were dissolved in 150 ml. of hexane at 20° and developed on a 27 × 8 cm. column with a 1:3 mixture of benzene–hexane (the following spectral maxima, in mμ, were observed visually, in hexane solutions):

48 minor zones and interzones
25 orange-red: all-*trans*-dehydro-β-carotene (504, 474)
50 reddish-purple: all-*trans*-bisdehydro β-carotene (522, 490)
25 purple: anhydro-eschscholtzxanthin (534, 499)
15 orange: neo-dehydro-β-carotene A (500, 469)
10 orange-red: a *cis*-bisdehydro-β-carotene (518, 489)
5 pale orange: neo-dehydro-β-carotene D (494, 461)
3 interzone
10 pale orange: a *cis*-bisdehydro-β-carotene (515, 484)
5 yellow-orange: a *cis*-dehydro-β-carotene (491, 460)
5 interzone
10 pale orange: a *cis*-bisdehydro-β-carotene (510, 481)

The identity of the stereochemical sets to which the respective *cis* forms belonged was established by iodine catalysis and mixed chromatography of the all-*trans* compound thus formed with an authentic sample of the corresponding substance. Each zone was eluted and transferred into benzene–hexane.

Dehydro-β-carotene.—The dried benzene–hexane solution was evaporated and the crystalline residue recrystallized from benzene–methanol as described above for the crude pigment mixture; yield 3–4 mg., m.p. 192°. This compound was identified by spectroscopic readings, mixed chromatogram with a sample *ex* β-carotene iodide, and by its behavior in isomerization experiments.

Anal. Calcd. for $C_{40}H_{54}$: C, 89.83; H, 10.17. Found: C, 89.79; H, 9.91.

Bisdehydro-β-carotene.—This fraction was evaporated, the residue dissolved in benzene and crystallized by cautious addition of methanol at 50°; yield 2–2.5 mg., m.p. 204°. From various experiments about 35 mg. of this compound was isolated as long quadrangular plates with slightly curved endings. Macroscopically the crystals appear to be definitely more purple than those of dehydro-β-carotene. Under the microscope single crystals are pale purple and crossings may appear very dark, almost black. Sparingly soluble in hexane, better in benzene, insoluble in methanol. When partitioned between hexane and 95% methanol, the pigment is found entirely in the epiphase. For the position on the lime–celite columns, *cf.*, the chromatogram above. Molecular extinction coefficient at $\lambda_{\max}$ in hexane: $E^{\text{mol.}}_{1\,\text{cm.}}$ 16.6 × 10⁴ at 487 mμ.

Anal. Calcd. for $C_{40}H_{52}$: C, 90.16; H, 9.84. Found: C, 89.40; H, 10.37.

Catalytic hydrogenation: 5.269 mg. substance in cyclohexane–glacial acetic acid (1:1) added, in the presence of 11.5 mg. of PtO_2, 2.76 ml. of hydrogen (0°, 760 mm.); calcd. 13 double bonds, found 12.5 double bonds. A parallel experiment carried out with β-carotene gave the following result: calcd. 11 and found 10.6 double bonds.

When bisdehydro-β-carotene is catalyzed with iodine in light, the three main *cis* forms (neos A-C) can be separated from the all-*trans* compound by developing with a 1:3 benzene–hexane mixture on lime–celite, whereby clear interzones are obtained. Visually observed maxima in hexane of the rechromatographed stereoisomers: all-*trans*-bisdehydro-β-carotene 521, 490, 457 mμ; neo A: 518, 485, 456 mμ; neo B: 514, 483 mμ; and neo C: 510, 481 mμ.

Anhydro-eschscholtzxanthin.—The benzene–hexane solution of this compound was evaporated and the pigment crystallized from benzene–methanol as described; yield 1 mg.; in all, 14 mg. was obtained from parallel experiments, dark purple crystals, m.p. 193°. Under the microscope bulky conglomerates appear but parallel twins and fan-like groupings are also found. Single crystals are purple with a brownish tinge while overlapping units are nearly black. The pigment is more soluble in hexane or benzene than bisdehydro-β-carotene; it is insoluble in methanol. When partitioned between hexane and 95% methanol, it shows entirely epiphasic behavior. It is adsorbed just below bisdehydro-β-carotene. The visually observed bands are located at 534, 499 mμ in hexane. Molecular extinction coefficient at $\lambda_{\max}$, in hexane: $E^{\text{mol.}}_{1\,\text{cm.}}$ 16.0 × 10⁴ at 499 mμ.

Anal. Calcd. for $C_{40}H_{50}$: C, 90.50; H, 9.50. Found: C, 89.89; H, 10.10.

The chromatogram of a solution that had been kept at 4° for 3 days showed two main *cis* forms, both adsorbed below the *trans* zone.

Acknowledgment.—We wish to thank Professor A. J. Haagen-Smit, Mr. G. Swinehart and Dr. A. Elek for analyses.

PASADENA, CALIF.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1813]

Conversion of Dehydro-β-carotene, *via* its Boron Trifluoride Complex, into an Isomer of Cryptoxanthin[1]

BY L. WALLCAVE AND L. ZECHMEISTER

RECEIVED APRIL 17, 1953

Dehydro-β-carotene and BF_3-etherate form a dark blue complex. Cleavage with water (or methanol) resulted in the isolation of a monohydroxy-β-carotene, termed isocryptoxanthin (or its methyl ether). Isocryptoxanthin when treated with acid chloroform undergoes dehydration to yield dehydro-β-carotene which indicates the presence of an allylic hydroxyl group. While naturally occurring cryptoxanthin is 3-hydroxy-β-carotene, isocryptoxanthin is the corresponding 4-compound. Its methyl ether or acetate can also be converted into dehydro-β-carotene.

Dehydro-β-carotene, $C_{40}H_{54}$, which so far as we know does not occur in nature, was obtained by Kuhn and Lederer[2] starting from β-carotene iodide. Its symmetrical structure was proposed by Karrer and Schwab[3] and is, in Oroshnik's terminology,[4] a "retro" structure (see the formula below), *i.e.*, the aliphatic section of the molecule and the rings are connected by double bonds.

A brief remark was made by Strain[5] concerning the formation of a dark blue coloration by the interaction of carotenoids and boron trifluoride. Somewhat earlier Lewis and Seaborg[6] reported on similar phenomena using boron trichloride. We observed that the dehydro-β-carotene structure is especially sensitive to BF_3, much more so than is β-carotene. When BF_3-etherate is added to a

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[1] Presented at the Meeting of the American Chemical Society, March 19, 1953, in Los Angeles, California.

[2] R. Kuhn and E. Lederer, *Ber.*, **65**, 637 (1932).

[3] P. Karrer and G. Schwab, *Helv. Chim. Acta*, **23**, 578 (1940).

[4] W. Oroshnik, G. Karmas and A. D. Mebane, THIS JOURNAL, **74**, 295 (1952).

[5] H. H. Strain, *ibid.*, **63**, 3448 (1941). "Boron trifluoride . . . converted carotenoids into unstable blue pigments . . . Alcohol reconverted these pigments into yellow substances that were strongly adsorbed on columns of magnesia and did not exhibit definite absorption maxima."

[6] G. N. Lewis and G. T. Seaborg, *ibid.*, **61**, 1886 (1939).

dehydro-β-carotene solution, the liquid is shaken for 1 min. and then cleaved by the addition of water, subsequent chromatography shows the absence of unchanged dehydro-β-carotene. About one half of the starting material is then present in form of a yellow-red pigment whose resolution yields two main crystalline polyenes, *viz.*, β-carotene, $C_{40}H_{56}$ (11–12% of the starting material), and a monohydroxy-β-carotene, $C_{40}H_{55}OH$ (34%). Thus, a hydroxyl group has been introduced into the β-carotene molecule *via* dehydro-β-carotene and its BF_3 complex.

The mechanism of the formation and cleavage of such complexes is unknown. One may tentatively assume that BF_3 is attached to the 4′-position of dehydro-β-carotene by means of an electron pair drawn from the terminal double bond of the chromophore. This would involve the rearrangement of the "retro" into a "normal" conjugated system as well as the polarization of the molecule with the appearance of a positive charge at the 4-position. Upon addition of water the BF_3 group would then be displaced by a proton while OH would enter the 4-position.

Parallel experiments in which methanol, instead of water, was used to decompose the complex yielded three main crystalline carotenoids, *viz.*, β-carotene (18%), a monomethoxy-β-carotene, $C_{40}H_{55}OCH_3$ (28%), and a dimethoxy-β-carotene, $C_{40}H_{54}(OCH_3)_2$ (6%).

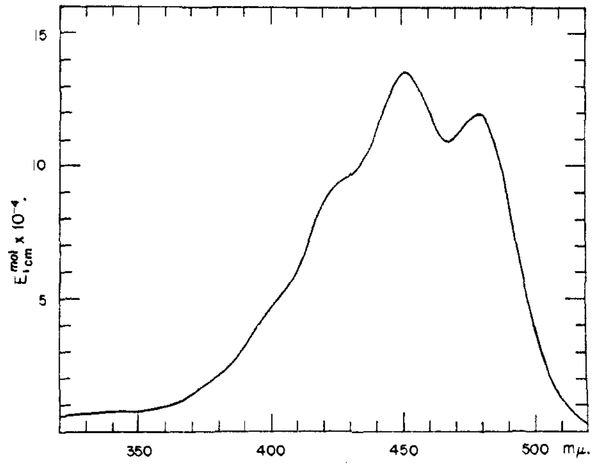
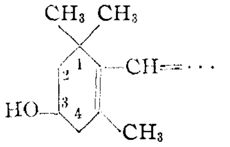


Fig. 1.—Molecular extinction curve of isocryptoxanthin in hexane.

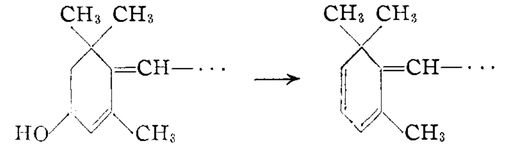
The hydroxy-β-carotene, termed "isocryptoxanthin," behaves in many respects like naturally occurring cryptoxanthin and shows a very similar spectral curve (Fig. 1). Nevertheless, the two monohydroxy-carotenes can be separated chromatographically. The accepted structure of cryptoxanthin[7] is that of 3-monohydroxy-β-carotene (I), although Goodwin and Taha[8] have proposed a 4-hydroxy structure which has been refuted by Karrer.[9] As will be shown below, our study indirectly confirms the 3-position of the hydroxyl group in cryptoxanthin.

In the isocryptoxanthin molecule the OH-group



I, end group of cryptoxanthin (the other end of the molecule is O-free).

can be located *a priori* in the position 2, 3 or 4. Of these only the 4-position is "allylic" with reference to the first double bond of the conjugated system. It has been shown recently by Karrer and Leumann[10] that a carotenoid containing the group —CHOH·CH=CH-, *viz.*, eschscholtzxanthin,[11] $C_{40}H_{54}O_2$, undergoes dehydration very easily when treated with acid chloroform at room temperature. This becomes manifest from the lengthening of the chromophore and displacement of the spectral maxima toward longer wave lengths (II, III).

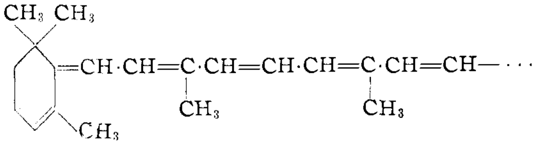


II III

4-Hydroxy-β-ionone also undergoes dehydration.[12]

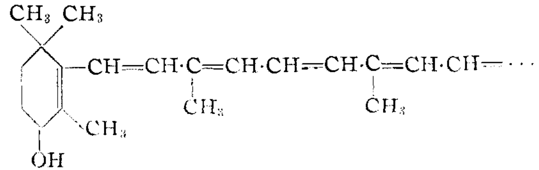
When isocryptoxanthin is treated with HCl in chloroform, it loses one molecule of water very rapidly. Deepening of the color can be noticed almost instantaneously, corresponding to the considerable spectral difference between the starting material and the main product, as illustrated by the following data ($E^{mol.}_{1\,cm.}$, in hexane): isocryptoxanthin, 13.4 × 10^4 at 451 mμ → dehydro-β-carotene, 16.6 × 10^4 at 471 mμ.

From the reaction mixture, crystalline pure dehydro-β-carotene was isolated in a yield of 70%, in addition to some β-carotene and a few minor pigments. This experiment strongly indicates the 4-hydroxy structure for isocryptoxanthin and also demonstrates the interconversion of "normal" and "retro" conjugated systems: β-carotene → dehydro-β-carotene (IV) → BF_3-complex → isocryptoxanthin (V) → dehydro-β-carotene (and, in part, β-carotene).



IV, ½ Dehydro-β-carotene
(the other half of the molecule is identical)

BF_3, H_2O ↓ ↑ HCl in $CHCl_3$



V, ½ Isocryptoxanthin
(the other half of the molecule is O-free)

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(7) R. Kuhn and C. Grundmann, *Ber.*, **66**, 1746 (1933).

(8) T. W. Goodwin and M. M. Taha, *Biochem. J.*, **48**, 513 (1951).

(9) P. Karrer, *Helv. Chim. Acta*, **34**, 2160 (1951).

(10) P. Karrer and E. Leumann, *ibid.*, **34**, 445 (1951).

(11) H. H. Strain, *J. Biol. Chem.*, **123**, 425 (1938).

(12) P. Karrer and C. H. Eugster, *Helv. Chim. Acta*, **34**, 1400 (1951)

The monomethoxy-β-carotene obtained by the cleavage with methanol of the BF_3 complex of dehydro-β-carotene can also be prepared by direct methylation of isocryptoxanthin. Furthermore, it is easily reconverted into dehydro-β-carotene by means of acid chloroform. Consequently, its structure is that of 4-methoxy-β-carotene. The dimethoxy-β-carotene mentioned behaves similarly; however, its structural clarification requires further experiments.

Finally, it should be noted on the basis of assays carried out in collaboration with Drs. H. J. Deuel, Jr., and J. Ganguly of the University of Southern California, that isocryptoxanthin and its methyl ether show equal provitamin A potencies in the rat, practically identical with that observed upon feeding cryptoxanthin.[12a]

Experimental

Materials and Methods.—The adsorbent was a 2:1 mixture of Sierra Hydrated Lime Superfine (U. S. Lime Products Corp., Los Angeles, Calif.) and Celite No. 545 (Johns-Manville Co.). Elutions were carried out with acetone, and the transfer of the pigments to hexane was effected in the continuous washing device designed by LeRosen.[13] Extinction curves were taken in the Beckman spectrophotometer (DU) while "visual" maxima were observed in a Zeiss Grating Spectroscope (Loewe-Schumm). Melting points (cor.) were taken in an electrically heated Berl block using evacuated capillaries.

Boron trifluoride etherate was prepared by passing the gas (Ohio Chemical and Manufacturing Co., Cleveland) into ice-cooled ether (Reagent Grade) until a weight increase of about 60 g. per 100 g. of ether was achieved (²/₃ mole BF_3 per mole ether). Upon distillation, the middle fraction (b.p. 122–125°) was collected and stored in a dark bottle in the cold room. The etherate remained colorless for several weeks; slightly discolored samples can also be used.

Isocryptoxanthin from Dehydro-β-carotene.—To a solution of 35 mg. of all-*trans*-dehydro-β-carotene[14] in 100 ml. of hexane 3 ml. of BF_3-etherate was added. The dark blue liquid, forming two phases, was shaken vigorously for exactly 1 min. and poured into a separatory funnel containing 400 ml. of acetone. Water was added cautiously, with swirling, to the homogeneous blue solution until two phases separated. The yellowish-brown upper phase contained practically the total pigment; the hypophase was discarded. The hexane solution was washed for ¹/₄ hr., *viz.*, until the yellowish-brown color turned dark red. The solution, about 100 ml., was decanted from some reddish-brown, gummy material (which had collected on the glass walls during the washing), dried with sodium sulfate, filtered, adsorbed on a 27 × 5.8 cm. column, and developed with hexane containing 7% acetone (figures on the left designate thickness of zones, in mm.; the quantities given were estimated photometrically):

13	brownish-red zones
15	interzone
18	several yellow and purple zones
10	interzone
40	reddish-orange: isocryptoxanthin (9 mg.)
2	interzone
12	yellow: *cis*-isocryptoxanthin (3 mg.)
150	interzone containing several pale yellow zones
15	intensely yellow: β-carotene (4 mg.)
7	colorless

Each of the three designated zones was cut out, eluted, transferred into hexane, dried and rechromatographed (developer, hexane and 8% acetone for the isocryptoxanthin zones and pure hexane for β-carotene). The *cis*-isocryptoxanthin was identified by its spectral properties as well as conversion into the all-*trans* form by iodine catalysis, in light. The hexane solutions of isocryptoxanthin and of β-carotene were evaporated *in vacuo* to dryness, dissolved in the minimum amount of benzene at room temperature, transferred into a small, conic centrifuge tube and, while kept in a bath of 40°, evaporated by blowing in dry nitrogen through a capillary. The residue was then dissolved in about 5 drops of benzene at 40° and 4–5 vol. of methanol was added cautiously, from a dropper, down the walls of the tube, with stirring. After standing at 20° for 30 min. the crystals were centrifuged, washed twice in the same tube with methanol and dried *in vacuo;* yields 5 mg. of isocryptoxanthin and 2 mg. of β-carotene. The yields originating from several experiments were combined.

Isocryptoxanthin.—When crystallized from benzene-methanol this pigment forms typically oval and leaf-like plates with mostly sawed contours. These forms are different from those of cryptoxanthin.[15] The glittery crystals are dark red; individuals appear orange-brown under the microscope, but crossed areas or thick plates are ruby red; m.p. 162–164°.

Anal. Calcd. for $C_{40}H_{56}O$: C, 86.87; H, 10.22. Found: C, 86.97, 86.52; H, 10.54, 10.24.

The compound is sparingly soluble in hexane, more easily in benzene or chloroform, only slightly in hot methanol. When partitioned between hexane and 95% methanol it is, like cryptoxanthin, about evenly distributed between the two phases. Adsorbed on a lime–celite column, it does not migrate when developed with hexane and requires hexane and 8% acetone. Prolonged development in such a system separates it from cryptoxanthin which then occupies the lower position. The spectral maxima observed in hexane are located at 484, 453 mμ (visual) or at 479, 451 mμ (Beckman).

Isocryptoxanthin Acetate.—The acetylation followed (in part) the directions given by Kuhn and Grundmann[7] for cryptoxanthin. To a solution of 30 mg. of substance in 2.5 ml. of dry pyridine, 1 ml. of acetic anhydride was added and the mixture kept at 70° for ³/₄ hr. After dilution with hexane, the washed and dried solution was adsorbed on a 27 × 5.8 cm. column and developed with hexane + 2% acetone. Some unreacted starting material remained near the top while the main migrating zone contained the acetate. It was eluted, transferred into hexane, evaporated, crystallized from benzene–methanol and dried at 55° *in vacuo* for 1 hr.; yield 4 mg., m.p. 108°; behavior in the partition test: epiphasic. Isocryptoxanthin was recovered after saponification with methanolic KOH at room temperature. Adsorption sequence: isocryptoxanthin (top), isocryptoxanthin acetate, and β-carotene (developer, hexane and 2% acetone).

Dimethoxy-β-carotene and Isocryptoxanthin Methyl Ether from Dehydro-β-carotene.—A solution of 60 mg. of substance in 250 ml. of hexane was treated with 5 ml. of BF_3-etherate as described, after which the complex was split by the addition of 300 ml. of 95% methanol. After having carried out the operations described for isocryptoxanthin, the following chromatogram appeared (column, 30 × 8 cm.; developer, hexane and 3% acetone):

30	several purple and pink minor zones
20	interzone
20	orange: dimethoxy-β-carotene (5 mg.)
15	interzone
25	yellow: *cis*-isocryptoxanthin methyl ether (3 mg.)
5	interzone
60	orange: isocryptoxanthin methyl ether (12 mg.)
2	interzone
25	yellow: *cis*-isocryptoxanthin methyl ethers and neo-β-carotene U (4 mg.)
2	interzone
15	orange: β-carotene (7 mg.)
2	interzone
30	*cis*-β-carotenes (2 mg.)

Each of the main zones was rechromatographed.

Dimethoxy-β-carotene.—This zone was eluted and crystallized as mentioned for isocryptoxanthin (see below), yield 3 mg., m.p. 152°. The spectrum was identical with β-carotene, $E^{\text{mol.}}_{1\text{ cm.}}$ 13.4 × 10^4 in hexane at $\lambda_{\max}$ (450–451 mμ). When partitioned between hexane and 95% methanol,

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(12a) *Arch. Biochem. Biophys.*, in press (1953).

(13) A. L. LeRosen, *Ind. Eng. Chem., Anal. Ed.*, **14**, 165 (1942).

(14) Samples containing some *cis* forms can also be used, although the yields then somewhat decrease.

(15) For a photomicrograph of cryptoxanthin *cf.* L. Zechmeister, "Carotinoide," Springer, Berlin, 1934, p. 290.

the compound is essentially epiphasic but less so than is β-carotene.

Anal. Calcd. for $C_{40}H_{54}(OCH_3)_2$: C, 84.50; H, 10.13; OCH_3, 10.37. Found: C, 84.33; H, 10.02; OCH_3, 9.45.

Isocryptoxanthin Methyl Ether.—The 60-mm. zone of the chromatogram was eluted, transferred into hexane and completely evaporated *in vacuo*. This residue should be powdery (if oily, the chromatographic purification should be repeated). It was dissolved in 10 drops of benzene and crystallized by the addition of methanol as described for the free alcohol; yield 9 mg., m.p. 133–135°. The color of the crystals is closely similar to that of isocryptoxanthin; however, the forms are quite different. The methyl ether is markedly more soluble in hexane than is the free alcohol. In the partition test it is epiphasic but less so than β-carotene.

Anal. Calcd. for $C_{40}H_{55}OCH_3$: C, 86.86; H, 10.31; OCH_3, 5.46. Found: C, 86.03, 86.11; H, 10.60, 10.09; OCH_3, 5.05.

When developed with hexane and 3% acetone the methyl ether appears below isocryptoxanthin but above the β-carotene zone. The spectral curves of isocryptoxanthin and its methyl ether are practically identical.

The same methyl ether was obtained by treating 8.6 mg. of isocryptoxanthin with 0.5 ml. of *t*-amyl alcohol in toluene and metallic potassium.[16] The product did not separate on the column from cryptoxanthin methyl ether. When, however, a mixture of the two compounds was treated with acid chloroform (which leaves the cryptoxanthin methyl ether unchanged) a chromatographic separation became possible.

β-Carotene was crystallized and identified by mixed chromatogram tests and spectroscopic comparison with an authentic sample *ex* carrots; yields 2 mg. from 35 mg. of dehydro-β-carotene (complex cleaved with water) or 6 mg. from 60 mg. (methanol experiment). The following analyses refer to samples obtained by these two routes.

Anal. Calcd. for $C_{40}H_{56}$: C, 89.48; H, 10.52. Found: C, 89.32, 89.35; H, 10.76, 10.37.

Reconversion of Isocryptoxanthin to Dehydro-β-carotene.—To a solution of 4 mg. of isocryptoxanthin (or its methyl ether) in 10 ml. of chloroform (C.P.) 4 drops of chloroform saturated with HCl gas was added. The color deepened within a few seconds. After standing in diffuse daylight for 25 min. the solution was deacidified by shaking with 10 ml. of 5% sodium bicarbonate. The dried filtrate was evaporated *in vacuo*, the red, powdery residue was dissolved in about 15 ml. of hexane, adsorbed on a 20 × 3.8 cm. lime-celite column and developed with hexane and 6% acetone:

1	brownish
25	interzone
15	red: all-*trans*-dehydro-β-carotene
3	interzone
69	four orange to red zones (with interzones): *cis*-dehydro-β-carotenes
60	interzone, with traces of pigment
5	yellow: β-carotene
22	empty section

The yields of dehydro-β-carotene (including stereoisomers) and of β-carotene amounted to 70% and 5%, respectively, while 25% of the starting material was unaccounted for. The corresponding fractions from several of these experiments were combined. The dehydro-β-carotene (and isomers) were crystallized and identified by crystal form, mixed chromatogram tests, spectroscopic data and behavior in the iodine catalysis experiment.

When dimethoxy-β-carotene was submitted to an acid-chloroform treatment, a color change similar to that mentioned was observed. However, chromatographic resolution of the product gave, besides dehydro-β-carotene, other pigments as yet unidentified, among them one with a much stronger chromophore than that of dehydro-β-carotene (visually observed maxima in hexane, 519, 487, 460 mμ).

Acknowledgment.—The authors wish to thank Dr. A. J. Haagen-Smit, Mr. G. Swinehart and Dr. A. Elek for microanalyses.

PASADENA, CALIFORNIA

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[16] P. Karrer and T. Takahashi, *Helv. Chim. Acta.*, **16**, 1163 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

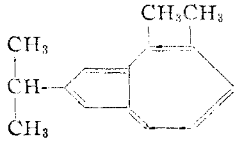
Azulenes. IV. 4,5-Substituted Azulenes[1]

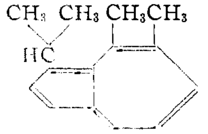
BY WERNER HERZ AND JOHN L. ROGERS

RECEIVED APRIL 13, 1953

4,5-Dimethyl-, 2,4,5-trimethyl- and 4,5-dimethyl-2-isopropylazulene, the latter a "regularly" constituted isoprenoid azulene, have been synthesized.

Although a considerable number of azulenes has been prepared in recent years,[2] the literature does not describe azulenes containing two substituents in the 4- and 5-positions of the basic azulene nucleus.[3] Two compounds with such substituents, 4,5-dimethyl-2-isopropylazulene (I) and 4,5-dimethyl-3-isopropylazulene (II), are of considerable interest. They may be thought of as consisting of three isoprene units linked together in "regular," or head-to-tail, fashion. It is therefore possible that either, or both, represents an azulene which occurs in nature or may appear among the dehydrogenation products of sesquiterpenes of unknown structure.[4]


I


II

The present communication reports the synthesis of I and two simpler homologs in an effort to assess the influence of substitution on the physical properties of the azulene system. Efforts dealing with the preparation of II are in progress.

The synthesis of the desired azulenes followed standard paths and is outlined in the flow sheet. Difficulties encountered when attempts were made to reduce 2-isopropyl-4,5-dimethylindanone to the corresponding indan by the Clemmensen or Wolff–Kishner reduction were circumvented as indicated. Lithium aluminum hydride reduction of the indanone yielded an alcohol which was dehydrated with

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[1] Paper III of this series, W. Herz, THIS JOURNAL, **75**, 73 (1953).

[2] M. Gordon, *Chem. Revs.*, **50**, 127 (1952).

[3] 4,5-Tetramethyleneazulene is listed in ref. 2; however, no details regarding its preparation and properties have been published.

[4] A. J. Haagen-Smit, Azulenes, "Fortschritte der Chemie Organischer Naturstoffe," Vol. 5, Springer Verlag, Vienna, 1948, p. 40.