(IX)[7] with sodium periodate in aqueous ethanol[8] 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: $\lambda_{\max}^{\mathrm{MeOH}}$ 208 mμ (log ε 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 isothianaphthene 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.

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[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. Gupte, *Tetrahedron Letters*, **No. 18**, 1953 (1966)], but the pure compound was not isolated.

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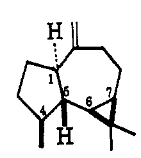
Received June 10, 1966

The Total Synthesis of (−)-Aromadendrene

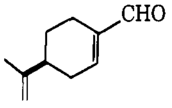
Sir:

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

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), $\lambda_{\max}^{\mathrm{EtOH}}$ 263 mμ (ε 11,700), $[\alpha]_D$ +108° ($CHCl_3$). Conversion to the diene **4**, $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ε 16,600), $[\alpha]_D$ −57° ($CHCl_3$), 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**, $[\alpha]_D$ −66° ($CHCl_3$), in essentially quantitative yield by consecutive treatments with lithium aluminum hydride, methanesulfonyl chloride, and lithium aluminum hydride.



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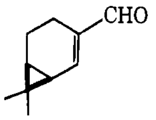

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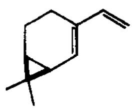

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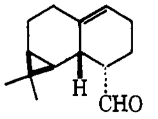

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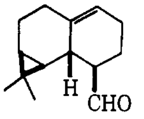

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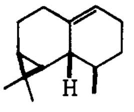

7

Oxidation of the olefin **7** with osmium tetroxide afforded a mixture of the diol **8** (84%), mp 132–133°, $[\alpha]_D$ +1° ($CHCl_3$), 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°, $[\alpha]_D$ −6° ($CHCl_3$), which on treatment with 1 equiv of potassium *t*-butoxide in *t*-amyl alcohol[6] or on chromatography over alumina was smoothly transformed to the ketone **12** (85%), mp 64–65°, $[\alpha]_D$ −21° ($CHCl_3$). Its infrared spectrum was different from those of apoaromadendrone[7] and its less stable epimer α-apoaromadendrone.[7] Similarly, the hydrocarbon **13**, $[\alpha]_D$ −31° ($CHCl_3$), prepared from **12** by a Wittig reaction (79%), was not identical with aromadendrene or its C-1 epimer, alloaromadendrene.[8,9]

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[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).

[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).

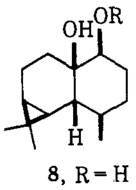
[6] Y. Mazur and M. Nussim, *J. Am. Chem. Soc.*, **83**, 3911 (1961); *Tetrahedron Letters*, 817 (1961), and earlier references cited.

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

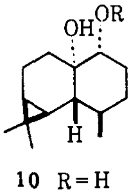
[8] L. Dolejš and F. Šorm, *Tetrahedron Letters*, **10**, 1 (1959).

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

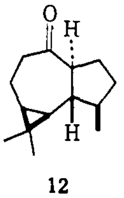
The tosylate **11**, mp 135–136°, [α]D −12° ($CHCl_3$), prepared from the isomeric diol **10**, has nmr absorption at δ 0.89 (3 H, doublet, J = 6 cps), while the corresponding methyl doublets are present at δ 1.18 in the diol **8** and at δ 1.15 in the tosylate **9**, respectively. The paramagnetic shifts observed[10] in the latter two compounds demand a 1,3-*cis*-diaxial relationship between methyl and tertiary hydroxyl groups, and this is only possible if the major glycol is the *cis*-decalin **8** and the minor glycol the *trans*-decalin **10**. Rearrangement of the tosylate **11** with 1 equiv of potassium *t*-butoxide in *t*-amyl alcohol followed by immediate condensation of the sensitive ketone with methylenetriphenylphosphorane gave a new hydrocarbon **14**, [α]D −40° ($CHCl_3$).



8, R = H
9, R = $C_7H_7SO_2$



10 R = H
11, R = $C_7H_7SO_2$



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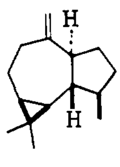

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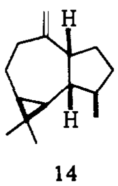
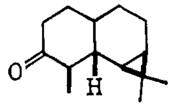


14

In another series of reactions the tricyclic ketone **15**[11] was transformed to the mesylate **16** which on exposure to potassium *t*-butoxide in hot *t*-butyl alcohol afforded a mixture of isomeric olefins from which epialloaromadendrene (**17**), [α]D +42° (EtOH), could be isolated by vapor phase chromatography.[12] The two enantiomers **14** and **17** were identical in vapor chromatographic behavior and infrared and mass spectra. This alternate synthesis left no doubt that the synthetic hydrocarbons **13** and **14** as well as their precursors have the configurations indicated, and as a corollary the previously proposed[1,2,7] stereochemistry of aromadendrene required revision. To provide new evidence on this point it was decided to synthesize hydrocarbon **22**.



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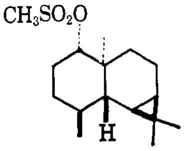

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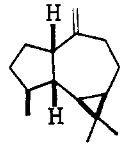
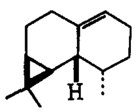


17

The tricyclic aldehyde **5** was transformed to the corresponding hydrocarbon **18** (77%), [α]D −188° ($CHCl_3$), by the sequence of reactions already used for the preparation of its epimer **7**. Oxidation with osmium tetroxide yielded a single diol **19** (86%), mp 124.5–125.5°, [α]D −9° ($CHCl_3$), which was converted to the tosylate **20** (89%), mp 129.5–130.5°, [α]D −21° ($CHCl_3$). The nmr spectra of both diol **19** and tosylate **20** reveal normally shielded secondary methyl groups (doublets at δ 0.87 and 0.83, respectively) demanding the presence of *cis*-decalins. When a solution of the tosylate **20** in chloroform was allowed to remain in contact with activated alumina, the ketone **21**, mp 82.5–83.5°, [α]D +4° ($CHCl_3$), was formed quantitatively. Its infrared and mass spectra were identical with those of apoaromadendrone, [α]D −4° ($CHCl_3$), and the two compounds were not separable by chromatographic techniques. When the tosylate **20** was rearranged by treatment with 1 equiv of potassium *t*-butoxide in *t*-butyl alcohol-OD, the resulting ketone **21** contained only 8.5% of one deuterium atom, thus confirming the presence of a substituted *trans*-bicyclo[5.3.0]decane. Condensation of the synthetic ketone **21** with methylenetriphenylphosphorane gave (−)-aromadendrene (**22**), [α]D −11° (EtOH), whose infrared and mass spectra were indistinguishable from those of aromadendrene, [α]D +9° (EtOH).



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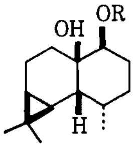
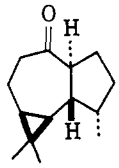


19, R=H
20, R=$C_7H_7SO_2$



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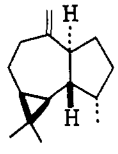

22

The synthesis just described leaves no doubt that natural aromadendrene is actually the C-4 epimer of structure **1**, but the source of error in the earlier deductions[1,2,7] has not yet been identified.

Acknowledgment. We are indebted to the National Institutes of Health (GM 09686) and to Firmenich & Cie, Geneva, for generous financial support.

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(10) R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963).

(11) R. B. Bates, G. Büchi, T. Matsuura, and R. R. Shaffer, *J. Am. Chem. Soc.*, **82**, 2327 (1960).

(12) G. Büchi, J. Kagan, T. Mukai, and A. Zschocke, to be published.

(13) National Institutes of Health Postdoctoral Fellow, 1964–1966.

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Received August 1, 1966

Organic Photochemistry. XVII.[1] Competition between Phenyl Migration, Type A Skeletal Rearrangement, and a New Rearrangement in 4,5-Diphenylcyclohexenone

Sir:

Two general types of photochemical cyclohexenone rearrangements are known. The first, conveniently termed "type A,"[2] involves skeletal change (note eq

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(1) For paper XVI of the series note H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, in press.

(2) (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 159 (1966); (b) *ibid.*, **88**, 1965 (1966).