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]

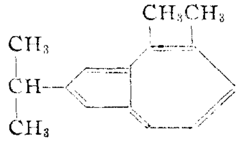
Azulenes. IV. 4,5-Substituted Azulenes[1]

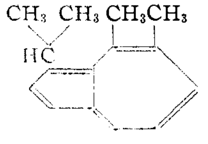
BY WERNER HERZ AND JOHN L. ROGERS

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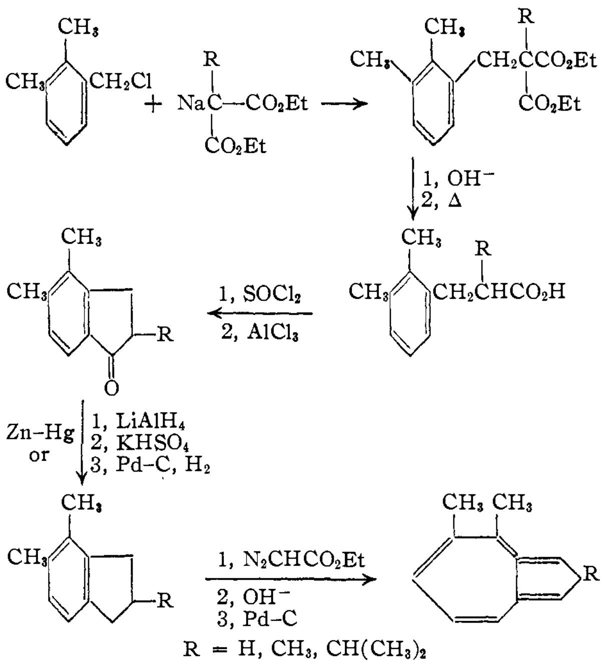
[1] Paper III of this series, W. Herz, THIS JOURNAL, **75**, 73 (1953).

[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.



potassium acid sulfate. The resulting indene was hydrogenated catalytically.

Treatment of the indans with diazoacetic ester followed by hydrolysis and simultaneous decarboxylation and dehydrogenation gave the desired azulenes. In accordance with the rules formulated by Plattner[5] 4,5-dimethylazulene is a blue oil which exhibits a violet tinge in solution.[6] The spectra of 2,4,5-trimethylazulene and of 2-isopropyl-4,5-dimethylazulene are shifted toward shorter wave lengths so that these azulenes are violet blue, in agreement with the previously observed effect of substituents in the 2-position. The strongest bands in the visible spectra of these compounds are found at 674, 612, 570 and 559 mμ.

Ultraviolet spectra of the newly-synthesized azulenes are given in Fig. 1.

Acknowledgment.—This work was supported in part by a grant from the Research Council of the Florida State University.

Experimental[8]

Hemimellityl Chloride.—This chloride was prepared from benzylmagnesium chloride by the sequence of reactions described by Smith and Spillane.[9] Although a considerable amount of the compound was required, it was found undesirable to carry out the Tiffeneau rearrangement of benzylmagnesium chloride and 2-methylbenzylmagnesium chloride in quantities larger than recommended by these authors. Nevertheless, the yields on the Grignard reactions were erratic. This resulted in a disappointing over-all yield of only 10–12%.

(2,3-Dimethylphenyl)-propionic Acid.—To a suspension of 35 g. of powdered sodium in 750 ml. of dry xylene was added dropwise 280 g. of redistilled malonic ester. The mixture was refluxed until dissolution of sodium was complete and 225 g. of hemimellityl chloride was added dropwise. After eight hours at reflux the mixture was acidified with acetic acid, diluted with water and extracted with ether. The dried ether extracts were distilled *in vacuo*. Following a forerun of malonic ester there was collected 255 g. (62%) of condensation product, b.p. 148–160° (2.7 mm.) which was hydrolyzed without further purification. A higher-boiling fraction (16 g.), boiling largely in the range 215–225° (4.5 mm.), solidified on stirring with a little ethanol. Two recrystallizations from ethanol yielded colorless needles, m.p. 84.5°. Analysis indicated that this material was the dialkylated ester, diethyl di-(2,3-dimethylbenzyl)-malonate.

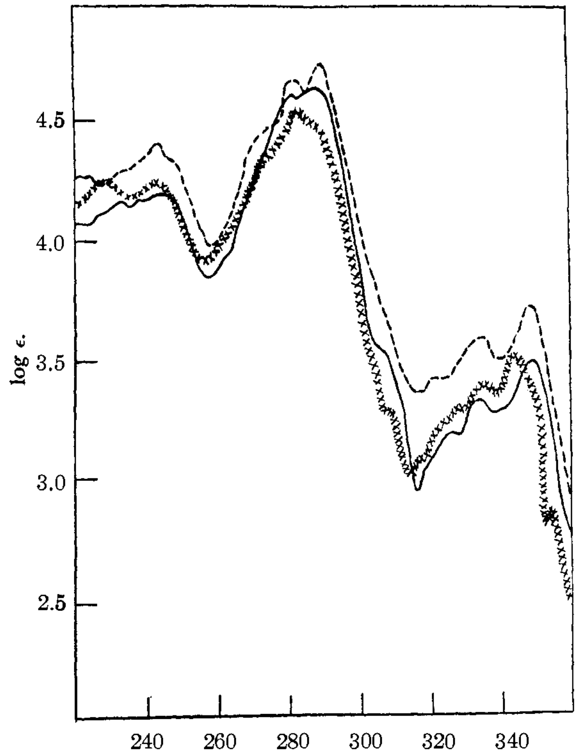


Fig. 1.—Ultraviolet spectra in isoöctane; x x x, 4,5-dimethylazulene; —, 2,4,5-trimethylazulene; - - -, 2-isopropyl-4,5-dimethylazulene.

Anal. Calcd. for $C_{25}H_{32}O_4$: C, 75.73; H, 8.11. Found: C, 75.68; H, 8.29.

The crude monoalkylated ester, wt. 136 g., was saponified by refluxing overnight with 70 g. of potassium hydroxide, 70 ml. of water and 200 ml. of ethanol. Water was added, the alcohol was removed by distillation and the residue was extracted with ether and acidified. The solid was filtered, dried and decarboxylated by distillation at reduced pressure. The acid was collected at 140–155° (2 mm.) and solidified on cooling. The yield was 77 g. (89%). Repeated recrystallization from ligroin afforded colorless needles, m.p. 116.5°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.27; H, 7.79.

The anilide was prepared in the usual way[10] and melted at 132–133° after recrystallization from ethanol–water.

Anal. Calcd. for $C_{17}H_{19}NO$: N, 5.53. Found: N, 5.46.

α-Methyl-(2,3-dimethylphenyl)-propionic Acid.—Condensation of diethyl sodiomethylmalonate, prepared from 191 g. of methylmalonic ester and 26.4 g. of powdered sodium in xylene, with 154 g. of hemimellityl chloride resulted in 192 g. (66%) of crude product, b.p. 140–180° (5 mm.). Hydrolysis and decarboxylation in the manner described

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[5] Pl. A. Plattner, *Helv. Chim. Acta*, **24**, 283E (1941).

[6] Measurements on a Beckman instrument indicate the presence of bands at 695, 630, 605, 578, 558 and 548 mμ. These values are in good agreement with the maxima of azulene and of 5,8-dimethyl- and 5-methyl-8-isopropylazulene[7] as predicted by theory,[5] but differ considerably from the figures given in ref. 2 for 4,5-tetramethyleneazulene which would be expected to absorb at the same wave lengths.

[7] H. Pommer, *Ann.*, **579**, 47 (1953).

[8] All melting points are uncorrected. Analyses by Clark Microanalytical Laboratory, Urbana, Ill., and Drs. Weiler and Strauss, Oxford, England.

[9] L. I. Smith and L. J. Spillane, THIS JOURNAL, **62**, 2639 (1940).

[10] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 158.

above furnished 106 g. (84%) of the desired acid, b.p. 140–155° (2.5 mm.). It did not solidify on cooling. The analytical sample boiled at 144–146° (2.5 mm.), $n^{22}\mathrm{D}$ 1.5221.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.98; H, 8.39. Found: C, 75.27; H, 8.17.

The anilide was recrystallized several times from ethanol–water and melted at 123.5°.

Anal. Calcd. for $C_{18}H_{21}NO$: N, 5.24. Found: N, 5.03.

α-Isopropyl-(2,3-dimethylphenyl)-propionic Acid.—In a similar way 222 g. of diethyl isopropylmalonate was converted to the sodium salt and condensed with 154 g. of hemimellityl chloride. The crude product, wt. 170 g. (53%), b.p. 130–175° (4 mm.), was hydrolyzed and decarboxylated, yielding 92 g. (85%) of the desired acid, b.p. 183–190° (9–10 mm.), which crystallized on cooling. The analytical sample was recrystallized from petroleum ether, m.p. 94.5–95.5°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.57; H, 9.16.

The anilide was recrystallized from ethanol, m.p. 143–144°.

Anal. Calcd. for $C_{20}H_{25}NO$: N, 4.73. Found: N, 4.42.

4,5-Dimethylindanone.—A mixture of 76 g. of the acid and 75 g. of thionyl chloride was heated on the steam-bath for two hours, allowed to stand overnight and distilled. The resulting acid chloride, b.p. 100–102° (2 mm.), wt. 79.5 g., was cyclized by slow addition to 60 g. of aluminum chloride in 350 ml. of dry thiophene-free benzene. The cherry-red solution was decomposed the next day and worked up in the usual manner. Difficulty was caused by solidification of the product, b.p. 115–130° (2.5 mm.), in the side-arm and condenser of the distilling apparatus, which necessitated considerable superheating of the distillate. The yield was 56 g. (82%), m.p. 99° after recrystallization from petroleum ether.

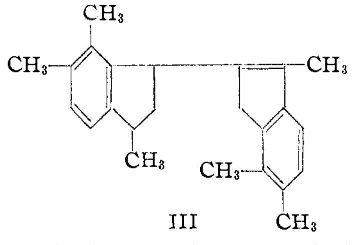
Anal. Calcd. for $C_{11}H_{12}O_2$: C, 82.46; H, 7.55. Found: C, 82.47; H, 7.47.

The dinitrophenylhydrazone was prepared in the usual way[11] and melted at 287–288° with gas evolution. Ethyl acetate served as the solvent for recrystallization.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: N, 16.46. Found: N, 16.20.

An attempt was made to prepare 1,4,5-trimethylindene by gradually adding 44.5 g. of 4,5-dimethylindanone in powdered form to methylmagnesium iodide prepared from 50 g. of methyl iodide and 9 g. of magnesium in 300 ml. of ether. The mixture was decomposed with ice and dilute sulfuric acid and worked up in the usual manner. On distillation from freshly fused potassium acid sulfate there was obtained not the expected indene, but 41 g. of a viscous red fraction boiling in the range 115–125° (4 mm.), which became colorless when dissolved in organic solvents. A portion (8 g.) of the oil was taken up in 150 ml. of hot ethanol and allowed to cool. The material which oiled out was dried in a high vacuum and then evaporatively distilled. The distillate crystallized slowly on standing, m.p. 80–81°. The analysis indicated that condensation of the indene to III had occurred, presumably under the influence of acid.

Anal. Calcd. for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 90.91; H, 8.89.



III

2,4,5-Trimethylindanone.—Cyclization of 107.5 g. of acid chloride, b.p. 115–120° (4.5 mm.), obtained from 103 g. of the corresponding acid, yielded 81 g. (87%) of indanone, b.p. 111–119° (2.5 mm.), which solidified on standing. It was recrystallized from petroleum ether and melted at 47.5–48°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.78; H, 8.60. Found: C, 82.88; H, 8.62.

The dinitrophenylhydrazone did not melt sharply, even after several recrystallizations from ethyl acetate, possibly due to the formation of stereoisomers. The product was dissolved in benzene and chromatographed over alumina. Recrystallization of the residue from ethyl acetate gave crystals which were powdered and then exhibited a sharp melting point at 225°.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: N, 15.85. Found: N, 15.94.

2-Isopropyl-4,5-dimethylindanone.—The acid chloride, wt. 133 g., b.p. 130–135° (5 mm.), obtained from 140 g. of the corresponding acid, was cyclized in the same manner, yielding 104 g. (81%) of indanone, b.p. 138–145° (4.5 mm.), which crystallized on standing. After recrystallization from petroleum ether it melted at 53–54°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.11; H, 8.97. Found: C, 83.77; H, 8.93.

The dinitrophenylhydrazone melted at 228–229°.

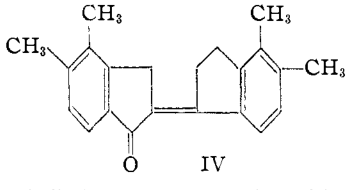
Anal. Calcd. for $C_{20}H_{22}N_4O_4$: N, 14.69. Found: N, 14.70.

4,5-Dimethylindan.—Reduction of 55 g. of 4,5-dimethylindanone with 200 g. of amalgamated zinc was carried out in the manner previously described.[12] On cooling the separation of a small amount of yellow crystalline material in the organic layer was noted. It was removed by filtration from the ether extract of the indan in which it was only partially soluble. Concentration of the ether extract and cooling yielded additional solid. The liquid fraction was distilled *in vacuo* and 37 g. (74%) of indan, b.p. 65–68° (2.3 mm.) was collected. The analytical sample boiled at 60–62° (1.5 mm.), $n^{23}\mathrm{D}$ 1.5367.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.36; H, 9.65. Found: C, 90.59; H, 9.58.

The solid, wt. 4.1 g., was recrystallized several times from ethanol. The long yellow needles decomposed at 221–222° (previous darkening above 210°). A solution in chloroform absorbed bromine with the formation of a yellow-orange precipitate. Analysis and chemical behavior indicated that the yellow solid was 2-[1-(4,5-dimethylindanylidene)]-4,5-dimethylindanone (IV). The formation of an analogous compound on treatment of indanone with sulfuric acid has been reported.[13]

Anal. Calcd. for $C_{22}H_{22}O$: C, 87.34; H, 7.33. Found: C, 87.60; H, 7.32.



IV

2,4,5-Trimethylindan.—The reduction of 78 g. of 2,4,5-trimethylindanone proceeded normally and gave 42 g. of product, b.p. 67–70° (2 mm.), $n^{25}\mathrm{D}$ 1.5282, and 15 g. of a fraction boiling in the range 71–83° (2 mm.), presumably partially reduced material.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.95; H, 10.07. Found: C, 89.78; H, 9.92.

2-Isopropyl-4,5-dimethyl-1-indanol and 2-Isopropyl-4,5-dimethylindene.—Clemmensen reduction of 2-isopropyl-4,5-dimethylindanone resulted in material which boiled over a considerable range. Analysis and chemical behavior of the lowest-boiling fraction, b.p. 100–112° (4 mm.), indicated that it consisted largely of the desired indan, but the yield was unsatisfactory. Hence the following procedure was adopted. A solution of 86 g. of the indanone in 500 ml. of dry ether was added dropwise, with stirring, to a slurry of 12 g. of lithium aluminum hydride in 800 ml. of dry ether. The reaction was worked up in the usual manner. Removal of the ether on the steam-bath yielded a residue, wt. 82 g., which crystallized on standing. A portion of the colorless

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(11) Ref. 10, p. 171.

(12) W. Herz, THIS JOURNAL, **73**, 4923 (1951).

(13) F. S. Kipping, *J. Chem. Soc.*, **65**, 480 (1894).

material was recrystallized several times from low-boiling petroleum ether and then melted at 120.5–121°.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.46; H, 9.27. Found: C, 82.43; H, 9.47.

The remainder of the crude product was transferred to a distilling flask and distilled from freshly fused potassium acid sulfate. The fraction boiling at 120–130° (4–5 mm.) was collected, wt. 54 g. (70%). The analytical sample boiled at 89–90° (0.7 mm.), n^{26}_{D} 1.5495.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.27; H, 9.73. Found: C, 90.21; H, 9.58.

2-Isopropyl-4,5-dimethylindan.—A solution of 8.9 g. of the above indene in 70 ml. of ethanol was reduced with 5% palladium–charcoal at 2–3 atmospheres until hydrogen uptake ceased. Removal of solvent followed by fractional distillation *in vacuo* yielded 6.3 g. of the indan, b.p. 102–105° (3 mm.). The analytical sample boiled at 95–96° (1.5 mm.), n^{24}_{D} 1.5180.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.25; H, 10.96.

4,5-Dimethylazulene.—Reaction of 36 g. of 4,5-dimethylindan with seven 8-g. portions of ethyl diazoacetate in the manner previously described[9] resulted in recovery of 19 g. of the crude indan and isolation of 37 g. of highly colored ester, b.p. 130–180° (2 mm.). This was saponified by refluxing with 140 ml. of ethanol, 30 ml. of water and 20 g. of potassium hydroxide. From the acid fraction was obtained 12.5 g. of green viscous material, b.p. 165–185° (2.5 mm.) which was dehydrogenated and decarboxylated by mixing with 2 g. of 10% palladium-on-charcoal and distilling over an open flame. The blue product was fractionated at reduced pressure, about 1.5 ml. of material boiling in the range 110–160° (1.7 mm.) being collected. The forerun and the residue were combined and dehydrogenated once more. This resulted in an additional 0.6 ml. of the crude azulene. The azulene was dissolved in 25 ml. of ethanol and mixed with a solution of 2 g. of trinitrobenzene in 75 ml. of warm ethanol. On cooling 1.25 g. of complex separated. Chromatography over alumina, eluent cyclohexane–benzene (3:1), resulted in 0.29 g. of blue dimethylazulene, b.p. 105–120° (1.5 mm.).

The trinitrobenzene complex, violet-black needles from ethanol, was recrystallized twice and melted at 157.5°.

Anal. Calcd. for $C_{18}H_{15}N_3O_6$: C, 58.54; H, 4.09. Found: C, 59.25; H, 4.39.

2,4,5-Trimethylazulene.—In a similar way, 42 g. of 2,4,5-trimethylindan, after treatment with seven 8-g. portions of diazoacetic ester, yielded 32 g. of deeply colored ester, b.p. 130–180° (1.5 mm.), and 24 g. of crude starting material. On saponification there was obtained 13.2 g. of greenish viscous acid, b.p. 150–175° (1.5 mm.) which, when subjected to two treatments with 10% palladium-on-charcoal, afforded 5.3 ml. of a crude azulene, b.p. 105–160° (2.5 mm.). This was dissolved in 50 ml. of ethanol and treated with a solution of 3 g. of trinitrobenzene in 100 ml. of warm ethanol. The complex, wt. 1.95 g., was decomposed by chromatography in the usual way. The violet-blue trimethylazulene, wt. 0.78 g., boiled at 110–120° (1.3 mm.).

The trinitrobenzoate, violet-black needles, was recrystallized twice from ethanol and melted at 160.5–161.5°.

Anal. Calcd. for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47. Found: C, 60.12; H, 4.66.

The trinitrotoluene complex, violet-black needles from ethanol, melted at 86–87°.

Anal. Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82. Found: C, 60.52; H, 4.89.

2-Isopropyl-4,5-dimethylazulene.—Treatment of 50 g. of 2-isopropyl-4,5-dimethylindan with seven 10-g. portions of diazoacetic ester yielded 49.5 g. of crude product, b.p. 125–170° (1.5 mm.) and 19 g. of recovered material. The yield of acid, b.p. 170–190° (2 mm.), after saponification with 25 g. of potassium hydroxide and 200 ml. of 80% ethanol was 20 g. On treatment with 3 g. of palladium–charcoal there was obtained 8.8 ml. of distillate, b.p. 100–160° (1.5 mm.), which was dissolved in 50 ml. of ethanol and added to a solution of 3 g. of trinitrobenzene in 100 ml. of warm ethanol. Decomposition of the complex, wt. 3.3 g., by chromatography over alumina followed by distillation gave 1.13 g. of violet-blue azulene, b.p. 115–125° (1 mm.).

The trinitrobenzene complex, violet-black needles, was recrystallized several times from ethanol and then melted at 136.5–137°.

Anal. Calcd. for $C_{21}H_{21}N_3O_6$: C, 61.34; H, 5.14; N, 10.24. Found: C, 61.50; H, 5.41; N, 9.90.

The picrate, black needles, was recrystallized from ethanol and melted at 117–118°.

Anal. Calcd. for $C_{21}H_{21}N_3O_7$: C, 59.00; H, 4.96. Found: C, 59.13; H, 5.02.

The trinitrotoluene complex was recrystallized from ethanol, m.p. 59.5–61°.

Anal. Calcd. for $C_{22}H_{23}N_3O_6$: C, 62.11; H, 5.45. Found: C, 62.25; H, 5.47.

TALLAHASSEE, FLORIDA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, BLOCKSON CHEMICAL COMPANY]

Direct Reduction of Aldoses and Ketoses by Raney Nickel

BY J. V. KARABINOS AND A. T. BALLUN

RECEIVED MAY 7, 1953

Aldoses and ketoses can be effectively reduced to the corresponding polyhydric alcohols by refluxing with Raney nickel aqueous alcohol. This affords a convenient laboratory preparative method for the polyols.

In connection with reductive desulfurization of thiazolidine derivatives[1] of aldoses and cysteine, it was found that good yields of the polyhydric alcohols corresponding to the original sugar could be obtained with Raney nickel.[2] In addition, the earlier reported reduction of aldonic acid thiolesters to the corresponding polyols by Jeger and co-workers[3] prompted us to investigate the direct conversion of aldoses and ketoses to the polyols from a preparative standpoint. Such a method would eliminate the use of pressure equipment in the customary catalytic methods and would also eliminate the troublesome removal of inorganic ions as in the sodium amalgam reduction of aldoses and ketoses. When D-mannose and D-galactose were refluxed with a large excess of Raney nickel in 70% ethanol, D-mannitol and D-galactitol were obtained in high yield and in good purity. Subsequent quantitative investigation of this reaction, by measurement of loss in reducing power using "aged" Raney nickel, indicated that the rate of conversion varied somewhat with different types of carbohydrates.

It is obvious that the above described method offers certain advantages in the reduction of radio-

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[1] See M. P. Schubert, *J. Biol. Chem.*, **130**, 601 (1939); G. Ägren, *Enzymologia*, **9**, 321 (1941).

[2] These data were reported by Irene Vadopalaite and J. V. Karabinos at the Illinois Academy of Sciences Meeting, Macomb, Illinois, May 9, 1953.

[3] O. Jeger, J. Norymberski, S. Szpilfogel and V. Prelog, *Helv. Chim. Acta*, **29**, 684 (1946).