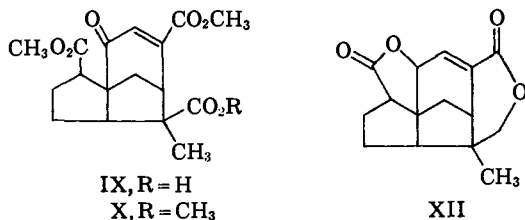
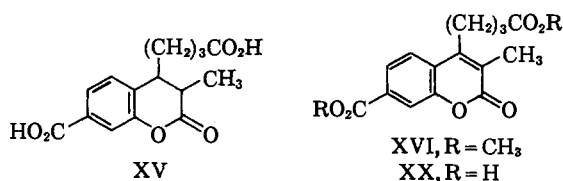


readily converted to a five-membered lactone, XI, m.p. 145–147.5°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.65, 5.75  $\mu$ , no high intensity ultraviolet absorption, no n.m.r. bands at  $\tau < 6$ . Treatment of I with acetic anhydride and sodium acetate formed a dilactone, XII, m.p. 147–151°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.65 (sh), 5.74  $\mu$ , ultraviolet end-absorption only. It regenerated I on treatment with warm aqueous sodium bicarbonate. It was hydrolyzed by hot water to a lactone acid,  $\lambda_{\text{max}}^{\text{KBr}}$  2.83, 3–4, 5.59, 5.85, 6.20  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  227 m $\mu$  ( $\epsilon$  5,500), in which the strained six-membered lactone ring of XII was opened. Hydrogenation of II and treatment with *p*-toluenesulfonic acid

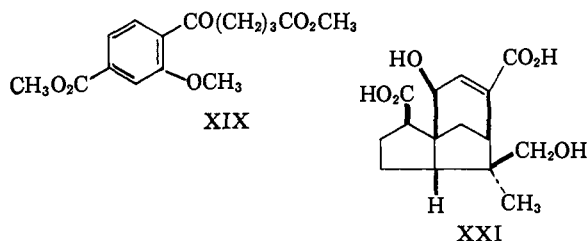


in benzene gave the dihydrodilactone analog of XII, m.p. 151–152.5°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.63, 5.72  $\mu$ , which did not hydrolyze with unusual readiness.

Fusion of II with alkali provided information concerning the skeleton of shellolic acid. The major product, which retained all of the carbon atoms of I, was a lactone diacid, XV, m.p. 199–201°,  $\lambda_{\text{max}}^{\text{KBr}}$  3–4, 5.63, 5.88, 6.31  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  ( $\epsilon$ ) 237 (10,000), 282 (1900), 290 (1800) m $\mu$ . Dehydrogenation over palladium/charcoal and then treatment with diazomethane gave the coumarin XVI, m.p. 115–116°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.75, 5.90, 6.20  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  ( $\epsilon$ ) 275 (sh, 13,300), 284 (18,200), 296 (16,200) 315 (sh, 7,700), 324 (8,300), 336 (sh, 5,300) m $\mu$ . The structure of XVI was proved by its independent synthesis from 4-(2-hydroxy-*p*-toluoyl)-butyric acid (XVII), m.p. 140–141.5°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  3–4, 5.83, 6.10 (s) $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  ( $\epsilon$ ) 262 (13,400), 325 (4,370) m $\mu$ , obtained from the Fries rearrangement of the ester from *m*-cresol and  $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_3\text{COCl}$ . Treatment of XVII with methyl iodide and



potassium carbonate gave methyl 4-(2-methoxy-*p*-toluoyl)-butyrate (XVIII), m.p. 38.5–39°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.78, 5.99, 6.22  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  ( $\epsilon$ ) 215 (18,700), 255 (10,200), 307 (4,360) m $\mu$ , which was converted, without purification of intermediates, to XIX, m.p. 78–79°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.79, 5.96, 6.22, 6.36  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  ( $\epsilon$ ) 254 (12,800), 320 (3,860), by the following sequence of reagents: N-bromosuccinimide in  $\text{CCl}_4$  with ABIN, silver nitrate in aqueous acetonitrile, chromic acid in acetic acid, methanolic HCl. Reaction of XIX with ethyl  $\alpha$ -bromopropionate and zinc, then treatment with hydrobromic acid in acetic acid gave XX, m.p. 248–249.5°,  $\lambda_{\text{max}}^{\text{KBr}}$  3–4, 5.8–5.9, 6.21  $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  ( $\epsilon$ ) 284 (17,600), 296 (15,400), 315 (sh, 7,500), 323 (8,000), 335



(sh; 5,100) m $\mu$ . This was converted with diazomethane to XVI, m.p. 115–116°, undepressed on admixture with the degradative sample; the spectra of the two samples were identical.

The formation of XV from dimethyl shellolate and the evidence for the functional group relationships permits the assignment to shellolic acid of structure I, which also serves to rationalize previous oxidation and bromination experiments.<sup>8</sup> The tentative relative configurational assignment XXI can be made on the basis of the present and earlier observations.

We thank the American Bleached Shellac Manufacturers Association for a generous supply of Kusmi seedlac.

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#### UNSATURATED MACROCYCLIC COMPOUNDS. XV.<sup>1</sup> CYCLOTETRADECAHEPTAENE

Sir:

Cyclotetradecaheptaene (CTH) (*e.g.*, IV) is a fully conjugated cyclic polyene which is of considerable interest, since it contains  $(4n + 2)$   $\pi$ -electrons ( $n = 3$ ) but cannot exist in a planar form. It therefore complies with only one of the two criteria which have been postulated for aromaticity in such systems<sup>2</sup> and its availability would make it possible to evaluate the relative significance of these criteria. The synthesis of cyclotetradecaheptaene has now been accomplished and it has been found that this substance in fact is quite unstable. This provides an experimental demonstration of the importance of planarity for aromaticity in conjugated cyclopolyolefins, especially in view of the much greater stability of cyclooctadecanonaene which also contains  $(4n + 2)$   $\pi$ -electrons ( $n = 4$ ), but in addition is planar or near planar.<sup>3</sup>

Reaction of *trans*-1,4-dibromo-2-butene (from butadiene and bromine) with excess ethynylmagnesium bromide<sup>4</sup> in tetrahydrofuran in the presence

(1) Part XIV, see Y. Amiel and F. Sondheimer, *Chemistry & Industry*, in press (1960).

(2) *Inter al.* W. Baker and J. P. W. McOmie in Ginsburg "Non-benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter IX.

(3) F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, No. 3, 3 (1959).

(4) E. R. H. Jones, L. Skattebøl and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); *Org. Syntheses*, **39**, 56 (1959).

of cuprous chloride<sup>5</sup> yielded besides other products 12% of *trans-trans*-4,10-tetradecadiene-1,7,13-triene (I) [m.p. 71–72°; C<sub>14</sub>H<sub>14</sub> (found: C, 92.15; H, 8.00; act. H, 1.06); no high-intensity absorption in the ultraviolet; converted on full hydrogenation to *n*-tetradecane, m.p. and mixed m.p. 5–6°]. The hydrocarbon I (1 part) was coupled with cupric acetate (15 parts) in pyridine (100 parts)<sup>6</sup> at 50° for 1 hr. and then treated directly with potassium *t*-butoxide in *t*-butyl alcohol-benzene at 60° for 1 minute. Chromatography of the product on alumina gave ca. 2% of 1,3,5,7,9,11-cyclotetradecahexaen-13-yne (III or a stereoisomer) as bright red plates from pentane (light red in solution), m.p. 148–149° (sample placed on block just before); C<sub>14</sub>H<sub>12</sub> (found: C, 92.68; H, 6.97);  $\lambda_{\max}^{\text{isoctane}}$  312, 365 and 392 m $\mu$  ( $\epsilon = 92,000, 7,100$  and 4,700);  $\lambda_{\max}^{\text{benzene}}$  319, 369 and 396 m $\mu$ ; acetylene band at 4.76  $\mu$  in the infrared. Full hydrogenation (platinum, ethyl acetate) smoothly yielded cyclotetradecane, m.p. and mixed m.p. 54–55°.

A second substance, which appears to be another isomer of III, was eluted directly after the first one (here and in the sequel, III refers to the cyclotetradecahexaen-yne structure without any particular configuration being implied). This isomer, obtained in ca. 0.4% yield, formed red plates from pentane (red-green in solution); decomposes on heating; C<sub>14</sub>H<sub>12</sub> (found: C, 92.51; H, 6.64);  $\lambda_{\max}^{\text{isoctane}}$  (principal bands) 309, 402, 410, 424 and 586 m $\mu$  ( $\epsilon = 175,000, 6,900, 7,500, 23,600$  and 2,900);  $\lambda_{\max}^{\text{benzene}}$  (principal bands) 317, 407, 414, 429 and 586 m $\mu$ . The infrared spectrum (acetylene band at 4.70  $\mu$ ) differed considerably from that of the first isomer. Full hydrogenation as previously again yielded cyclotetradecane, m.p. and mixed m.p. 54–55°. This isomer could be kept with little change in light and air for 1 day, unlike the first one which had decomposed completely after this time.

The coupling of I in addition yielded other conjugated substances, as will be reported subsequently.

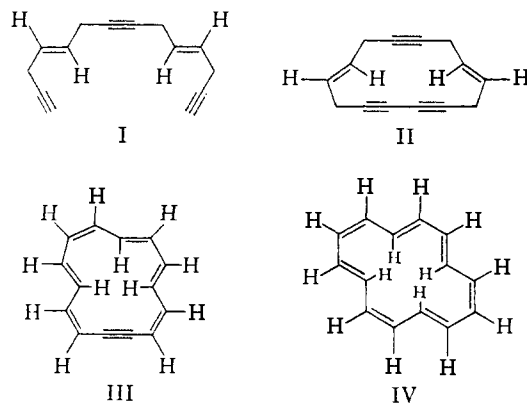
Both isomers of III were formed most probably via II, the cyclic "monomer" of I. However no attempt was made to isolate this intermediate prior to the potassium *t*-butoxide treatment, since the ultraviolet spectrum of the material at that stage indicated that partial isomerization already had taken place during the coupling reaction. The yields of the two isomers of III were not improved when the coupling of I was carried out under conditions of high dilution.<sup>6a</sup>

Partial hydrogenation of the first-described isomer of III in benzene over a "Lindlar" palladium

(5) See J. P. Daneby, D. B. Kijlian and J. A. Nieuwland, *THIS JOURNAL*, **58**, 611 (1936).

(6) See (a) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959); (b) F. Sondheimer, Y. Amiel and R. Wolovsky, *THIS JOURNAL*, **81**, 4600 (1959).

catalyst, followed by chromatography on alumina, yielded ca. 15% of cyclotetradecaheptaene. This substance crystallized from ethanol as long dark-brown needles (red-brown in solution); m.p. 134–135° (sample placed on block just before); C<sub>14</sub>H<sub>14</sub> (found: C, 92.55; H, 7.63);  $\lambda_{\max}^{\text{isoctane}}$  314 and 374 m $\mu$  ( $\epsilon = 69,000$  and 5,700);  $\lambda_{\max}^{\text{benzene}}$  321 and 378 m $\mu$ . The infrared spectrum no



longer showed the acetylene band at 4.76  $\mu$ . Full hydrogenation (platinum, ethyl acetate) once more yielded cyclotetradecane, m.p. and mixed m.p. 54–55°.

Cyclotetradecaheptaene was completely destroyed after being allowed to stand in light and air for 1 day. A dilute isoöctane solution suffered ca. 10% decomposition after 1 day, 30% after 9 days and 45% after 14 days. By comparison, both isomers of III in isoöctane were stable for several weeks.

It is not known with certainty whether the synthetic CTH in fact possesses the configuration IV or exists in one of the other possible ones (*e.g.*, as in the periphery of phenanthrene or anthracene). However, since none of the possibilities can be planar, the observed instability of cyclotetradecaheptaene demonstrates the importance of planarity for aromaticity in conjugated cyclic polyenes, irrespective of its actual configuration. It is of interest to note that whereas the conjugated cyclopolyolefins containing 18, 24 and 30 carbon atoms<sup>7,8</sup> (which are presumably planar or near planar) are *more* strongly adsorbed on alumina than their respective dehydro-compounds, the non-planar CTH as might be expected is *less* strongly adsorbed than its precursor.

(7) F. Sondheimer and R. Wolovsky, *ibid.*, **81**, 4755 (1959).

(8) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **83**, 755 (1960).

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