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OPTICALLY ACTIVE CUMULENE

SYNTHESIS AND RESOLUTION OF 1,5-DI-p-CHLOROPHENYL-1,5-DI-t-BUTYL-PENTATETRAENE

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AS early as 1875, van t'Hoff had predicted that an unsymmetrically substituted cumulene should be resolvable into optical antipodes, when the number of its cumulative double bonds is even,[1] but this prediction has not been verified up to now except for allenes.[2] With regard to pentatetraenes, having four cumulative double bonds, even the synthesis of a symmetrically substituted product has not yet been attained.[3] The isolation of *cis*- and *trans*-isomers of butatrienes which contain an odd number of cumulative double bonds has been reported recently by Kuhn[4]. But their geometrical stability is so small that they can be interconverted very easily.

It is now of interest to clarify whether pentatetraenes can be resolved

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[1] J.H. van t'Hoff, *La Chimie dans L'Espace*, Rotterdam (1875).

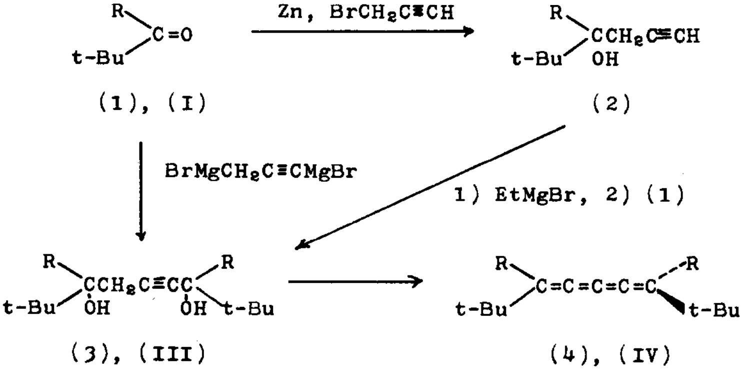
[2] P. Maitland and W.H. Mills, *Nature, Lond.* **135**, 994 (1935); *J.Chem. Soc*. 879 (1936); E.P. Kohler and M. Tischler, *J.Amer.Chem.Soc*. **57** 1743 (1935).

[3] The first report on the synthesis of *bis*-pentatetraene [*Angew.Chem.* **70**, 705 (1958)] has been corrected, see R. Kuhn and H. Fischer, *Chem.Ber*. **92**, 1849 (1959).

[4] R. Kuhn and K.L. Scholler, *Chem.Ber*. **87**, 598 (1954); R. Kuhn and D. Blum, *Ibid*. **92**, 1483 (1959).

into enanthiomorphs as in the case of allenes, or whether the resolution of them is possible in view of the extreme ease of interconversion of butatrienes.

We have now achieved the synthesis of pentatetraenes according to the following route*.



Starting from phenyl t-butyl ketone (1), we have obtained the acetylenic glycol (3) via the acetylenic alcohol (2) or directly by means of Kuhn's method[3]. Dehydration of (3) by the action of p-toluenesulphonic acid in boiling benzene and subsequent purification on chromatography yielded (4) as colourless prisms (from methanol), m.p. 99~100°C, $C_{25}H_{28}$ (Found: C, 90.77; H, 8.50%).

The ultra-violet spectrum of this hydrocarbon shows the following absorption maxima in ethanol. λ_{max} : 229; 261; 304; 312 and 340 (inflexion) mμ (ε = 14,700; 36,600; 10,200; 9500 and 3400). The infra-red spectrum of (4) shows a strong band at 1940 cm^{-1} which is characteristic of the cumulene structure. The formula of (4) was assigned to this hydrocarbon on the basis of the above-mentioned spectroscopic data and the following evidence.

This hydrocarbon absorbed 3 moles of hydrogen in ethyl acetate and

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* Arabic numerals: R=phenyl ; Roman numerals: R=p-chlorophenyl.

acetic acid over palladium oxide. When platinum oxide was used as catalyst, the absorption did not stop at 4 moles, but slow absorption continued without appreciable change in the absorption rate. This anomalous behaviour in catalytic reduction is not inconsistent with the assigned formula, since the reference compound, 1,4-diphenyl-1,4-di-t-butyl-butatriene, synthesized according to the method of Bohlmann[5] also absorbed only 2 moles of hydrogen over palladium oxide, and the absorption did not stop at 3 moles over platinum oxide.

The NMR spectrum of (4) in carbon tetrachloride (0.5 mole solution) shows two lines arising from methyl protons in the aliphatic region (+141 cps and +146 cps at 40 MC using water as external standard). The doublet methyl resonance would be due to the bulky t-butyl group, which tends to fix the methyl groups to a certain extent. The fact that the NMR spectrum of the similarly substituted butatriene also shows two lines with the same chemical shift as (4) indicates that the t-butyl groups in both compounds are in very similar environments.

In order to obtain the pentatetraene (4) in optically active form we applied the method of asymmetric dehydration of the glycol (3) by the action of _d_-bromocamphorsulphonic acid. The fractional recrystallization of the dehydration product afforded (4), colourless prisms, m.p. 95-96°C, showing the specific rotation $[\alpha]_{5461} = +11^{\circ}$ in benzene solution. Owing to the low optical yield and the minor differences[3] of solubility between the active form and the racemate, we were unable to obtain the optically pure enanthiomorph.

To overcome the above-mentioned difficulties, the synthesis of the _p_-chloro-substituted analogue of (4) was carried out according to the same sequence of reactions. Treatment of the glycol (III) with _d_-bromocamphor-

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[5] F. Bohlmann and K. Kieslich, _Chem.Ber._ _88_, 1211 (1955).

sulphonic acid in benzene afforded the dehydration product. Chromatographic purification of the product furnished pale yellow crystals, $C_{25}H_{26}Cl_2$, m.p. 171~172°C, (Found: C, 75.87; H, 6.64%). The ultra-violet spectrum of this substance (in ethanol, λ_{max} : 207.5; 234; 267; 300 and 311 mμ (ε = 33,000; 17,300; 39,200; 9900 and 8100) closely resembles that of (4). Also the infra-red spectrum exhibits a strong absorption at 1940 cm^{-1} indicating the presence of the cumulene structure. From these observations the structure of 1,5-di-p-chlorophenyl-1,5-di-t-butylpentatetraene (IV) was given to the pale yellow hydrocarbon.

Fortunately, spontaneous partial resolution was observed in the fractional recrystallization of IV (m.p. 171~172°C, $[\alpha]_{5461}$ = +0.3° (c = 4.40)* from a mixture of ethanol and methanol (1 : 3.3). The laevorotatory crystals (first crop, $[\alpha]_{5461}$ = -27.2°, second crop, $[\alpha]_{5461}$ = -29.3°) were obtained on cooling the solution. These two crops were combined and fractionally recrystallized from the same solvent. Increasing values of rotation in the more soluble fractions was observed, and finally pale yellow crystals, m.p. 157~158.5°C, $[\alpha]_{5461}$ = -467° (c = 0.120) were obtained from the most soluble fraction. The dextrorotatory mother liquor of the above-mentioned laevorotatory first and second crops was fractionally concentrated in the same way. Pale yellow crystals (m.p. 158~159°C, $[\alpha]_{5461}$ = +447° [c = 0.518]) were obtained from the most soluble fraction. Further recrystallization of the laevo-IV caused a minor change in the optical rotation and therefore, the optical purity of these antipodes seems to be fairly high. The ultraviolet and infra-red spectra of d-, l- and rac-IV were found to be completely identical over the entire region of the spectrum. The rate of racemization of the laevo-isomer was measured in bromobenzene at 156°C and the half-life period was found to be ca. 700 min.

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* The optical rotation was measured in benzene solution throughout this experiment.

The optical stability of (IV) is similar to that of the optically active allenes[2] in sharp contrast to the geometrical instability of butatrienes.[4] The marked difference of the stability between the two series of compounds (even number and odd number of the cumulative double bonds) seems to be reflected in the ultra-violet spectra. As we have synthesized a number of variously substituted pentatetraenes, the discussion about this point will be presented separately.

The van't Hoff's prediction of the existence of the optically active higher homologues of allene is now verified experimentally by the above-mentioned resolution of 1,5-di-p-chlorophenyl-1,5-di-t-butyl-pentatetraene (IV).

The details of this research will be reported elsewhere.