur at 142–147°. Pertinent infrared stretching frequencies are as follows: NH, 3172 cm^{-1}; SO, 1057 cm^{-1}; nmr spectrum (in TFA) 2.83–3.20 three phenyl protons), 6.25–6.55 (doublet, terminal methylene protons), 7.05–7.20 (multiplet, $H_{2,3}$), 7.60 (broad, H_4 and methyl protons), 8.00, ($H_{1,6,7\,syn,\,7\,anti}$).

Anal. Calcd for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40; S, 12.36. Found: C, 69.30; H, 6.68; N, 5.54; S, 12.57.

Constituents of *Helenium* Species. XX. Virginolide, a New Guaianolide from *Helenium virginicum* Blake[1,2]

WERNER HERZ AND P. S. SANTHANAM

Department of Chemistry, The Florida State University, Tallahassee, Florida 32306

In 1936, Blake[3] reported the discovery in Augusta County, Va., of a *Helenium* colony closely related to, but apparently different from, *Helenium autumnale* L. and accorded it separate species status as *Helenium virginicum* Blake. This separation has been questioned.[4]

Through the courtesy of Dr. B. H. Braun we came into possession of *H. virginicum* which had been collected near the type locality. It appeared possible

(1) Supported in part by grants from the United States Public Health Service (GM-05814) and the Mallinckrodt Chemical Works.

(2) Previous paper: A. Romo de Vivar, L. Rodriguez-Hahn, J. Romo, M. V. Lakshmikantham, R. N. Mirrington, J. Kagan, and W. Herz, *Tetrahedron*, **22**, 3279 (1966).

(3) S. F. Blake, *Claytonia*, **3**, 13 (1936).

(4) Private communication from the late Dr. H. F. L. Rock, Department of Biology, Vanderbilt University, who concluded that this geographically severely restricted material possesses "no sound morphological features which are distinctive."

that the taxonomic problem could be resolved chemically since when the matter first came to our attention perusal of the literature indicated that extraction of *H. autumnale* had invariably resulted in isolation of the pseudoguaianolide helenalin (1).[5,7] In the present paper we report the results of our study of *H. virginicum* Blake. This led to the isolation of a new guaianolide which we have called virginolide and the flavone hispidulin (6-methoxy-4',5,7-trihydroxyflavone)[10] and afforded no indication of the presence of helenalin. *H. virginicum* Blake is thus at least chemically distinct from previously reported collections of *H. autmnale* L.

Virginolide ($C_{15}H_{16}O_3$, mp 133–135°, $[\alpha]D$ +4.45°), which was isolated from the whole plant or, in somewhat better yields, from the flowers, possessed spectral characteristics [λ_{max} 257 mμ (ϵ_{max} 14600), infrared bands at 1680, 1640, and 1625 cm^{-1}] characteristic of the dienone chromophore present in lactucin (3),[11] matricarin (4),[12] and analogous guaianolides isolated from *Achillea*,[13] *Artemisia*,[14] and *Sonchus*[15] species. The presence of a third exocyclic double bond conjugated with a γ-lactone group (infrared band at 1765 cm^{-1}) was suggested by strong end absorption near 205 mμ, was demonstrated chemically by ozonolysis (liberation of formaldehyde) and preparation of a pyrazoline, and was confirmed by microhydrogenation which resulted in the uptake of 3 mole equiv of hydrogen. The product was a mixture of hexahydrovirginolides from which a very small amount of a solid isomer (6) could be isolated. The infrared spectrum of this material exhibited bands at 1775 (γ-lactone) and 1740 cm^{-1} (cyclopentanone), the latter group being flanked by CH_2 (positive Zimmermann test).
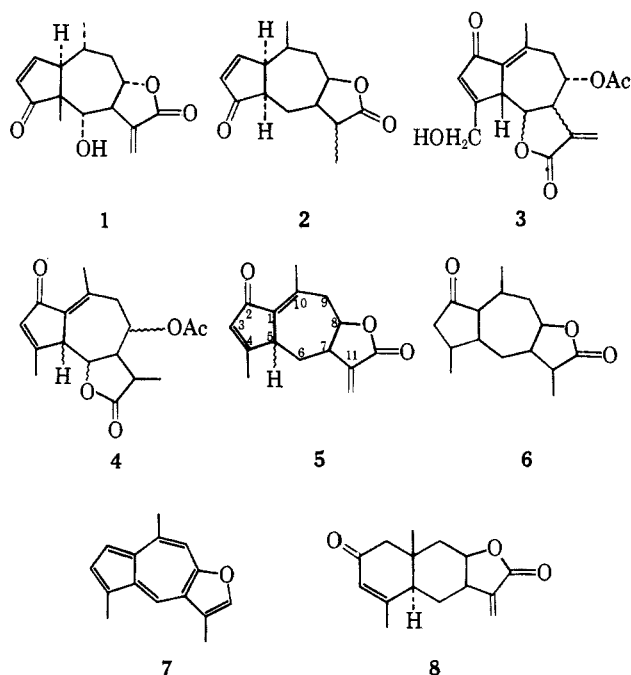
The nmr spectrum of virginolide corroborated these conclusions and led to the tentative formulation of virginolide as 5. Two low-field doublets at 6.15 and 5.49 ppm (J = 4 cps) were characteristic of the exocyclic methylene group conjugated with the lactone.[16] A third vinyl resonance at 6.09 (narrowly split quadruplet, J = 1 cps), was coupled to a narrowly split (J = 1 cps) vinyl methyl resonance at 2.15 ppm. This feature and a second, sharp vinyl methyl resonance at 2.45 ppm clearly revealed partial structure A also present in matricarin and achillin.[13] Virginolide also

exhibited a complex multiplet centered at 3.78 ppm characteristic of hydrogen on carbon carrying lactone oxygen which because of the multiplicity was spin

A
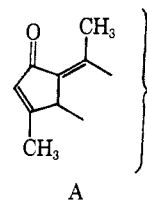
coupled to more than two adjacent hydrogens. Hence, if virginolide were a "normally-constituted" isoprenoid sesquiterpene derivative, it was clear that the lactone ring must be closed toward C-8 as in formula 5 rather than toward C-16.[17]

Confirmation for this structure was obtained by dehydrogenation. The hexahydrovirginolide mixture was reduced with lithium aluminum hydride. The crude triol on dehydrogenation with palladized charcoal afforded guaiazulene and a small amount of linderazulene (7), thus establishing the carbon skeleton of virginolide and the orientation of the lactone ring.

1   2   3

4   5   6

7   8

Virginolide is the second "normally-constituted" sesquiterpene lactone isolated from a *Helenium* species, the first being the eudesmanolide pinnatifidin from *H. pinnatifidum* (Nutt.) Rydb.,[18] and continues the pattern of lactone ring closure toward C-8 characteristic of compounds isolated from *Helenium* and related species. Because of the obvious relationship between virginolide and pinnatifidin and because all sesquiterpene lactones of established absolute configuration

(5) For leading references[6] see W. Herz, A. Romo de Vivar, J. Romo, and N. Viswanathan, *J. Am. Chem. Soc.*, **85**, 19 (1963).

(6) Unfortunately the previous workers did not detail the source of *H. autumnale* used for the isolation of helenalin. Two articles thank individuals, in the southeastern United States, for supplying material; other plants were grown from seed supplied by herbaria and botanical gardens.

(7) A more recent paper,[8] however, describes the isolation of dihydromexicanin E (2)[9] from a North Carolina collection of *H. autumnale*. Helenalin appeared to be absent. This suggests that an examination of other *H. autumnale* collections might be in order.

(8) R. A. Lucas, R. G. Smith, and L. Dorfman, *J. Org. Chem.*, **29**, 2101 (1964).

(9) A. Romo de Vivar and J. Romo, *J. Am. Chem. Soc.*, **83**, 2326 (1961); J. Romo, A. Romo de Vivar, and W. Herz, *Tetrahedron*, **19**, 2317 (1963); C. N. Caughlan, Mazhar-ul-Haque, and M. T. Emerson, *Chem. Commun.*, 151 (1966).

(10) W. Herz and Y. Sumi, *J. Org. Chem.*, **29**, 3438 (1964).

(11) D. H. R. Barton and C. R. Narayanan, *J. Chem. Soc.*, 963 (1958).

(12) W. Herz and K. Ueda, *J. Am. Chem. Soc.*, **83**, 139 (1961).

(13) E. H. White and R. E. K. Winter, *Tetrahedron Letters*, 137 (1963).

(14) K. S. Rybalko and P. S. Massagetov, *Med. Prom. SSSR*, **15**, 25 (1961); M. Holub and V. Herout, *Collection Czech. Chem. Commun.*, **27**, 2980 (1962).

(15) J. Bermejo Barrera, J. L. Breton Funes, and A. Gonzalez Gonzalez, *J. Chem. Soc.*, 1298 (1966).

(16) W. Herz, H. Watanabe, M. Miyazaki, and Y. Kishida, *J. Am. Chem. Soc.*, **84**, 2601 (1962); W. Herz, A. Romo de Vivar, J. Romo, and N. Viswanathan, *ibid.*, **85**, 19 (1963).

(17) This conclusion was strongly supported by the spectrum of a methanolic solution of virginolide containing a small amount of alkali which developed a strong maximum at 430 mμ owing to β elimination, with a corresponding decrease in intensity of the 256-mμ band. The acidic material isolated after the usual work-up could not be crystallized.

(18) W. Herz, R. B. Mitra, K. Rabindran, and N. Viswanathan, *J. Org. Chem.*, **27**, 4041 (1962).

contain a β-oriented C-7 side chain we suggest the partial stereochemistry implied in **5**.[19]

Experimental Section[20]

Extraction of *Helenium virginicum* Blake. A.—Aboveground material, 8.3 kg., collected by Dr. B. H. Braun on June 30, July 14, July 28, and Aug 11, 1963, near Hatton's Chapel, Staunton Quadrangle, Va., at *ca.* 1480 ft, was powdered and extracted with chloroform for 3 days. The chloroform extract was concentrated to dryness and the residual gum was taken up in 3 l. of ethanol and mixed with a solution of 75 g of lead acetate in 3 l. of water and 20 ml of acetic acid. After 4 days the clear supernatant liquid was decanted (through glass wool) and the residue was washed twice with ethanol. The ethanol-water mixture was concentrated to small volume and extracted thoroughly with chloroform. The extract was dried, filtered, and evaporated at reduced pressure and the residual gum (100 g) was chromatographed over silicic acid (500-ml fractions). Benzene (eight fractions) and benzene–chloroform (5:1, eight fractions, 5:3, eight fractions) eluted small amounts of oils or gums which contained no helenalin (tlc analysis). Benzene–chloroform (1:1, 16 fractions) gave a gum which solidified on treatment with ether (yield 5 g). Recrystallization from hexane–acetone afforded white needles of virginolide, mp 134°. Virginolide polymerized gradually on exposure to light or on standing, but can be separated from polymeric material by treatment with chloroform and passing the chloroform-soluble portion through a column of acid-washed alumina. Chloroform (ten fractions) and chloroform–methanol (99:1) eluted 0.2 g of a yellow flavone which melted at 292° after recrystallization from methanol. Conversion to the triacetate (mp 168–170°) and trimethyl ether (mp 164–165°) and direct comparison of the parent compound and its derivatives with hispidulin and its derivatives (infrared, nmr, tlc, mixture melting point) established the flavone as hispidulin. The more polar material was a gum which contained no helenalin.

B.—Flowers and flowers buds of *H. virginicum* (0.9 kg), collected by Dr. Braun at Hatton's Chapel on July 25 and Aug 8, 1965, were powdered and extracted with hexane and then with chloroform for 3 days. The extracts were worked up separately. Removal of hexane at reduced pressure yielded 10 g of gum which contained no helenalin (tlc analysis), and was chromatographed over silicic acid. Benzene eluted nothing. Benzene–chloroform (1:1) eluted a gum which solidified on titration with ether. Two recrystallizations from acetone–hexane gave 0.6 g of virginolide, mp 134°. Elution of the column with chloroform gave nothing.

The chloroform extract was worked up in the usual way and the residual gum (50 g) which contained no helenalin (tlc analysis) was chromatographed over silicic acid. Elution with benzene gave an oil. Further elution with benzene–chloroform (1:1 and 1:2) afforded crude virginolide. Rechromatography over silicic acid afforded 0.85 g of pure virginolide (mp 133–134°) from the benzene–chloroform (1:3) eluate. Elution of the column with chloroform–methanol (99:1) afforded hispidulin, (20 mg).

C.—Powdered leaves and stems, exclusive of flowers, collected at Hatton's Chapel on July 25 and Aug 8, 1965 (1.95 kg) were extracted with chloroform in the usual manner. The crude gum (40 g) was chromatographed over silicic acid as described in the previous paragraph; yield of pure virginolide was 2.4 g; yield of hispidulin was 25 mg.

Properties of Virginolide.—Analytically pure virginolide melted in the range 133–135°; $[\alpha]^{25}D$ +4.45° (*c* 1.00); infrared bands at 1765 (γ-lactone), 1680 (cyclopentenone), 1640 (double

bond), and 1625 cm^{-1} (strong, cisoid double bond); λ_{max} 256 mμ (ε 14,600), strong end absorption at 200 mμ (ε 11,200).

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; O, 19.65. Found: C, 73.25; H, 6.80; O, 20.02.

The pyrazoline was prepared by mixing a solution of 0.2 g of virginolide in 15 ml of tetrahydrofuran with 10 ml of an ethereal solution of diazomethane. After 3 days in the refrigerator the solvents were removed. The residue was recrystallized from chloroform–hexane and acetone–hexane, mp 144–147°.

Anal. Calcd for $C_{18}H_{18}N_2O_3$: C, 67.11; H, 6.34; N, 9.78. Found: C, 67.26; H, 6.30; N, 9.71.

A soluton of 0.4 g of virginolide in 20 ml of acetic acid was ozonized at 0° for 30 min, diluted with water, and steam distilled into a chilled, saturated, aqueous solution of dimedone. After standing there precipitated 0.12 g of the dimedone derivative of formaldehyde, mp 182–184°.

A solution of 0.3 g of virginolide in 65 ml of ethanol was allowed to stand with 5 ml of 5% ethanolic potassium hydroxide solution. The ultraviolet spectrum of the solution developed a maximum at 430 mμ while the 256-mμ maximum characteristic of virginolide disappeared. After 24 hr the solvent was removed and the residue was mixed with ice water, and extracted with chloroform. The aqueous extract was acidified and again extracted with chloroform. Evaporation of the acid fraction afforded an oily acid which could not be crystallized or converted to a solid ester, but appeared to be homogeneous (tlc).

Hexahydrovirginolide.—A suspension of 0.1 g of platinum oxide in 60 ml of ethanol was saturated with hydrogen and mixed with 0.4 g of virginolide, and the hydrogenation was continued at atmospheric pressure. Hydrogen absorption stopped after consumption of 3 mole equiv of hydrogen (rapid uptake). Removal of solvent after filtration gave a gummy residue (infrared bands at 1775 and 1740 cm^{-1}) whose nmr spectrum exhibited no vinyl proton or vinyl methyl resonances. The distribution of methyl resonances in the range 0.8–1.3 ppm indicated the presence of a mixture. Chromatography over 40 g of silicic acid and elution with benzene–chloroform (1:2) gave a gum first, followed by semicrystalline material. Trituration of the latter with cold ether afforded approximately 10 mg of a solid which was recrystallized from acetone-hexane, mp 140–145° (previous shrinking). Infrared bands were at 1775 and 1740 cm^{-1}; apparently homogeneous on tlc; ORD curve (*c* 0.075, methanol) $[\alpha]_{400}$ −53°, $[\alpha]_{314}$ 1080°, $[\alpha]_{272}$ −1520°, $[\alpha]_{250}$ −133° (last reading).

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86; O, 19.17. Found: 72.17; H, 8.75; O, 19.00.

The gummy material could not be separated chromatographically. Hydrogenation of virginolide with palladized charcoal afforded a gum which consisted of at least three very similar compounds (three very close spots on tlc) and could not be separated into crystalline components.

Dehydrogenation of Virginolide. A.—A solution of 0.4 g of virginolide in 30 ml of tetrahydrofuran was reduced with 0.25 g of sodium borohydride at room temperature for 3 hr, chilled to 0°, acidified with acetic acid, and concentrated *in vacuo.* The residue was diluted with water and extracted with chloroform. The chloroform extract was evaporated and the residue which could not be induced to crystallize was mixed with 3.5 ml of Nujol and dehydrogenated with 0.4 g of 10% palladium-charcoal at 330° for 5 min (bluish violet vapors). The cooled contents were extracted thoroughly with hexane and the extracts were concentrated to small volume. The residue was extracted repeatedly with 85% phosphoric acid, the combined extracts were diluted with ice water and extracted again with hexane. The dried hexane extract was dried, concentrated (blue residue), filtered through alumina, and converted to a few milligrams of the trinitrobenzene adduct, mp 128° (lit.[21] for chamazulene trinitrobenzene adduct mp 133°). The visible spectrum of the azulene regenerated from the adduct was superimposable on that of chamazulene.

B.—A solution of 1 g of virginolide in 15 ml of tetrahydrofuran was added dropwise to 2.5 g of lithium aluminum hydride in 30 ml of tetrahydrofuran. After 10 hr at room temperature, the mixture was worked up in the usual way. The product, a viscous gum (no carbonyl band, 1 g) was mixed intimately with 1 g of 10% palladium–charcoal and heated in a metal bath at 320–330° for 5 min (blue vapors). The crude azulene was

(19) Attempts to verify this for C-8 by applying the Hudson-Klyne rule to virginolide failed because of the chemical change on base treatment alluded to in footnote 16. Because of the possibility of base-catalyzed epimerization at C-1 (*vide* our experiences with matricarin described in ref 12) and the scarcity of crystalline material, further work on the configuration of **6** could not be undertaken at this time. The ORD curve of **6** (moderately strong positive cotton effect, *a* +26) does not permit an unambiguous assignment, but suggests that the absolute configuration of the ring junction differs from that of tetrahydromatricarin and is perhaps similar to that of tetrahydrolactucin.[12]

(20) Melting points are uncorrected. Nmr spectra were run in deuteriochloroform with tetramethylsilane serving as internal standard; infrared spectra and rotations were run in chloroform; ultraviolet spectra were determined in 95% ethanol. Analyses were by Dr. F. Pascher, Bonn, Germany.

(21) M. Gordon, *Chem. Rev.*, **50**, 127 (1952).

separated as described in the previous section and chromatographed over alumina. Elution with hexane afforded 3 mg of a less polar blue azulene, mp of TNB adduct 141–145°; with TNB adduct of guaiazulene mmp 141–145°. The visible spectrum of azulene was superimposable on that of guaiazulene. Further elution of the alumina column with benzene–hexane (1:1) afforded an azulene mixture. Elution with benzene yielded 2 mg of a more polar azulene; TNB adduct mp 151°; with authentic linderazulene adduct mmp 149–152°. The visible spectrum of the azulene liberated from the TNB adduct was superimposable on that of linderazulene.

A Convenient Synthesis of *cis-* and *trans-*Cyclodecene

JAMES G. TRAYNHAM, DEWITT B. STONE,[1]
AND JOHN L. COUVILLION

*Coates Chemical Laboratories, Louisiana State University,
Baton Rouge, Louisiana 70803*

Although both *cis-* and *trans-*cyclodecene have been prepared by several different routes, none of the published routes is truly convenient in the sense of requiring few steps from cheap starting materials.[2] Cyclodecane is now available,[3] it is easily chlorinated, and the chlorocyclodecane can be dehydrochlorinated by potassium *t*-butoxide in dimethyl sulfoxide to 97% *cis-*cyclodecene and by lithium dicyclohexylamide in hexane to 96% *trans-*cyclodecene.[4]

Because of the ease with which these preparations can be carried out, and because the isomeric cyclodecenes may be used for the preparation of numerous

(1) National Aeronautics and Space Administration Trainee, 1964–1966.

(2) Illustrative examples are (a) 87% *cis* and 85–94% *trans* from bromocyclodecane [A. C. Cope, M. Brown, and G. L. Woo, *J. Am. Chem. Soc.*, **87**, 3107 (1965)]; (b) *cis* only from 10,10-dibromobicyclo[7.1.0]decane [J. G. Traynham and P. M. Greene, *ibid.*, **86**, 2657 (1964)]; (c) 83% *trans* from cyclodecyl tosylate [V. Prelog, W. Küng, and T. Tomljenović, *Helv. Chim. Acta*, **45**, 1352 (1962)]; (d) 98% *trans* from cyclodecyltrimethylammonium hydroxide [A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960)]; (e) 98% *trans* from cyclodecyldimethylamine oxide [A. C. Cope, D. C. McLean, and N. A. Nelson, *ibid.*, **77**, 1628 (1955)]; (f) *cis* only from *cis,trans*-1,5-cyclodecadiene [G. A. Knesel, Ph.D. Dissertation, Louisiana State University, 1966].

(3) From Columbian Carbon Co., Lake Charles, La. We gratefully acknowledge the gift of a generous sample of cyclodecane from this company.

(4) Other reagents tried gave mixtures containing more of the minor component; for example, silver nitrate in DMSO gave a mixture consisting of 92% *cis-* and 8% *trans-*cyclodecene.

cyclodecane derivatives otherwise difficult or expensive to obtain, these procedures promise to be particularly useful.

Experimental Section

Chlorocyclodecane.—A 1-l., three-neck Pyrex flask equipped with a condenser, stirrer, and gas dispersion tube was charged with cyclodecane (420 g, 3.0 moles) and irradiated with a 150-w light bulb in a reflector about 4 in. from the flask. Chlorine gas (71 g, 1.0 mole) was passed through a trap containing concentrated sulfuric acid, through an empty trap, and into the stirred cyclodecane during 4 hr. Irradiation was continued for 35 min longer, and air was then bubbled through the mixture for 30 min to sweep out chlorine and hydrogen chloride. Distillation of the mixture at reduced pressure gave the following three well-separated fractions.

Recovered cyclodecane amounted to 286 g (2.04 moles), bp 72–73.5° (12 mm), $n^{25}D$ 1.4697.

Chlorocyclodecane was obtained in 64% yield (based on Cl_2) (111.4 g), bp 109–110.5° (12 mm), $n^{25}D$ 1.4923. *Anal.* Calcd for $C_{10}H_{19}Cl$: C, 68.74; H, 10.96. Found: C, 68.55; H, 10.75.

Dichlorocyclodecane was formed in small amount (14.1 g, 13.5%), bp 135–137° (12 mm), $n^{25}D$ 1.5078. *Anal.* Calcd for $C_{10}H_{18}Cl_2$: C, 57.42; H, 8.67. Found: C, 58.00; H, 8.92.

Dehydrochlorination. A. *cis-*Cyclodecene.—A solution of chlorocyclodecane (105 g, 0.60 mole), dimethyl sulfoxide (500 ml), and potassium *t*-butoxide (100.8 g, 0.90 mole) was stirred for 3 hr. The mixture was diluted with water (750 ml) and extracted with four 200-ml portions of petroleum ether (bp 60–70°). The combined organic material was dried with Drierite and concentrated by rotary evaporation. Distillation of the residue gave *cis-*cyclodecene (66.0 g, 80%), bp 44–45° (2 mm). Analysis by gas chromatography on a $1/8$ in. × 15 ft Ucon column at 110° indicated that the sample contained 97% *cis-* and 3% *trans-*cyclodecene.

B. *trans-*Cyclodecene.[5]—A solution of butyllithium in hexane (400 ml, 1.6 *M*) was added to a solution of dicyclohexylamine (124 g, 0.68 mole) in anhydrous ethyl ether (200 ml) contained in a 2-l. flask fitted with a condenser, magnetic stirrer, and nitrogen atmosphere. To the resulting mixture was added a solution of chlorocyclodecane (105 g, 0.60 mole) in hexane (200 ml). The mixture was refluxed for 24 hr, allowed to cool, washed with four 50-ml portions of water, and dried with Drierite. Removal of solvent by rotary evaporation and distillation of the residue gave *trans-*cyclodecene (58.0 g, 70%), bp 53–55° (4 mm). Analysis by gas chromatography on a $1/8$ in. × 15 ft Ucon column at 110° indicated that the sample contained 96% *trans-* and 4% *cis-*cyclodecene. Dicyclohexylamine was recovered in good yield by continuing the distillation.[6]

(5) This procedure parallels that for dehydrobromination of bromocyclodecane with lithium di-*sec*-butylamide.[2a]

(6) Dicyclohexylammonium chloride is sparingly soluble in water. When attempts were made to remove the amine (as its salt) from the organic layer by washing with aqueous acid, a heavy, white precipitate formed and made subsequent work-up difficult.