

ylang oil, and a chloranthus oil.^{2a} The analogous spectra of (\pm)-8-isocopaene (**16**) were quite similar to those of copaene, but contained significant differences.¹⁷

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(17) NOTE ADDED IN PROOF. Compound **16** has now been shown, by direct comparison, to be identical with a sample of ylangene from *Schizandra chinensis* (Turcz.) Baill.^{9c} We wish to thank Dr. Herout for supplying the sample.

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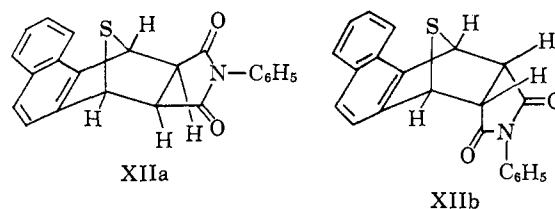
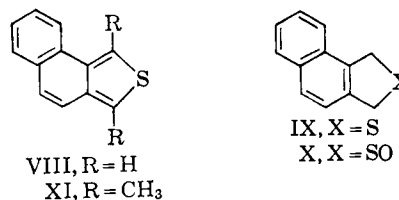
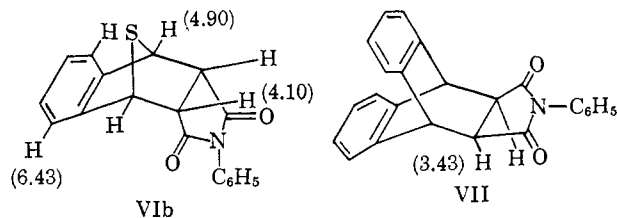
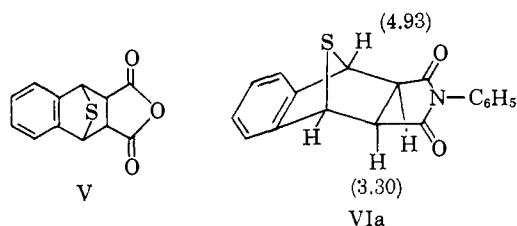
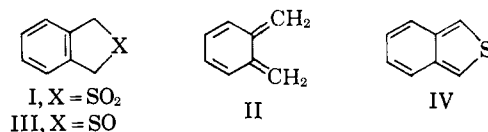
A Novel Synthesis of Isothianaphthenes

Sir:

The thermal decomposition of 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (I) is a convenient and simple method for the generation of the unstable *o*-quinodimethane (II), sulfur dioxide being extruded in the process.¹ We have now studied the thermal decomposition of 1,3-dihydrobenzo[*c*]thiophene 2-oxide (III).^{2,3} Contrary to our original expectation, III gave no evidence of decomposition into sulfur monoxide and *o*-quinodimethane, but underwent dehydration under remarkably mild conditions to give benzo[*c*]thiophene (IV, "isothianaphthene"). Thus, when a 1:2 mixture of III and neutral alumina was heated under 20-mm pressure at 100–125° in a sublimator, IV condensed on the cold finger in 94% yield as a white crystalline crust, mp 47–56° (mp 53–55° after resublimation; lit.⁴ mp 50–51°). The spectral properties of IV prepared in this way were in agreement with those previously described,⁴ and the compound reacted with maleic anhydride to give the expected adduct V, mp 148–152° (lit.⁴ mp 153–154°).

Adduct V could be prepared directly (25% yield) from sulfoxide III (without isolation of IV) by refluxing a mixture of III and maleic anhydride in acetic anhydride solution. Similarly, dehydration of III with acetic anhydride in the presence of *N*-phenylmaleimide gave a mixture of stereoisomeric adducts (86% total yield) which was separated, by fractional crystallization, into the *exo* isomer, mp 203–204° (VIa), and the *endo*

isomer, mp 236–239° (VIb). Structures VIa and VIb were distinguished on the basis of their nmr spectra.⁵



The nmr spectrum of VIa shows the two protons α to the imide carbonyls at δ 3.30, a position similar to that (3.43) of the corresponding protons of the *N*-phenylmaleimide-anthracene adduct (VII);⁶ molecular models indicate no shielding of these protons in VIa and VII. Other features of the nmr spectrum of VIa include the bridgehead protons at δ 4.93 and a broad band of nine aromatic protons in the δ 7.0–7.5 region. The nmr spectrum of the *endo* isomer VIb shows, in addition to the bridgehead protons at δ 4.90 and seven aromatic protons in the δ 7.0–7.5 region, two aromatic protons at δ 6.43; the appearance of the latter two protons at an unusually high-field position is the result of shielding by the carbonyls of the imide system. Also, the protons α to the imide carbonyls in VIb appear at δ 4.10, indicating a strong deshielding of these protons by the sulfide bridge.

The generality of our method to the synthesis of higher benzologs of IV is exemplified by the synthesis of the previously unreported naphtho[1,2-*c*]thiophene (VIII). Thus, oxidation of 1,3-dihydronaphtho[1,2-*c*]thiophene

(1) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

(2) S. F. Birch, R. A. Dean, and E. V. Whitehead, *J. Inst. Petrol.*, **40**, 76 (1954).

(3) The structure of III is confirmed by an infrared band at 1035 cm⁻¹, characteristic of sulfoxides, and by its nmr spectrum, which is in agreement with that previously reported (R. F. Watson and J. F. Eastham, *J. Am. Chem. Soc.*, **87**, 664 (1965)). In addition, oxidation of III with peracetic acid gives sulfone I.

(4) R. Meyer, H. Kleinert, S. Richter, and K. Gewald, *J. Prakt. Chem.*, **20**, 244 (1963).

(5) All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds reported. Nmr spectra were determined in CDCl₃; ultraviolet spectra were determined in methanol.

(6) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965).

(IX)⁷ with sodium periodate in aqueous ethanol⁸ afforded the corresponding sulfoxide X,⁹ mp 141–143°, in 50% yield. Pyrolysis of a mixture of X and neutral alumina at 160–180° (25 mm) afforded a 47% yield of thiophene VIII as colorless plates, mp 110–112°. The ultraviolet spectrum of VIII shows the following complex series of bands: $\lambda_{\text{max}}^{\text{MeOH}}$ 208 m μ ($\log \epsilon$ 4.45), 223 (4.32), 253 sh (4.38), 257 (4.39), 266 (4.43), 271 (4.53), 277 (4.56), 314 sh (3.78), 318 (3.79), 326 sh (3.71), 332 (3.67), and 348 (3.27); this spectrum is very similar to that reported for 1,3-dimethylnaphtho[1,2-*c*]thiophene (XI).¹⁰

The reaction of N-phenylmaleimide with sulfoxide X in refluxing acetic anhydride afforded a mixture of stereoisomeric adducts (89% total yield) which was separated, by fractional crystallization, into the *exo* isomer, mp 246–247° (XIIa), and the *endo* isomer, mp 174–175° (XIIb); the same products were formed by direct reaction of VIII with N-phenylmaleimide. Structures XIIa and XIIb were distinguished on the basis of their nmr spectra, which differed qualitatively in a manner similar to that of isomers VIa and VIb. It is of interest to note that the only definitely characterized derivatives of VIII previously reported (*i.e.*, the 1,3-dimethyl derivative XI and its 7-carboxy derivative) were obtained in low yield by a lengthy synthetic route.^{10,11}

Studies relating to the scope of the new isothianaphene synthesis and to the chemistry of isothianaphthene adducts are in progress and will form the subject of subsequent reports.

Acknowledgment. We thank the National Science Foundation for Grant GP-4931 in support of this work.

(7) M. P. Cava, R. L. Shirley, and B. W. Erickson, *J. Org. Chem.*, **27**, 755 (1962).

(8) N. J. Leonard and C. R. Johnson, *ibid.*, **27**, 282 (1962).

(9) The structure of X is confirmed by a sulfoxide band in the infrared at 1030 cm^{-1} , and by its nmr spectrum, which shows six aromatic protons in the δ 7.2–8.0 region and four methylene protons in a complex pattern between δ 4.0 and 4.6. Oxidation of X with peracetic acid gives the corresponding sulfone.

(10) O. Dann and H. Distler, *Chem. Ber.*, **87**, 365 (1954).

(11) Ultraviolet evidence for the formation of the 1-carbomethoxy derivative of VIII has been reported [B. D. Tilak, H. S. Desai, and S. S. Gupta, *Tetrahedron Letters*, No. 18, 1953 (1966)], but the pure compound was not isolated.

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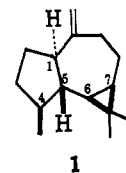
The Total Synthesis of (–)-Aromadendrene

Sir:

Aromadendrene is a representative of a group of tricyclic sesquiterpenes structurally characterized by the fusion of a cyclopropane ring to a hydroazulene nucleus. Degradative studies^{1,2} led to the proposal of the complete structure **1**, and the purpose of this communication is to describe a stereoselective synthesis of (–)-aromadendrene and some of its stereoisomers.

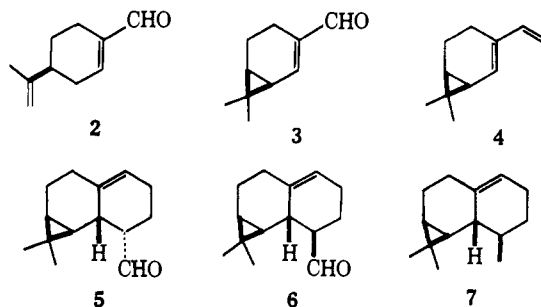
(1) G. Büchi, S. W. Chow, T. Matsuura, T. L. Popper, H. H. Rennhard, and M. Schach von Wittenau, *Tetrahedron Letters*, **6**, 14 (1959).

(2) L. Dolejš and F. Šorm, *ibid.*, **17**, 1 (1959); *Collection Czech. Chem. Commun.*, **25**, 1837 (1960).



1

Conformational uncertainties associated with perhydroazulenes led us to first prepare a decalin derivative which subsequently could be rearranged to a hydroazulene. Addition of hydrogen bromide to (–)-perillaldehyde (**2**)³ in glacial acetic acid followed by treatment of the crude bromide with potassium *t*-butoxide in *t*-amyl alcohol yielded the bicyclic aldehyde **3** (41% yield), $\lambda_{\text{max}}^{\text{EtOH}}$ 263 m μ (ϵ 11,700), $[\alpha]_{\text{D}} +108^\circ$ (CHCl_3). Conversion to the diene **4**, $\lambda_{\text{max}}^{\text{EtOH}}$ 245 m μ (ϵ 16,600), $[\alpha]_{\text{D}} -57^\circ$ (CHCl_3), was accomplished in 98% yield using a modified Wittig reaction.⁴ Condensation with acrolein in benzene solution at 100° furnished a mixture of adducts (98%) containing 75% of the aldehyde **5** and 15% of the epimer **6**.⁵ Exposure of either epimer to potassium *t*-amylate (5 min, 20°) in *t*-amyl alcohol lead to an equilibrium mixture containing 83% of **6** and 17% of **5**. The more stable aldehyde **6** was transformed to the tricyclic hydrocarbon **7**, $[\alpha]_{\text{D}} -66^\circ$ (CHCl_3), in essentially quantitative yield by consecutive treatments with lithium aluminum hydride, methanesulfonyl chloride, and lithium aluminum hydride.



Oxidation of the olefin **7** with osmium tetroxide afforded a mixture of the diol **8** (84%), mp 132–133°, $[\alpha]_{\text{D}} +1^\circ$ (CHCl_3), and the epimeric diol **10** (*ca.* 10%), which was not obtained in pure form. The major epimer **8** was converted to the tosylate **9** (82%), mp 130.5–131.5°, $[\alpha]_{\text{D}} -6^\circ$ (CHCl_3), which on treatment with 1 equiv of potassium *t*-butoxide in *t*-amyl alcohol⁶ or on chromatography over alumina was smoothly transformed to the ketone **12** (85%), mp 64–65°, $[\alpha]_{\text{D}} -21^\circ$ (CHCl_3). Its infrared spectrum was different from those of apoaromadendrone⁷ and its less stable epimer α -apoaromadendrone.⁷ Similarly, the hydrocarbon **13**, $[\alpha]_{\text{D}} -31^\circ$ (CHCl_3), prepared from **12** by a Wittig reaction (79%), was not identical with aromadendrene or its C-1 epimer, alloaromadendrene.^{8,9}

(3) A. Kergomard, S. Philibert-Bigon and M. T. Geneix, French Patent 1,813,849 (July 15, 1959); T. R. Keenan, B.Sc. Thesis, Massachusetts Institute of Technology, 1966.

(4) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(5) For similar condensations using vinylcyclohexene see A. S. Onishchenko, "Diene Synthesis," Daniel Davey & Co. Inc., New York, N. Y., 1964 (translated from Russian).

(6) Y. Mazur and M. Nussim, *J. Am. Chem. Soc.*, **83**, 3911 (1961); *Tetrahedron Letters*, 817 (1961), and earlier references cited.

(7) A. J. Birch and F. N. Lahey, *Australian J. Chem.*, **6**, 379 (1953).

(8) L. Dolejš and F. Šorm, *Tetrahedron Letters*, **10**, 1 (1959).

(9) A. S. Birch, J. Grimshaw, R. N. Speake, R. M. Gascoigne, and R. O. Hellyer, *ibid.*, **3**, 15 (1959).