C.—Samples of crude **5** showed large increases in the amount of **8** (by glc and nmr analysis) when subjected to the following conditions: (1) refluxed for 3 hr in 20% NaOH; (2) heated to 150° for 5 hr; and (3) a solution of **5** in ethylene dichloride is stirred overnight at room temperature in the presence of stannic chloride.

The products from procedures A and B gave similar ir and nmr spectra as described in the text. The presence of some **8** in the higher boiling fractions could be determined by the presence of an ir band at 1685 cm^{-1} and a peak in the nmr at τ 8.13 (see Table II).

6-Acetyl-4-isopropyl-1-methylcyclohexene (6 and 7).—1-*p*-Menthene (100 g, 0.72 mol) was added to a mixture of 98 g (0.96 mol) of acetic anhydride and 8.0 ml of $BF_3 \cdot O(C_2H_5)_2$ over a 40-min period at 36°. After an additional stirring period of 2 hr, 150 ml of H_2O was added and the mixture stirred for 2 hr. The layers were separated, washed with 10% NaOH, and then made neutral to litmus with water. Distillation yielded a main fraction, 25.2 g (19% theory), bp 95–96° (7 mm), which was composed of 5.1% hydrocarbons, 52.0% **6**, 32.7% **7**, and 10.2% **8**. These glc retention times were identical (peak enhancement) with those produced in the glc of **5**. Spinning band distillation of the above yielded purified samples of **6** (98.5% by glc) and **7** (95.2% by glc).

Registry No.—**1**, 6876-13-7; **5a**, 30338-42-2; **5b**, 30338-43-3; **6**, 30338-44-4; **7**, 30338-45-5; **8**, 30338-46-6.

Acknowledgment.—We are indebted to Professors J. A. Marshall and W. G. Dauben for valuable discussions, Mr. P. Porcaro for spectroscopic determinations, and Dr. H. U. Daeniker for his support and encouragement during this project.

A Synthesis of *N*-Methyl-1,9-ethenophenothiazine, a Bridged *syn*-Metacyclophane[1,2]

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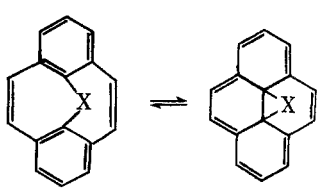
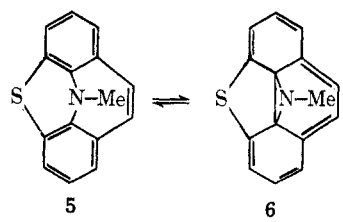
A synthesis of *N*-methyl-1,9-ethenophenothiazine (**5**) is described. Analogously to the two other known examples of bridged *syn*-metacyclophanes, **5** undergoes thermal extrusion of the methylamino bridge to give **19**.

As part of our studies of 15,16-dihydropyrene derivatives,[4] we have been concerned with the synthesis of such derivatives in which the internal substituents at the 15 and 16 positions are oriented cis to each other.[5] In particular we have studied those examples where a bridging heteroatom, as part of a three-membered ring, constitutes the cis substituents.[6,7] In the approach employed, the synthesis of the bridged *syn*-[2.2]metacyclophane-1,9-dienes (**1** and **2**) was first accomplished and then their possible valence tautomerization to the corresponding pyrene *cis*-15,16-epoxide (**3**) and pyrene *cis*-15,16-imine (**4**) was studied.



1, X = O
2, X = N,R
3, X = O
4, X = N,R

Although substitution of a sulfur atom for a carbon–carbon double bond is well known in aromatic heterocyclic systems, examination of molecular models suggested that the substitution of a sulfur atom for a carbon–carbon double bond in **1** or **2** would lead to a very marked increase in ring strain. We undertook the synthesis of the sulfur analog **5**, therefore, both to see whether it could exist and, if so, what effect the additional ring strain might have on the equilibrium between the valence tautomers **5** and **6**.[8]



5 **6**

The synthesis of **5** was modeled after that employed for the synthesis of 8,16-imino[2.2]metacyclophane-1,9-diene.[7] Treatment of phenothiazine (**7**) with oxalyl chloride and aluminum chloride, following the Stollé isatin procedure,[9] gave **8** in 75% yield. Hydrolysis of **8** with aqueous base followed by addition of hydrogen peroxide gave the corresponding acid **9**, which was converted by reaction with diazomethane to the methyl ester **10** for isolation and purification. The overall yield for these three steps was 65%.

When **10** was subjected to the Stollé isatin synthesis followed by a repetition of the above sequence, the diester **12** was readily formed. The nmr spectrum of **12** exhibited three types of aromatic protons: a pair of doublets at τ 2.33 (J = 7.5, J = 2 Hz), a pair of doublets at τ 3.03 (J = 7.5, J = 2 Hz), and a triplet at τ 3.29 (J = 7.5, J = 7.5 Hz), each of equivalent integrated area, as would be expected for **12**.

Treatment of **12** with sodium hydride followed by an excess of methyl iodide gave the *N*-methyl derivative **13** in 95% yield. Lithium aluminum hydride reduction of **13** led to the corresponding diol **14** in 96% yield. This, on reaction with phosphorus tribromide in ben-

(1) We thank the National Science Foundation for their support of this work.

(2) This is paper XXVIII in our series on Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud. For the preceding communication, see V. Boekelheide and J. Lawson, *Chem. Commun.*, 1558 (1970).

(3) NDEA Fellow, 1967–1970.

(4) For a review, see V. Boekelheide, *Proc. Welch Foundation*, **12**, 83 (1968).

(5) R. H. Mitchell and V. Boekelheide, *Chem. Commun.*, 1555 (1970).

(6) B. A. Hess, Jr., A. S. Bailey, B. Bartusek, and V. Boekelheide, *J. Amer. Chem. Soc.*, **91**, 1665 (1969).

(7) B. A. Hess, Jr., and V. Boekelheide, *ibid.*, **91**, 1672 (1969).

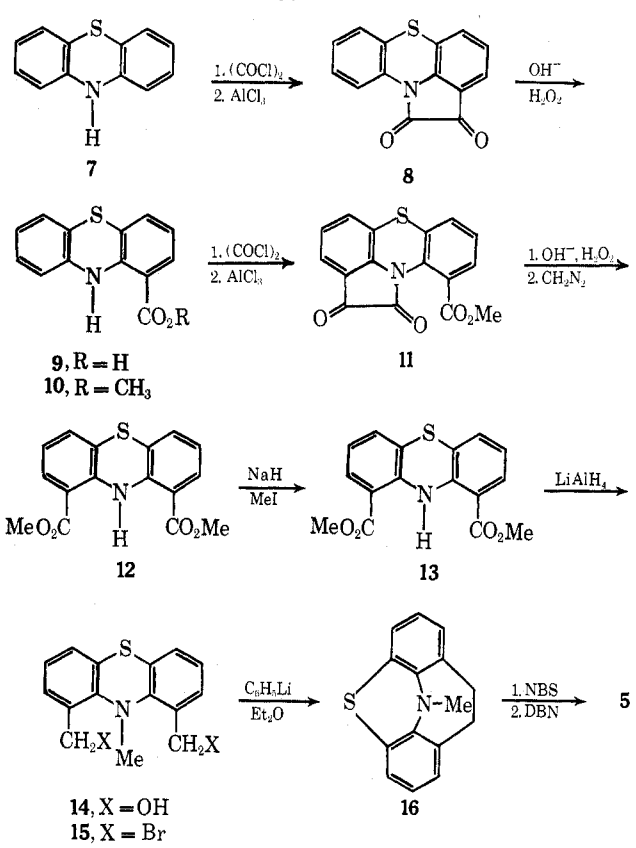
(8) Because of the importance of physiologically active phenothiazine derivatives, it was also of interest in this regard to prepare a phenothiazine derivative having a rigid, butterfly geometry.

(9) R. Stollé, *Ber.*, **46**, 3915 (1913).

zene, was converted in quantitative yield to the dibromide **15**. It is of interest that the steric crowding of the *N*-methyl group is sufficiently large to prevent free rotation about the carbon–carbon bonds at the 1 and 9 positions. Thus, the methylene protons of the hydroxymethyl groups in **14** appear in its nmr spectrum as an AB quartet rather than a singlet. Similarly, the methylene protons of the bromomethyl groups in **15** appear as an AB quartet.

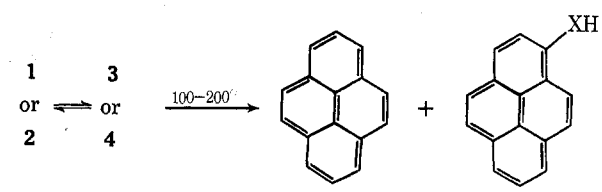
When a solution of the dibromide **15** in ether was treated with phenyllithium, a Wurtz cyclization occurred to give the bridged *syn*-metacyclophane **16** in 16% yield. The spectral properties of **16** are in good accord with its assigned structure. To effect dehydrogenation of the ethano bridge, **16** was treated with *N*-bromosuccinimide (NBS) and the resulting bromo derivative was heated with 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN). This gave the desired *N*-methyl-1,9-ethenophenothiazine (**5**) as a pale yellow oil in 35% yield. The reactions leading to the synthesis of **5** are summarized in Scheme I.

SCHEME I



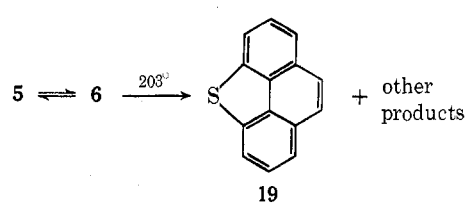
The properties of the final product were clearly in accord with structure **5** and not that of its valence tautomer **6**. Thus, its longest wavelength absorption in the ultraviolet was a broad band centered around 350 nm and there was no absorption in the visible region analogous to that of the dihydropyrenes.[4] Similarly, its nmr spectrum showed the signal for the aromatic protons in the usual region, with the vinyl protons as a singlet at τ 3.28 and the NCH_3 protons as a singlet at τ 6.98. These properties are in accord with structure **5** and indicate that valence tautomerization to **6** is not occurring to any significant degree at room temperature. In this respect the behavior of *N*-methyl-1,9-ethenophenothiazine is quite analogous to that of 8,16-oxido[2.2]metacyclophane-1,9-diene (**1**)[6] and 8,16-imino[2.2]metacyclophane-1,9-diene (**2**).[7]

Both **1** and **2** underwent thermal rearrangements which were most readily explained by postulating isomerization to the corresponding valence tautomers **3** and **4** followed by either expulsion of the heteroatom to give pyrene (**17**) or migration of the heteroatom to the periphery as in **18**. It was of interest to see whether



5 would exhibit a similar rearrangement or expulsion of the bridging nitrogen atom.

The first evidence was derived from the mass spectrum of **5**. In addition to the expected molecular ion at *m/e* 237, there was a signal of major intensity at *m/e* 208, corresponding to loss of NCH_3. When **5** was heated at 203° in benzene, analysis by thin layer chromatography showed five products were formed with the major one being phenanthro[4,5-*bcd*]thiophene (**19**).[10] A plausible interpretation for the formation of **19** at elevated temperatures would be valence tautomerization of **5** to **6** followed by expulsion of the bridging NCH_3 group. Whether any of the other products formed in this thermal reaction correspond to the various structures possible for migration of the NCH_3 group was not determined due both to lack of material and lack of authentic samples for comparison.



Despite the additional ring strain which must be present in **5**, as indicated from molecular models, the formation of **5** and its thermal behavior are quite analogous to the corresponding metacyclophane derivative **2**.

Experimental Section[11]

1,10-Oxalylphenothiazine (8).—To a boiling solution of 30 ml of oxalyl chloride in 200 ml of benzene under a nitrogen atmosphere there was added dropwise over a period of 45 min a solution of 44.0 g of phenothiazine in 600 ml of benzene. The resulting solution was boiled under reflux an additional 4.5 hr and then concentrated under reduced pressure. The remaining pale green solid was taken up in 500 ml of carbon disulfide and added dropwise with stirring over a 2-hr period to a boiling slurry of

(10) We thank Professor Klemm for his kindness in providing us with a sample of phenanthro[4,5-*bcd*]thiophene (**19**) for comparison. For the preparation of **19**, see L. H. Klemm, D. R. McCoy, and D. R. Olson, *J. Heterocycl. Chem.*, **7**, 1347 (1970).

(11) Microanalyses were performed by Micro-Tech Laboratories and A. Bernhardt Microanalytical Laboratories. Spectral measurements were made with a Cary Model 15, a Beckman IR-5A, a Varian A-60, and a CEC-110-21B. We thank the National Science Foundation for funds used toward the purchase of the Varian A-60 and the CEC-110-21B mass spectrometer.

50 g of aluminum chloride in 300 ml of carbon disulfide. When addition was complete, the reaction mixture was boiled under reflux an additional 16 hr. After the mixture had cooled to room temperature, the carbon disulfide was removed by decantation. To the remaining solid residue cooled in an ice bath there was added slowly 200 ml of concentrated hydrochloric acid followed by 200 ml of water. The resulting mixture was extracted repeatedly with chloroform (6 l., total). The combined chloroform extracts were washed with water, dried, and concentrated to give 56 g of a black solid. This was recrystallized from a benzene–methanol mixture to give 42 g (75%) of black crystals, mp 200–203°. A small sample was chromatographed over silica gel using a 1:1 benzene–hexane solution for elution to give black crystals: mp 203.0–203.5°; uv max (95% ethanol) 246 nm (ϵ 40,700) and 302 (6490); ir ($CHCl_3$) 1740 and 1725 cm^{-1} (C=O); nmr ($CDCl_3$) τ 1.28–1.47 (m, 1, Ar H), 2.54–3.12 (m, 6, Ar H).

Anal. Calcd for $C_{14}H_7NO_2S$: C, 66.39; H, 2.79; N, 5.53; S, 12.66. Found: C, 66.12; H, 2.83; N, 5.92; S, 12.71.

1-Carbomethoxyphenothiazine (10).—To a solution of 44.0 g of sodium hydroxide in 8 l. of water there was added with stirring 42.0 g of **8**. Solution was complete in about 1 hr. There was then added over a period of 20 min with stirring a solution of 40 ml of 30% hydrogen peroxide in 500 ml of water. The resulting solution was stirred at room temperature for 1 hr before acidification with concentrated hydrochloric acid. The yellow solid, which precipitated, was collected by filtration, dried, and redissolved in 10 l. of ether. To this was added dropwise with stirring an ethereal solution of diazomethane until there was no longer evidence of reaction. Concentration of the ethereal solution gave a yellow oil which was chromatographed over silica gel using a 1:1 benzene–hexane mixture as solvent. Elution of the main yellow band gave 37.0 g (65%) of yellow crystals: mp 114.0–114.5°; uv (95% ethanol) 241 nm (ϵ 21,900), 257 (22,100), 261 (22,300), and 320 (3540); ir ($CHCl_3$) 3330 (NH) and 1670 cm^{-1} (C=O); nmr ($CDCl_3$) τ −0.13 (s, 1, NH), 2.41 (q, 2, J = 8.0, J' = 1.8 Hz, Ar H), 2.90–3.52 (m, 6, Ar H), and 6.15 (s, 3, OCH_3).

Anal. Calcd for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44; S, 12.46. Found: C, 65.41; H, 4.30; N, 5.43; S, 12.48.

1-Carbomethoxy-9,10-oxalylphenothiazine (11).—To a boiling solution of 10 ml of oxalyl chloride in 10 ml of benzene there was added dropwise a solution of 3.2 g of **10** in 50 ml of benzene and the resulting mixture was boiled under reflux overnight. After concentration the residual green solid was taken up in 50 ml of carbon disulfide and added dropwise over a period of 1 hr with stirring to a slurry of 4.0 g of aluminum chloride in 20 ml of carbon disulfide. The mixture was boiled under reflux with stirring for an additional 1 hr before removal of the carbon disulfide by decantation. The residual solid was cooled in an ice bath and decomposed by addition of 10 ml of concentrated hydrochloric acid with stirring followed by 20 ml of water. The mixture was extracted repeatedly with chloroform (600-ml total). After it had been dried over magnesium sulfate, the chloroform extract was concentrated to give a black solid. This was taken up in benzene and chromatographed over silica gel to give 0.8 g of recovered **10** plus 1.1 g (39%, based on unrecovered **10**) of black crystals. A sample of these was recrystallized from a benzene–methanol mixture giving very dark red crystals: mp 236–238°; uv (95% ethanol) 222 nm (ϵ 25,900), 253 (24,000), and 327 (3740); ir ($CHCl_3$) 1730 and 1750 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_9NO_4S$: C, 61.74; H, 2.91; N, 4.50; S, 10.31. Found: C, 61.72; H, 3.00; N, 4.36; S, 10.21.

1,9-Dicarbomethoxyphenothiazine (12).—To a solution of 15 g of sodium hydroxide in 300 ml of water there was added 7.8 g of **11** with stirring. As soon as solution was complete, the mixture was diluted by addition of 200 ml of water and a solution of 8 ml of 30% hydrogen peroxide in 30 ml of water was added with stirring. When the mixture had been stirred for 15 min, it was acidified with concentrated hydrochloric acid and the yellow precipitate was collected by filtration. The carefully dried yellow solid was taken up in 200 ml of ether and an ethereal solution of diazomethane was added with stirring until no further reaction ensued. After concentration, the residual solid was taken up in benzene and chromatographed over silica gel to give 4.4 g (56%) of yellow crystals, mp 133–135°. A sample recrystallized from ether gave yellow plates: mp 134.5–135.5°; uv (95% ethanol) 225 nm (ϵ 24,800), 244 (19,500), 262 (17,300), and 390 (7250); ir ($CHCl_3$) 3260 cm^{-1} (NH) and 1710 (C=O); nmr ($CDCl_3$) τ −0.79 (s, 1, NH), 2.33 (q, 2, J = 7.5, J = 2.0 Hz, Ar H), 3.03 (q, 2, J = 7.5, J = 2.0 Hz, Ar H), 3.29 (t, 2, J = 7.5, J = 7.5 Hz, Ar H), and 6.04 (s, 6, OCH_3).

Anal. Calcd for $C_{16}H_{13}NO_4S$: C, 60.95; H, 4.16; N, 4.44; S, 10.15. Found: C, 61.07; H, 4.38; N, 4.44; S, 10.00.

***N*-Methyl-1,9-dicarbomethoxyphenothiazine (13).**—To a solution of 8.0 g of **12** in 300 ml of dry dioxane there was added 9 g of sodium hydride (59% dispersion in oil) and 70 ml of methyl iodide The resulting mixture was boiled under reflux for 8 hr before destroying the excess sodium hydride by addition of methanol. Then, water was added and the mixture was extracted with ether. The combined ether extracts were washed with water, dried, and concentrated. The residual yellow solid was recrystallized from an ether–hexane mixture to give 8.0 g (95%) of pale yellow crystals: mp 104–105°; uv (95% ethanol) 223 nm (ϵ 20,900), 259 (17,100), and 338 (3280); ir ($CHCl_3$) 1725 cm^{-1} (C=O); nmr ($CDCl_3$) τ 2.58 (q, 2, J = 7, J = 2 Hz, Ar H), 2.78 (q, 2, J = 7, J = 2 Hz, Ar H), 3.03 (t, 2, J = 7, J = 7 Hz, Ar H), 6.03 (s, 6, OCH_3), and 6.75 (s, 3, NCH_3).

Anal. Calcd for $C_{17}H_{15}NO_4S$: C, 62.00; H, 4.59; N, 4.25; S, 9.72. Found: C, 61.89; H, 4.59; N, 4.24; S, 9.93.

***N*-Methyl-1,9-bis(hydroxymethyl)phenothiazine (14).**—A solution of 6.1 g of **13** in 350 ml of ether was added dropwise with stirring over a period of 20 min to a boiling slurry of 4.5 g of lithium aluminum hydride in 450 ml of ether. After the mixture had boiled under reflux an additional 1 hr, it was cooled to 0° and 10 ml of a saturated aqueous sodium sulfate solution was added with stirring. The ether solution was decanted from the precipitated crystalline solid and the precipitate was washed twice with ether by decantation. Then the combined ether extracts were dried and concentrated yielding 5.2 g of a white solid. This, on recrystallization from an ether–hexane mixture gave 4.8 g (96%) of white needles: mp 118.0–119.5°; uv (95% ethanol) 245 nm (ϵ 16,500) and 283 (3300, sh); ir ($CHCl_3$) 3390 cm^{-1} (OH); nmr ($CDCl_3$) τ 2.72–3.18 (m, 6, Ar H), 5.38 (q, 4, CH_2OH), 5.77 (s, 2, OH), and 7.08 (s, 3, NCH_3).

Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.93; H, 5.53; N, 5.13; S, 11.73. Found: C, 65.86; H, 5.63; N, 4.92; S, 11.68.

***N*-Methyl-1,9-bis(bromomethyl)phenothiazine (15).**—A solution of 4.7 g of **14** and 8 ml of phosphorus tribromide in 250 ml of benzene was boiled under reflux for 1 hr. After the solution had been cooled to 0°, 100 ml of ice water was added, the benzene layer was separated, and the aqueous layer was extracted with benzene. The combined benzene extracts were washed with water and then concentrated to give 6.9 g (100%) of a yellow solid. This was satisfactory for use in the next step without further purification. However, a sample was recrystallized from an ether–hexane mixture to give white crystals: mp 125.0–125.5°; nmr ($CDCl_3$) τ 2.52–3.05 (m, 6, Ar H), 5.15 (q, 4, CH_2Br), and 6.83 (s, 3, NCH_3).

Anal. Calcd for $C_{15}H_{13}Br_2NS$: C, 45.09; H, 3.31; N, 3.60; Br, 39.96; S, 8.04. Found: C, 45.27; H, 3.28; N, 3.51; Br, 40.06; S, 8.13.

***N*-Methyl-1,9-ethanophenothiazine (16).**—To a boiling solution of 5.5 ml of a 2.11 *N* solution of phenyllithium in benzene in 800 ml of ether was added dropwise with stirring a solution of 1.45 g of **15** in 80 ml of ether. The mixture was boiled under reflux an additional 1 hr and cooled, and water was added. Separation of the ether layer followed by concentration gave a tan solid. This was chromatographed over silica gel using hexane for elution to give 130 mg (16%) of white crystals. These, on recrystallization from methanol, gave white needles: mp 164–165°; uv (95% ethanol) 216 nm (ϵ 18,900), 234 (20,700), 267 (5720, sh), and 308 (3140); nmr ($CDCl_3$) τ 2.58–3.55 (m, 6, Ar H), 6.82 (q, 4), and 7.02 (s, 3, NCH_3); mass spectrum (70 eV) m/e 239.077 (mol wt calculated for $C_{15}H_{13}NS$, 239.077).

Anal. Calcd for $C_{15}H_{13}NS$: C, 75.30; H, 5.48; N, 5.85; S, 13.37. Found: C, 75.15; H, 5.33; N, 5.96; S, 13.42.

***N*-Methyl-1,9-ethenophenothiazine (5).**—A mixture of 100 mg of **16**, 75 mg of *N*-bromosuccinimide, and a small amount of azobisisobutyronitrile in 30 ml of carbon tetrachloride was boiled under reflux for 1.5 hr. After the solution had cooled, it was filtered to remove the solids present and the filtrate was concentrated. The residual solid from the filtrate was taken up in 125 ml of benzene, 125 mg of 1,5-diazabicyclo[4.3.0]non-5-ene was added, and the mixture was boiled under reflux for 30 min. After the solution had cooled, it was washed with water and concentrated. The residual yellow oil was chromatographed over silica gel using a 1:9 benzene–hexane mixture as solvent. Elution of the main band gave 35 mg of a pale yellow oil: uv (cyclohexane) 248, 272.5, 284, 297, 309, 334, 342, and 362 nm

(because of the instability of **5** toward handling in the pure state, quantitative extinction coefficients were not obtained); nmr ($CDCl_3$) τ 1.95–3.50 (m, 6, Ar H), 3.28 (s, 2, CH=CH), and 6.98 (s, 3, NCH_3); mass spectrum (70 eV) *m/e* (rel intensity) 237 (100) and 208 (26).

Anal. Calcd for $C_{15}H_{11}NS$: mol wt, 237.061. Found: (high-resolution mass spectrum), 237.061.

Thermal Decomposition of 5.—A solution of 8 mg of **5** in 0.5 ml of benzene was placed in a thick-walled tube, degassed, sealed, and heated in an oil bath maintained at 203 ± 0.5° for 20 hr. After the tube had been cooled, it was opened and the solution was concentrated. Analysis of the residue by tlc over silica gel using benzene for elution showed five components. The major component, also the one of highest R_f value (0.8), had a characteristic bright blue fluorescence. This was separated and rerun in a tlc comparison with an authentic sample of **19**. Both showed the same blue fluorescence and both were identical in their tlc behavior.

Registry No.—**5**, 29939-42-2; **8**, 29939-43-3; **10**, 4063-33-6; **11**, 29939-45-5; **12**, 29939-46-6; **13**, 29939-47-7; **14**, 30115-51-6; **15**, 29939-48-8; **16**, 29939-49-9.

Intramolecular Nitrone–Olefin Cycloadditions. The Stereochemistry of Hexahydro-2,1-benzisoxazoline Formation[1]

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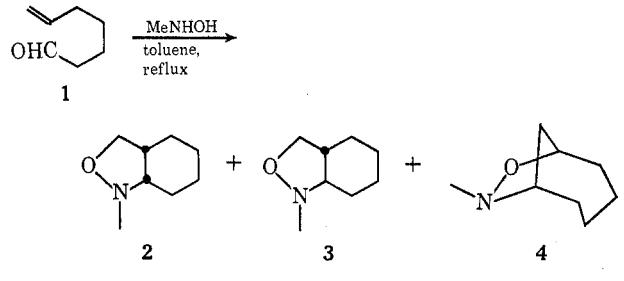
Received February 4, 1971

The stereochemistry of the intramolecular, 1,3-dipolar cycloaddition of several methyl-substituted *N*-methyl-*C*-6-heptenylnitrones was studied. The major product isoxazolidines were confirmed to have the 7-aza-8-oxabicyclo[4.3.0]nonane (3a,4,5,6,7,7a-hexahydro-2,1-benzisoxazoline, hydrindan) skeleton. The stereochemistry at the ring fusion was assigned primarily on the basis of nmr spectral evidence. It was found that cyclization of the nitrones at 76° gave primarily the trans-fused isomers in all cases, and the ratio between cis and trans isomers was influenced mainly by substitution in the five-membered isoxazolidine ring. Interconversion of the isoxazolidines in the temperature range 180–300° occurred by retro-1,3-dipolar cycloaddition. At these temperatures the thermodynamically more stable cis-fused isomers predominated. These results correlate well with what is known concerning the relative stabilities of *cis*- and *trans*-hydrindan. The retro-1,3-dipolar cycloaddition of bicyclic isoxazolidines promises to be a valuable method for relative stability studies of fused heterobicyclo[*n*.3.0] derivatives.

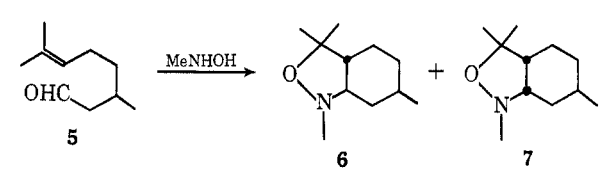
Part A

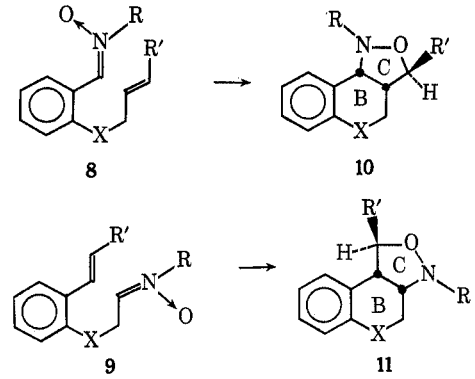
In the intramolecular 1,3-cycloaddition of *N*-alkyl-*C*-5-hexenyl- and -6-heptenylnitrones to give fused bicyclic isoxazolidine products, cis–trans isomerism at the ring juncture is a source of configurational ambiguity. For every case of product formation involved with the creation of a 2-aza-3-oxabicyclo[3.3.0]octane skeleton (*N*-alkyl-*C*-5-hexenylnitrones) a cis fusion was noted. Ring closure to give the more highly strained trans isomer would require a transition state of prohibitive energy.[2] However, with the homologous series mixtures of isomers having the azaoxabicyclo[4.3.0]nonane (5-aza-6-oxahydrindanyl, 3a,4,5,6,7,7a-hexahydro-2,1-benzisoxazoline) ring system were obtained,[2a] and the relative amounts of the isomers were shown to be temperature dependent in at least one case.[2b]

For example, the unsubstituted compound **1** led to a 3:1:1 mixture of cis (**2**), trans (**3**), and bridged bicyclic isomers **4**, respectively.[2a] On the other hand,



condensation of (+)-citronellal (**5**) with *N*-methylhydroxylamine gave isomer ratios for **6**:**7** ranging from 97:3 at 25° to 87:13 at 138°.[2] In this case, predominant formation of the trans isomer is found. Very recently, a series of papers has revealed the intramolecular cyclizations of nitrones of the types **8** and **9**.[3] The products, tetrahydrobenzopyrano[4,3-*c*]isoxazoles (**10**, X = O), the analogous quinoline analogs (**10**, X = NH), and the tetrahydrobenzopyrano[3,4-*c*]isoxazoles (**11**, X = O), were found in almost every case to contain a cis juncture between the B and C rings. In only





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(2) (a) N. A. LeBel, M. E. Post, and J. J. Whang, *J. Amer. Chem. Soc.*, **86**, 3759 (1964); (b) M. E. Post, unpublished data.

(3) (a) W. Oppolzer and K. Keller, *Tetrahedron Lett.*, 1117, 4313 (1970); (b) W. Oppolzer and H. P. Weber, *ibid.*, 1121 (1970).