ment of the aziridine **5** to the carbamate **7** in the injection port of the gas chromatograph. For example, analysis of the chilled reaction mixture without the water extraction step gives **4** (0.8%), **5** (55%), **6** (7.0%), and **7** (2.8%).

1-Chloro-2,3-dimethyl-2-butene-*4*-d_1 (11). DCl was generated from 566 g (4.02 mol) of benzoyl chloride and 16.1 g (0.805 mol) of D_2O according to the method of Brown and Groot.[15] This was directed through a gas dispersion tube into a stirred, three-neck, 250-ml flask containing 120.1 g (1.46 mol) of 2,3-dimethyl-1,3-butadiene cooled to −80°.[16] After DCl generation was complete, the contents were purged with nitrogen and allowed to warm to room temperature and stand for 3 days. Distillation gave three fractions, 30.0 g (0.253 mol) of 3-chloro-2,3-dimethyl-1-butene-*4*-d_1 (**12**), bp 35° (45 mm) [lit.[16] bp 32° (45 mm)], 97 g of an unknown fraction, bp 37–53° (45 mm), and 48.6 g (0.410 mol) of the chloride **11**, bp 53–55° (45 mm) [lit.[16] bp 57.7° (45 mm)]. Mass spectra: **11**, 7% d_0, 88% d_1, 5% d_2; **12**, 7% d_0, 89% d_1, 4% d_2.

2,3-Dimethyl-2-butene-d_1 (13). The chloride **11** was reduced using the method of Brown and Bell.[17] A three-neck 1-l. flask was fitted with an addition funnel, a magnetic stirring bar, a thermometer, and a water-cooled condenser. It was charged with 390 ml of glyme, 210 ml of water, and 24 g (0.60 mol) of sodium hydroxide. The mixture was stirred and heated to 55°. To this was added 90.6 g (2.40 mol) of sodium borohydride. When dissolved, 8.75 g (0.0739 mol) of the chloride **11** was added over a 15-min period. Some cooling was necessary to maintain the temperature at 50–55°. There was considerable gas evolution. The mixture was allowed to cool and stirred overnight. It was then extracted with two 400-ml aliquots of water. The organic phase was then dried over $CaSO_4$ and distilled on a spinning band column giving 11.6 g (46%) of **13**, bp 71–72°, NMR ($CDCl_3$) 1.63 ppm (s).

1-Carbethoxy-2-methyl-d_1-2,3,3-trimethylaziridine (8). A solution of 1.57 g (13.6 mmol) of ethyl azidoformate in 21 ml of the butene **13** was photolyzed in the usual way. Distillation gave 1.14 g (49%) of aziridine **8**: NMR ($CDCl_3$) same as that of aziridine **5**; mass spectrum, 10% d_0 (σ 1.3), 85% d_1 (σ 1.4), 5% d_2 (σ 1.2).

Kinetics of 1-Carbethoxy-2,2,3,3-tetramethylaziridine (5) Thermolysis. This experiment was carried out by proton NMR using a sealed 30-μl Kontes microcell charged with aziridine **5**. The cell was placed in a constant-temperature bath at 150° and periodically removed for analysis. The rate of carbamate **7** formation was followed by measuring the change in the combined area of the two vinylic protons in **7** relative to the total area of the methylene quartet of the ethoxy groups present. The final spectrum, at 88% conversion, was that of the carbamate **7**.

Kinetics of Ethyl Azidoformate Thermolysis. Cyclohexane and 2,3-dimethylbutane were purchased and further purified by distillation from Na–K under nitrogen. Solutions of ethyl azidoformate were prepared, charged into several 7-mm glass tubes, evacuated, and sealed with a torch. These were placed in a constant-temperature bath and individual samples taken periodically for analysis. The rate of ethyl azidoformate decomposition was followed by infrared using the disappearance of the 2140-cm^{-1} band.

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Registry No.—**4**, 56488-01-8; **5**, 56488-02-9; **6**, 1611-51-4; **8**, 56488-03-0; **10**, 2955-74-0; **11**, 56488-04-1; **12**, 56488-05-2; **13**, 56488-06-3; ethyl azidoformate, 817-87-8; 2,3-dimethyl-2-butene, 563-79-1; DCl, 7698-05-7; 2,3-dimethyl-1,3-butadiene, 513-81-5.

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Dehydrogenation of Heterohelicenes by a Scholl Type Reaction. The Dehydrohelicenes[1]

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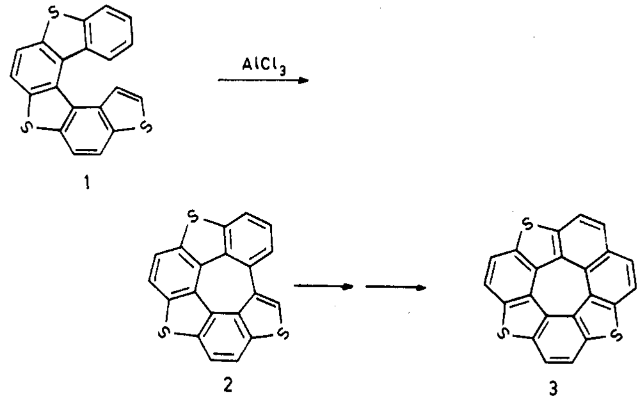
The reaction of seven heterohelicenes with $AlCl_3$ is described. The products are compounds in which the two helical termini of a helicene are connected by a σ bond. They are called dehydrohelicenes. The intramolecular ring closure is limited to hetero[5]- and -[6]helicenes. In addition to the synthesis, the spectral properties of dehydrohelicenes are discussed.

In our study of the synthesis, resolution, and chemistry of heterohelicenes,[2] the preparation of dehydrohelicenes by a Scholl reaction became of importance. The Scholl reaction has been defined by Balaban and Nenitzescu[3] as the elimination of two aryl-bound hydrogens accompanied by the formation of an aryl–aryl bond under the influence of Friedel–Crafts catalysts. Groen and Wynberg used this reaction in preparing **2** in low yield from the heterohexahelicene **1**[4] (Scheme I). The conversion of **2** to the [7]heterocirculene **3**[5] prompted us to undertake a more systematic study of the Scholl reaction of heterohelicenes. Compounds such as **2**, in which the two helical termini of a helicene are connected by a σ bond, will be called dehydrohelicenes.[6]

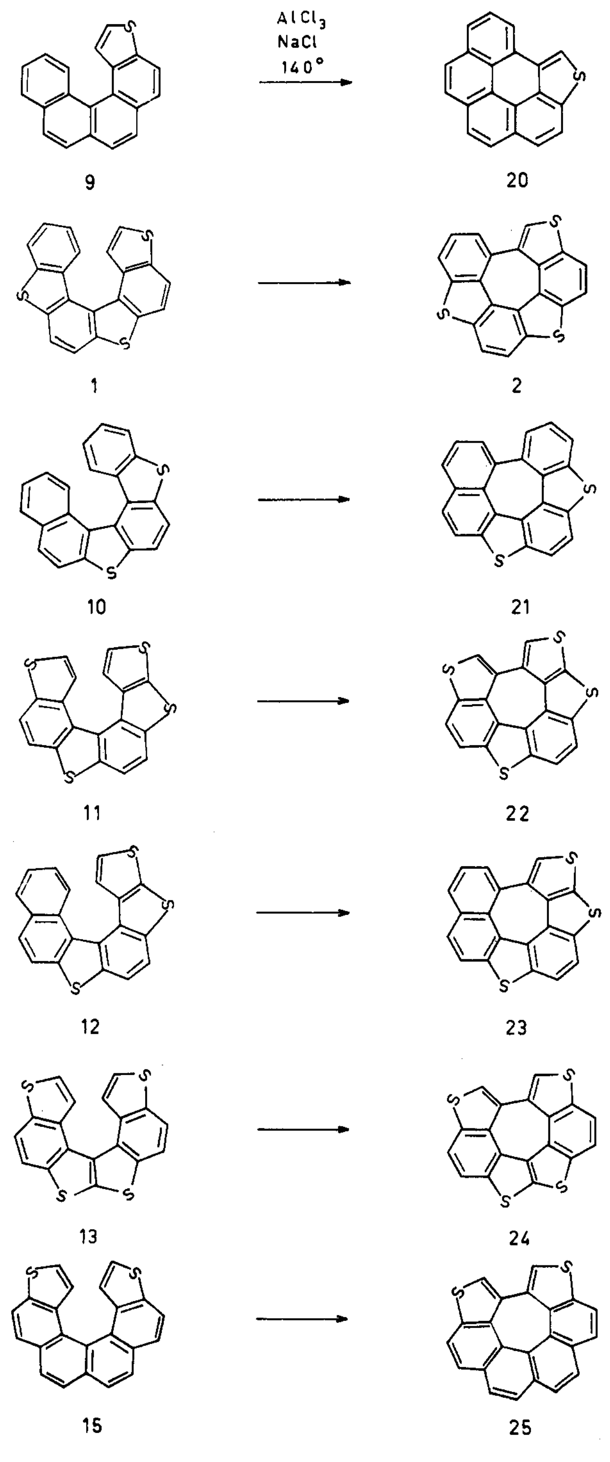
Results

Most of the heterohelicenes used in this study (Schemes II and III) have been described previously.[4,7] The new compounds **4**, **6**, **7**, **9**, and **16** were prepared by standard methods.[1] In the original "Scholl" method employed by Groen,[4] **1** was dissolved in benzene at room temperature and to this solution an excess of $AlCl_3$ was added. The mixture was allowed to stand for 24 hr prior to isolating **2**. This method is improved when a mixture of $AlCl_3$ and NaCl is used.[8] When **1**, $AlCl_3$, and NaCl were mixed together and heated to 140°, a black melt was formed immediately. After hydrolysis of this melt **2** was obtained in 95% yield. The other dehydrohelicenes were obtained in a similar manner. A

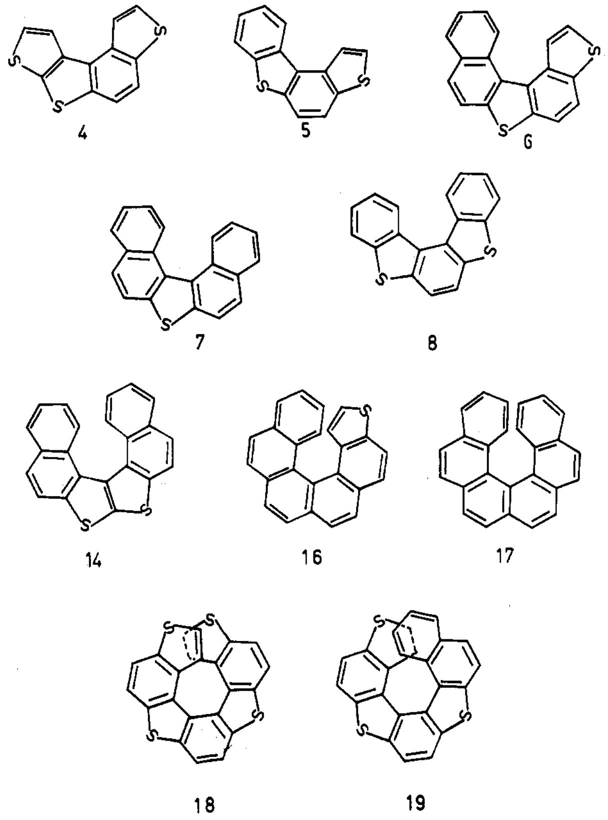
Scheme I



Scheme II



Scheme III



summary of the successful ring closures is given in Scheme II. Clearly, the reaction is limited to hetero[5]- and -[6]helicenes.

The helicenes **4–8**, **14**, **16**, **17**,[9] **18**, and **19** (Scheme III) when subjected to similar reaction conditions gave no well-defined products.

Attempts to perform the Scholl reaction with proton acids as catalysts[3,10] were unsuccessful. Treatment of **13** with FSO_3H or 98% H_2SO_4 yielded only water-soluble products, presumably resulting from sulfonation of the helicene. No reaction could be obtained with 40% HF, benzenesulfonic acid, trifluoroacetic acid, 5% H_2SO_4 in THF, or liquid hydrochloric acid. This might be due to the inhomogeneity of the medium or to the insufficient acidity of the acids used.

Properties of Dehydrohelicenes. The dehydrohelicenes are extremely insoluble in most organic solvents. In benzene and carbon disulfide they are sparingly soluble. They dissolve in $AsCl_3$ under the formation of paramagnetic species. They crystallize from *p*-xylene in long needles and have high melting points. In solution they fluoresce weakly. Owing to their extreme insolubility no well-resolved NMR spectra could be obtained. The mass spectra of the dehydrohelicenes resemble those of the corresponding helicenes.[4,7] In addition to high-intensity singly and double charged molecular ions, only small-intensity fragments were observed. The results are collected in Table I.

The uv spectra of the dehydrohelicenes are drawn in Figure 1. In these spectra a large shift of the α band (±30 nm) is observed when compared with the uv spectra of the corresponding helicenes. In contradistinction to the α band, only a small shift of the p band is observed. Those dehydrohelicenes (**22–24**) containing a thieno[2,3-*b*]thiophene moiety **26** behave differently.[7] Relative to the corresponding helicenes (**11–13**) there is only a moderate red shift of the longest wavelength band. The red shift depends upon the place of **26** in the molecule. In order to understand this

Table I
Mass Spectra of the Dehydrohelicenes, Relative Abundance ($M^+ = 100$)

Compd	$-S^+$	$-H_2S^+$	$-CS^+$	$-CHS^+$	$-CHS_2^+$	$-C_2S_2^+$	M^{2+}	$M\text{-}C_2S_2^{2+}$
20			8	12			32	
2	4	6	4	10	2		32	
21							40	
23	5	5	5	10	10	4	20	5
25	7	10		10			28	
22			10	10	3	10	15	10
24			10	10	4	10	30	15

phenomenon in a more quantitative way, the uv spectra of **2**, **22**, and **24** were calculated by PPP type of semiemperical SCF–MO calculations.[11] The results are given in Tables II and III.

Table II
Experimental and Calculated Transitions of the Dehydrohelicenes 2, 22, and 24

Dehydrohelicene	Experimental, nm (log ε)	Calculated, nm (*f*)
2	413 (2.88), 392 (3.32),	384 (0.05), 350 (0.10), 332 (0.74),
	372 (3.56), 356 (3.89),	320 (0.33), 299 (0.09), 285 (0.46),
	343 (4.07), 334 (4.36),	280 (0.65), 269 (0.54), 265 (0.03),
	321 (4.19), 309 (4.07),	258 (0.56), 250 (0.39), 246 (0.01),
		235 (0.03), 223 (0.10)
22	376 (4.00), 359 (3.91),	360 (0.29), 341 (0.10), 310 (0.39),
	343 (4.14), 328 (4.12)	309 (0.20), 294 (0.33), 277 (0.86),
		271 (0.11), 267 (0.33), 259 (0.59),
		256 (0.01), 247 (0.41), 241 (0.05),
		235 (0.11), 230 (0.00)
24	363 (4.00), 347 (4.08),	350 (0.49), 325 (0.51), 319 (0.10),
	333 (4.00), 312 (4.09),	304 (0.08), 288 (0.05), 286 (0.01),
	300 (4.12)	269 (0.09), 262 (0.79), 258 (1.48),
		254 (0.02), 250 (0.01), 239 (0.27),
		232 (0.20), 231 (0.03)

All absorptions calculated by this PPP method gave energies higher than those observed. Only an approximate correspondence between calculated and experimental data was obtained.

Experimental Section

All reagents were purified where necessary by standard methods. For column chromatography neutral alumina (Merck A1) for silica gel (B. D. H.) was used. Melting points (corrected) up to 300° were determined on a Mettler FP$_1$ microscope and between 300 and 350° (uncorrected) on a Reichert hot-stage apparatus.

Uv spectra were measured on a Zeiss PMQ 11 or recorded with a Beckman DB-G grating spectrophotometer. Mass spectra were obtained with a AEI MS 902 instrument and recorded by Mr. A. Kiewiet. Elemental analysis were carried out by Mr. H. Draayer, Mr. J. Ebels, and Mr. J. Vos in the microanalytical department of this laboratory.

The preparation of dehydrohelicenes is illustrated by a detailed procedure for the preparation of **24**.

6,7-Epithio-2,5,10-trithiabenz[1.8]azuleno[4,5,6,7-*jkl*]-*as*-indacene (24). To a mixture of **13** (100 mg, 0.28 mmol) and sodium chloride (300 mg, 5.1 mmol) was added as quick as possible 1500 mg (11.2 mmol) of finely powdered aluminum chloride. The three compounds were mixed thoroughly, the reaction flask was provided with a CaCl$_2$ drying tube, and the flask was inserted into an oil bath preheated to 140°. Immediately the flask contents turned black and after 5 min the mixture started to melt. As soon as the melt was completed (10 min) the flask was taken out of the oil bath and the reaction mixture was hydrolyzed directly with distilled water. A slightly yellow precipitate was formed, which was filtered off and washed with water until neutral. After drying in vacuo over P$_2$O$_5$ the mixture was taken up in a minimum amount of benzene and chromatographed on alumina with benzene as eluting agent. In this way 92 mg (92%) of pure **24** was obtained. An analytically pure sample of **24** (mp 318° dec) was obtained by recrystallization from *p*-xylene, from which it crystallizes in long white needles.

Anal. Calcd for $C_{18}H_6S_4$: C, 61.69; H, 1.73; S, 36.59. Found: C, 61.8; H, 1.9; S, 36.4.

Pyreno[5,4,3-*cde*]benzo[*b*]thiophene (20). The pyrenobenzo[*b*]thiophene **20** was obtained by treatment of **9** (100 mg, 0.35 mmol) with sodium chloride (300 mg, 5.1 mmol) and aluminum chloride (1500 mg, 11.2 mmol). After hydrolysis of the melt and working up of the reaction mixture a yellow-orange precipitate was formed which was taken up in benzene (200 ml). The benzene layer was washed with water and NaHCO$_3$ solution and dried over MgSO$_4$. After filtering and evaporation of the solvent the residue was chromatographed on alumina with benzene. After removal of the solvent the residue was recrystallized twice from methylcyclohexane. The analytically pure compound (long orange yellow needles) melted at 298–299°. The yield was 95 mg (95%).

Table III
The Red Shift of the Longest Wavelength Absorption of the Dehydrohelicenes Relative to the Corresponding Helicenes

Compd	Observed, nm	Calculated, nm
1 ⟶ 2	29	29
11 ⟶ 22	10	13
13 ⟶ 24	24	13

Anal. Calcd for $C_{20}H_{10}S$: C, 85.09; H, 3.57; S, 11.35. Found: C, 85.0; H, 3.8; S, 11.4.

1,11-Etheno-2,5,10-trithiabenz[1.8]azuleno[4,5,6,7-*jkl*]-*as*-indacene (2). The dehydrohelicene **2** was obtained by treatment of **1** (262 mg, 0.76 mmol) with sodium chloride (800 mg, 13.6 mmol) and aluminum chloride (4 g, 30 mmol). After hydrolysis of the melt a yellow precipitate was formed which was filtered, washed, and dried. After drying the product was sublimed in vacuo (220°/0.001 mm) and recrystallized from benzene. The yield of analytically pure **2** (mp 344–345°, lit.[4] 359–363°) was 180 mg (69%).

Anal. Calcd for $C_{20}H_8S_3$: C, 69.73; H, 2.34; S, 27.92. Found: C, 69.7; H, 2.3; S, 27.8.

4,7-Dithianaphth[2′,1′,8′:3,4,5]azuleno[1,8,7,6-*cdef*]fluorene (21). The dehydrohelicene **21** was obtained by treatment of **10** (300 mg, 0.88 mmol) with sodium chloride (900 mg, 15.2 mmol) and aluminum chloride (4.5 g, 33.6 mmol). After hydrolysis of the melt a brown-yellow precipitate was formed which was taken up in 200 ml of benzene. The benzene solution was washed with water and sodium bicarbonate solution and dried over MgSO$_4$. After evaporation

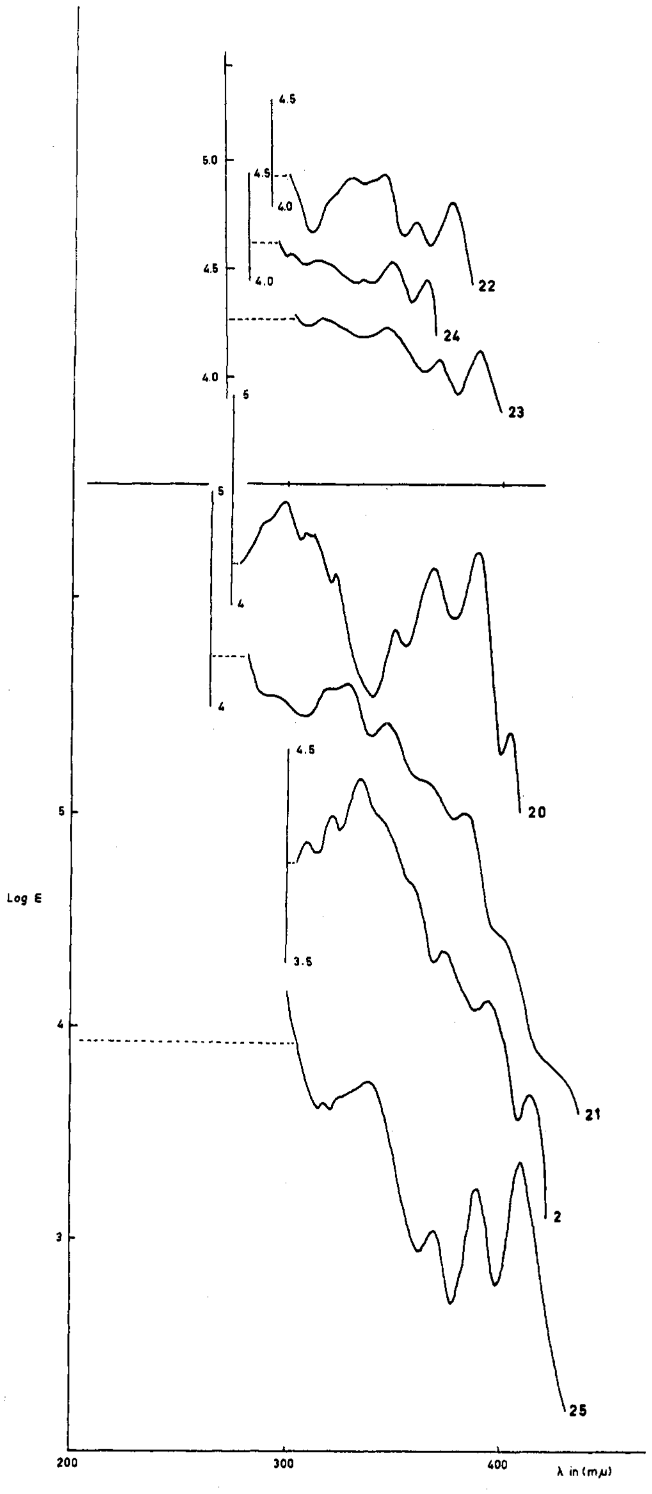


Figure 1. The uv spectra of the dehydrohelicenes in C_6H_6.

of the solvent the yellow residue was taken up in a minimum of hot *p*-xylene and chromatographed on alumina with benzene. After removal of the solvent the yellow residue (105 mg, 35%) was recrystallized from methylcyclohexane. The analytically pure compound melted at 284–290° (lit.[4] 267–280°).

Anal. Calcd for $C_{22}H_{10}S_2$: C, 78.07; H, 2.98; S, 18.95. Found: C, 77.9; H, 3.2; S, 18.8.

5,6:9,10-Diepithio-2,11-dithiabenz[7.8]azuleno[4,5,6-*cd*]indene (22). The dehydrohelicene **22** was obtained by treatment of **11** (262 mg, 0.74 mmol) with sodium chloride (1 g, 17.1 mmol) and aluminum chloride (4 g, 30 mmol). After hydrolysis of the melt a slightly green precipitate was formed which was filtered, washed, and dried. The product was taken up in a minimum of hot *p*-xylene and chromatographed on alumina with benzene. After removal of the solvent the residue was recrystallized from *p*-xylene. In this way 241 g (92%) of analytically pure **38** (mp 347–350° dec) was obtained.

Anal. Calcd for $C_{18}H_6S_4$: C, 61.69; H, 1.73; S, 36.59. Found: C, 61.8; H, 1.9; S, 36.1.

7,8-Etheno-2,5,6-trithiabenz[4.5]azuleno[1,8,7,6-*ijkl*]-*as*-indacene (23). The dehydrohelicene **23** was obtained by treatment of **12** (280 mg, 0.81 mmol) with sodium chloride (1.04 g, 17.7 mmol) and aluminum chloride (5.0 g, 37.4 mmol). After hydrolysis of the melt a yellow-brown precipitate was formed which was filtered, washed, and dried. After drying the product was chromatographed on alumina with benzene. After removal of the solvent the yellow residue (223 mg, 80%) was recrystallized from methylcyclohexane. The analytically pure compound sublimed between 250 and 300° and decomposed slowly above 290°.

Anal. Calcd for $C_{20}H_8S_3$: C, 69.73; H, 2.34; S, 27.92. Found: C, 69.7; H, 2.5; S, 27.9.

5,6-Etheno-2,11-dithianaphth[2′,1′,8′:3,4,5]azuleno[8,7,6-*cd*]indene (25). The dehydrohelicene **25** was obtained by treatment of **15** (150 mg, 0.44 mmol) with sodium chloride (450 mg, 7.6 mmol) and aluminum chloride (2.25 g, 16.8 mmol). After hydrolysis of the melt a yellow precipitate was formed which was filtered, washed, and dried. After drying the product was taken up in a minimum of hot *p*-xylene and chromatographed on alumina with benzene–chloroform (1:1). After removal of the solvent the yellow residue (139 mg, 93%) was recrystallized from benzene. The analytically pure compound sublimed between 280 and 290° and decomposed slowly at 348–354°.

Anal. Calcd for $C_{22}H_{10}S_2$: C, 78.07; H, 2.98. Found: C, 77.6; H, 3.1.

Registry No.—**1**, 24132-27-2; **2**, 30689-70-4; **9**, 56488-32-5; **10**, 20841-66-1; **11**, 41784-95-6; **12**, 41784-96-7; **13**, 41784-97-8; **15**, 41784-99-0; **20**, 54844-63-2; **21**, 30689-69-1; **22**, 54844-57-4; **23**, 54844-60-9; **24**, 54844-54-1; **25**, 54844-52-9; aluminum chloride, 7446-70-0.

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(6) We prefer this nomenclature because these molecules are in fact dehydrogenated helicenes. However, we realize that the use of the word helicenes for almost planar molecules may be somewhat confusing.

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(11) For details of the calculations see ref 5b. They were carried out by Dr. P. B. Koster of this laboratory.