

${}^1A_1$ ), whereas the transition at 18 kk. ( $\log \epsilon = 3.5$ ) in acepleiadylyene is polarized along the symmetry axis ( ${}^1A_1 \leftarrow {}^1A_1$ ), as is shown in Fig. 1.

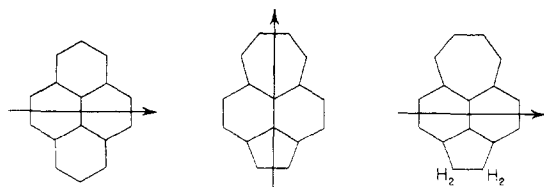


Fig. 1.—Polarization properties of the lowest electronic transitions in pyrene and in the pleiadienes.

The low intensity of the 17 kk. transition in acepleiadiene suggests a  ${}^1L_b \leftarrow {}^1A$  assignment. Elementary considerations based on the method of the polarization diagram<sup>8</sup> predict that the  ${}^1L_b \leftarrow {}^1A$  transition is polarized along the transverse direction, in agreement with observation.

The predictions based on the polarization diagram indicate that the  ${}^1L_b \leftarrow {}^1A$  transition in acepleiadylyene is polarized along the symmetry axis. The intensity appears somewhat high for a  ${}^1L_b \leftarrow {}^1A$  transition, but the polarization properties are not consistent with a  ${}^1L_a \leftarrow {}^1A$  assignment. The lowest transition in acepleiadylyene is therefore assigned as  ${}^1L_b \leftarrow A^1$ . The rather high intensity for this transition is ascribed to the long-field nature of the molecule.<sup>9</sup>

By treating the cata-condensed hydrocarbon as a perturbed cyclic polyene, Moffitt<sup>10</sup> has given an elegant account of the large energy decrease of the  ${}^1L_b \leftarrow A^1$  transition in azulene relative to its  $\pi$ -isomer, naphthalene. FEMO calculations lead to a  ${}^1L_b \leftarrow {}^1A$  assignment for the lowest absorption transition in pyrene at 27 kk.<sup>11</sup> The 9 kk. decrease in the transition in acepleiadylyene relative to its  $\pi$ -isomer, pyrene, is in agreement with Moffitt's perturbation theory. It therefore appears that Moffitt's description of a cata-condensed system may also be useful for a peri-condensed system, which may be thought of as a perturbed bicyclic polyene in which the inner atoms lie on a perimeter which is coaxial with the perimeter of the outer atoms. Both the inner and outer perimeters separately satisfy the Hückel ( $4n + 2$ ) rule in pyrene<sup>12</sup> and in acepleiadylyene.

I am grateful to Prof. V. Boekelheide and to Prof. M. Szwarc for gifts of the hydrocarbons.

(8) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

(9) J. R. Platt, *ibid.*, **18**, 1168 (1950).

(10) W. Moffitt, *ibid.*, **22**, 320 (1954).

(11) N. S. Ham and K. Ruedenberg, *ibid.*, **24**, in press.

(12) F. O. Rice and E. Teller, "The Structure of Matter," J. Wiley and Sons, New York, N. Y., 1949, p. 107.

DEPARTMENT OF CHEMISTRY  
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JEROME W. SIDMAN

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## TERPENES V. THE STRUCTURE OF PATCHOULY ALCOHOL

Sir:

Patchouly oil is one of the most important raw materials for the composition of fancy perfumes.

The mysterious scent of the essence is partly due to patchouly alcohol ( $C_{15}H_{26}O$ ), a tricyclic sesquiterpene first isolated by Gal in 1869. The early structural investigations of Gadamer, Semmler and Wallach<sup>1</sup> have been continued by Treibs<sup>2</sup> who proposed I as a structural expression for this natural product.

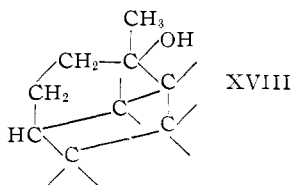
We would like to discuss evidence which shows that patchouly alcohol is represented by II. Acetylation of II with ketene produced the acetate (VIII), m.p.  $\sim 24^\circ$ , (*Anal. Calcd. for  $C_{17}H_{28}O_2$ : C, 77.22; H, 10.67. Found: C, 77.05; H, 10.64) which was reduced to II with lithium aluminum hydride. Pyrolysis of VIII at  $300^\circ$  led to a mixture of liquid patchoulenes (IX and X), b.p.  $141\text{--}142^\circ$  (17 mm.),  $[\alpha]^{20}_D -43^\circ$ , (*Anal. Calcd. for  $C_{15}H_{24}$ : C, 88.16; H, 11.84. Found: C, 88.34; H, 11.82) which on oxidation with osmium tetroxide was converted to two isomeric, saturated diols (XI and XII). Diol XI, m.p.  $95\text{--}96^\circ$ , (*Anal. Calcd. for  $C_{15}H_{26}O_2$ : C, 75.58; H, 11.00. Found: C, 75.75; H, 11.06) on cleavage with lead tetraacetate gave formaldehyde and a norketone (XIII), (*Anal. Calcd. for  $C_{14}H_{22}O$ : C, 81.50; H, 10.75. Found: C, 80.94; H, 10.45) infrared max.  $5.86\ \mu$ ; 2,4-DNP, m.p.  $144\text{--}145^\circ$ , (*Anal. Calcd. for  $C_{20}H_{26}N_4O_4$ : C, 62.16; H, 6.78. Found: C, 61.88; H, 6.85). Oxidation of diol XII, m.p.  $107\text{--}108^\circ$ , (*Anal. Calcd. for  $C_{15}H_{26}O_2$ : C, 75.58; H, 11.00. Found: C, 75.61; H, 10.84) with lead tetraacetate produced a ketocarboxylic acid (XIV), m.p.  $82.5\text{--}83.5^\circ$  (*Anal. Calcd. for  $C_{15}H_{24}O_3$ : C, 71.39; H, 9.59. Found: C, 71.30; H, 9.60), infrared max.  $3.1\text{--}4.0$ ;  $5.90$ ;  $8.25\ \mu$ ; oxime m.p.  $164\text{--}165^\circ$  (*Anal. Calcd. for  $C_{15}H_{25}NO_3$ : C, 67.38; H, 9.43. Found: C, 67.39; H, 9.44). Condensation of XIII with isoamyl nitrite in the presence of sodium ethoxide gave the oximinoketone (XV), m.p.  $131\text{--}132^\circ$ , (*Anal. Calcd. for  $C_{14}H_{21}NO_2$ : C, 71.45; H, 9.00. Found: C, 71.65; H, 9.04),  $\lambda_{max}$ .  $234\ m\mu$  ( $\epsilon$  8400) rather than an oximinoester. Examination of the infrared spectrum of XIII indicates the presence of a substituted cyclohexanone or a cycloheptanone. Convincing evidence for the size of ring A was obtained in the following way: Oxidation of a mixture of IX and X consecutively with potassium permanganate and with nitric acid led to a dicarboxylic acid (XVI), m.p.  $225\text{--}227^\circ$  (*Anal. Calcd. for  $C_{13}H_{20}O_4$ : C, 64.98; H, 8.39. Found: C, 64.92; H, 8.33). The corresponding anhydride (III), m.p.  $109\text{--}110^\circ$ , (*Anal. Calcd. for  $C_{13}H_{18}O_3$ : C, 70.24; H, 8.16. Found: C, 70.21; H, 8.04) with infrared peaks at  $5.60$  and  $5.73\ \mu$  is clearly a glutaric anhydride and ring A therefore six-membered.***********

Information as to the size of ring B was adduced by further degradation of XVI. The action of phenylmagnesium bromide on the dimethyl ester (*Anal. Calcd. for  $C_{15}H_{24}O_4$ : C, 67.13; H, 9.02. Found: C, 67.45; H, 8.90) of XVI followed by*

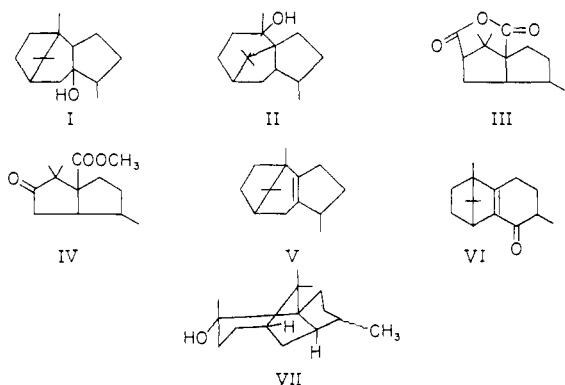
(1) An outline of previous investigations on the structure of patchouly alcohol is given in J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, London, 1952. For a complete and authoritative discussion on patchouly oil see E. Guenther, "The Essential Oils," Vol. III, Van Nostrand Co., Inc., New York, N. Y., 1949.

(2) W. Treibs, *Ann.*, **564**, 141 (1949).

dehydration gave the diphenylethylene ester (XVII), m.p. 154–155°,  $\lambda_{\max}$ . 227  $m\mu$  ( $\epsilon$  11200), (*Anal.* Calcd. for  $C_{26}H_{30}O_2$ : C, 83.38; H, 8.07. Found: C, 83.17; H, 7.91). After considerable experimentation we found that XVII can be oxidized to IV with ozone in acetic acid solution at 25°. Ketoester IV had an infrared peak at 5.79  $\mu$ , which is characteristic for a cyclopentanone and ring B is thus established to be five-membered. Analysis of the facts provided thus far leads to part-structure XVIII for patchouly alcohol.



We turned next to a reexamination of the patchoulene (V) described previously by Treibs,<sup>2</sup> from which information as to the size and attachment of ring C was forthcoming. Dehydration of II with sulfuric acid in ether solution at 35° gave a liquid hydrocarbon which is predominantly V as shown by its oxidation with osmium tetroxide to a saturated diol (XIX), m.p. 122.8–123.5°, (*Anal.* Calcd. for  $C_{15}H_{26}O_2$ : C, 75.58; H, 11.00. Found: C, 75.37; H, 10.77). Cleavage of XIX with lead tetraacetate produced diketone XX, m.p. 95–96°, infrared max. 5.90  $\mu$ , (*Anal.* Calcd. for  $C_{15}H_{24}O_2$ : C, 76.22; H, 10.24. Found: C, 76.12; H, 9.96) which gave a negative iodoform test. The formation of a cyclohexenone (VI), m.p. 79.5–80°,  $\lambda_{\max}$ . 260  $m\mu$  ( $\epsilon$  11000), infrared max. 6.04  $\mu$  (*Anal.* Calcd. for  $C_{15}H_{22}O$ : C, 82.51; H, 10.16. Found: C, 82.44; H, 10.27) by base catalyzed aldolization of XX is only possible with a  $\delta$ -diketone and V consequently must be a substituted cyclopentene. We have confirmed the finding of Treibs<sup>2</sup> who reported the formation of homocamphoric acid on ozonization of V and conclude that structure V proposed by this author is correct.



It had previously been assumed that V contains the carbon skeleton of patchouly alcohol and this thesis had led to the erroneous structure I. The

observations presented above clearly show that in the acid catalyzed dehydration of II a rearrangement had occurred. We have no degradative evidence for the location of the remaining methyl group and the structural argument rests solely on the formation of guaiazulene on dehydrogenation of II.<sup>2</sup> The reactions outlined above and others to be presented in a later paper provide evidence for the stereoformula VII of patchouly alcohol.

**Acknowledgments.**—We would like to thank Givaudan-Delawanna, Inc., for liberal financial support and Drs. Lüthy and Y. R. Naves of this firm for their continued interest. We are indebted to Dr. E. Guenther for a gift of patchouly oil and to Dr. M. Tishler for supplying the osmium tetroxide.

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#### PREPARATION OF ANHYDROUS ETHYLENIMINE: A CORRECTION

Sir:

It has been called to our attention<sup>1</sup> that the preparation of anhydrous ethylenimine by our published procedure<sup>2</sup> can lead to a violent reaction. This is the result of an unfortunate error in the quantity of water specified. In the interest of safety we should like to submit the following corrected procedure.

**Anhydrous Ethylenimine.**—A solution of 694 g. (6 moles) of 2-chloroethylamine hydrochloride in 1400 ml. of water was added with stirring to 600 g. (15 moles) of sodium hydroxide in 900 ml. of water. Solution temperatures were maintained below 50°. The resulting solution was then heated at 50° for 2 hours, after which time it was distilled at slightly reduced pressure (b.p. 30–35°) until 680 ml. of distillate had been collected. The cooled distillate was mixed with 350 g. of sodium hydroxide, and the ethylenimine was distilled at atmospheric pressure through a one-foot column packed with glass helices. A 50% sodium hydroxide solution was run in slowly at the top of the column during the distillation. The yield of ethylenimine was 187 g. (73%), b.p. 56–57°. The pot temperature did not exceed 70° during the distillation. The ethylenimine was stored over a few pellets of sodium hydroxide. Yields may be improved somewhat by increasing the efficiency of the ethylenimine removal operation as well as the condensation of the low-boiling distillate.

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F. C. SCHAEFER

RECEIVED FEBRUARY 16, 1956

(1) Personal communication from Professor Hakon Lund, Aarhus University, Denmark.

(2) V. P. Wystrach, D. W. Kaiser and F. C. Schaefer, *THIS JOURNAL*, **77**, 5915 (1955); specifically "Anhydrous Ethylenimine," p. 5917.