[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Azulene. IV. 1-Benzylazulene[1,2,3]

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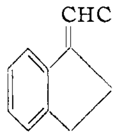
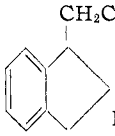
1-Benzylazulene, a new azulene derivative, has been synthesized from 1-indanone. Ring enlargement of the intermediate 1-benzylindane with ethyl diazoacetate and the final dehydrogenation went in low yield. No 2-benzylazulene was obtained from an attempted thermal rearrangement of 1-benzylazulene.

Although a number of 1-substituted azulene compounds have been prepared, no reference to 1-benzylazulene was found in the literature. As only a small amount of this substance was desired, what appeared to be the quickest route (1-indanone → 1-benzylindane → 1-benzyltetrahydroazuloic acid → 1-benzylazulene) was used.

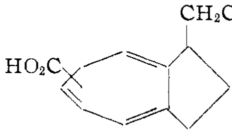
1-Indanone was converted to 1-benzylideneindane (I) in 44% yield by a modification of the Barbier method wherein the ketone and benzyl chloride were added simultaneously to the magnesium. The relative simplicity of the procedure made it preferable to the high dilution Grignard technique which is reported[4] to give a 65% yield. Catalytic hydrogenation of 1-benzylideneindane gave 1-benzylindane (II) in good yield. No attempt was made to separate the mixture of esters and, subsequently, acids obtained from the reaction of ethyl diazoacetate and 1-benzylindane as it was felt that the later separation of azulenic from non-azulenic compounds would be considerably easier. Thus, the yields of crude ester (67%), and corresponding acid (47%) gave no indication of the amount of the desired product (III) present.



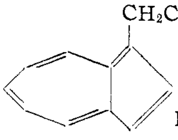
I



II



III



IV

Several examples of the rearrangement of 1-substituted to 2-substituted azulene by heat and in presence of palladium catalysts have been reported.[5] In the work with 1-phenylazulene[5a] it was shown that at lower temperatures (200–220°) and with sulfur as the dehydrogenation reagent no rearrangement occurred. In this same study a method of dehydrogenation with palladium–charcoal wherein the products were removed from the catalyst by rapid distillation was shown to give a ratio of 10:1 of non-rearranged to rearranged product. As it was felt that there was some chance that 1-benzylazulene would rearrange, both of these methods were tried.

As decarboxylation of the carboxylic acid derivatives at 220° was not satisfactory, it was necessary to remove carboxyl group with copper powder and quinoline before attempting the dehydrogenation with sulfur. The yield of 1-benzylazulene (IV) was low (0.79%). Direct dehydrogenation of the acid, with simultaneous decarboxylation by distillation from palladium–charcoal, also gave less than 1% yields. These low yields were not unexpected because the starting material, as mentioned above, was quite impure and liquid phase dehydrogenations frequently give low yields of azulenes.

Under the conditions which were found to give the best yields of 2-phenylazulene from 1-phenylazulene,[5a] no evidence was found for the rearrangement of 1-benzylazulene to 2-benzylazulene. A small amount of azulene was formed and also a minute quantity of material which was not identified. The visible absorption spectrum of this substance most nearly resembled that expected for 1,3-dibenzylazulene.

Experimental[6]

1-Benzylindane (II).—1-Benzylideneindane (I)[4] was prepared in 44% yield by a Barbier reaction procedure adapted from the modification of Davies and Kipping.[7] Hydrogenation of 330 g. (1.5 moles) of 1-benzylideneindane dissolved in 300 ml. of absolute alcohol over 10 g. of a 1% palladium–strontium carbonate catalyst at 2–3 atm. required 3.5 hours and 92% of the theoretical quantity of hydrogen was taken up. The dark viscous liquid remaining after removal of the catalyst and solvent was distilled and the fractions boiling between 175 and 187° at 17–20 mm. (n^{25}_{D} 1.5796 to 1.5799) were combined. The total yield was 316.5 g. (95%). The analytical sample (b.p. 165–165.5° at 10 mm., n^{25}_{D} 1.580, d^{20}_{4} 1.033) was a colorless liquid which turned yellow after several days.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.25; H, 7.75; M_D, 66.70. Found: C, 92.27; H, 8.01; M_D, 67.10.

Reaction of Ethyl Diazoacetate with 1-Benzylindane.—Two hundred and seventy-nine grams (1.25 moles) of once-distilled 1-benzylindane was subjected to six successive treatments with ethyl diazoacetate as described by Herz[8] for similar reactions. For each run 30 g. (28 ml., 0.26 mole) of the diazoacetic ester was used. In the separation of starting material from products, the reaction mixture was distilled until the vapor temperature reached about 190° at water aspirator (15–20 mm.) pressure. The final treatment yielded 153 g. (55%) of recovered crude 1-benzylindane. The accumulated still residues (240.5 g.) were fractionally distilled to give 119 g. (67% net yield) of material boiling at 162–192° at 0.2–0.3 mm. This fraction, a viscous dark green oil with the final portion a blue color, was heated under reflux for two hours with 200 ml. of 95% ethanol, 80 ml. of water and 40 g. of potassium hydroxide. About 400 ml. of

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(1) From the Ph.D. thesis of Edward J. Cowles.

(2) For paper III in this series see A. G. Anderson, Jr., J. A. Nelson and J. J. Tazuma, THIS JOURNAL, **75**, 4980 (1953).

(3) This work was supported in part by a grant from the Research Corporation.

(4) A. A. Plentl and M. T. Bogert, THIS JOURNAL, **63**, 989 (1941).

(5) (a) Pl. A. Plattner, A. Fürst, M. Gordon and K. Zimmerman, *Helv. Chim. Acta*, **30**, 1320 (1947); (b) W. Herz, THIS JOURNAL, **75**, 73 (1953); (c) T. Ukita, H. Watanabe and M. Miyazaki, *ibid.*, **76**, 4585 (1954).

(6) Melting points are not corrected.

(7) A. I. C. Davies and F. S. Kipping, *Trans. Chem. Soc.*, **99**, 296 (1911).

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

water was then added and the alcohol removed under reduced pressure. The cooled solution was extracted with ether, acidified with hydrochloric acid, and the oil which separated extracted with ether. The crude acidic product (75 g., 70%) obtained from the dried extracts was a viscous, greenish-black oil.

1-Benzylazulene. (IV). A. Dehydrogenation of 1-Benzyltetrahydroazulene with Sulfur.—The crude acid product (5 g., 0.019 mole) from the above procedure, 15.3 g. (14 ml.) of quinoline and 1 g. of copper powder were heated in a fused salt-bath at 210–220° as described by Shepard, Winslow and Johnson[9] until the evolution of gas ceased (15–20 minutes). The quinoline was removed by distillation and an ether solution of the cooled residue extracted with two 15-ml. portions of 6 *N* sulfuric acid, one 20-ml. portion of water, three 50-ml. portions of saturated salt solution, and then dried over calcium chloride. Removal of the solvent left 1.4 g. (34%) of a brown oil.

A tube containing a mixture of 0.44 g. (2 millimoles) of the brown oil and 0.13 g. of flowers of sulfur was placed in a fused salt-bath preheated to 180° and the bath temperature raised to 220° over a period of 20 minutes, at which time the evolution of hydrogen sulfide had ceased. The cooled residue was broken up and dissolved by treatment with a number of portions of boiling benzene. Chromatography of the concentrated benzene solution on alumina with benzene as the eluent afforded a separation of a light brown zone from a dark brown, more tightly adsorbed, fraction. The residue from the first eluate fraction was taken up in petroleum ether–benzene and rechromatographed with petroleum ether as the solvent. A small blue band was eluted rapidly and the residue from this rechromatographed (petroleum ether) to give a blue oil which could not be crystallized. A colorimetric analysis[10] of a petroleum ether solution of the oil indicated a yield of 3.4 mg. (0.79%) of 1-benzylazulene.

The crude blue product (10.5 mg.) from the total 1.4 g. of brown oil was treated with 20 ml. of a saturated solution of 1,3,5-trinitrobenzene in 95% ethanol, the solution concentrated to a volume of about 1 ml. and left in a refrigerator (10°) overnight. The precipitate, a mixture of trinitrobenzene and a brown solid, was washed by decantation with two 0.5-ml. portions of 95% ethanol and dried between filter papers. Extraction with 30–60° petroleum ether gave a blue solution and a residue of trinitrobenzene. Chromatography of the concentrated extracts on alumina with petroleum ether afforded a blue solid which crystallized readily (m.p. 70–75°). Five recrystallizations from petroleum ether by sudden chilling (Dry Ice-acetone-bath) of a saturated solution raised the melting point to 75–76.6° and reduced the amount of product to 2–3 mg.

B. Dehydrogenation of Crude 1-Benzyltetrahydroazuloic Acid with Palladium–Charcoal.[5a]—In a 10-ml. one-piece distilling apparatus was placed 100 mg. of a 10% palladium–charcoal[11] catalyst and 1 g. (3.76 millimoles) of the crude acid prepared above dissolved in 2.4 ml. of chloroform. After careful removal of the solvent by distillation, the residual material was distilled rapidly. When the vapors changed from a blue-green to a yellowish color, the flask was cooled, a second portion of catalyst and acid (in chloroform) added, and the process repeated. The combined distillates from ten such operations, plus the residue from the chloroform distillates, were taken up in petroleum ether and this solution washed with 1 *N* ammonium hydroxide and saturated salt solutions. Chromatography of the concentrated organic solution on alumina with petroleum ether as the eluent gave a blue band which was separated and rechromatographed twice more. The third chromatogram showed four bands (violet-blue, blue-green, blue, yellow-green) which were not sharply defined. Rechromatography of these gave four well defined fractions. Only the first (violet-blue) and third (blue) bands contained sufficient material to characterize. Colorimetric analysis[10] of petroleum ether solutions of these showed the violet-blue fraction to contain 9.5 mg. (0.2%) of azulene and the blue fraction to contain 77.5 mg. (0.95%) of 1-benzylazulene.

Evaporation of the solvent from the blue fraction left a partially crystalline material which was fractionally sublimed (*ca.* 0.05 mm. and 55°), the middle fraction resublimed and then recrystallized as described above (A) three times from petroleum ether. The final product of 1-benzylazulene, m.p. 72–74°, amounted to 19.5 mg. (0.24%) of blue needles. A petroleum ether solution showed clearly defined absorption maxima in mμ (log ϵ) at 238 (4.28), 280 (4.76), 285 (4.74), 290 (4.62), 331 (3.43), 338 (3.50), 346 (3.72), 362 (3.52), 605 (ϵ 327), 660 (ϵ 284), 730 (ϵ 115) and points of inflection (shoulders) at 298 (3.80), 325 (319), 562 (ϵ 239), 585 (ϵ 282), 628 (ϵ 282) and 708 (ϵ 95). The infrared spectra of the products from (A) and (B) were identical.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.59; H, 6.66.

Attempted Thermal Rearrangement of 1-Benzylazulene.—A sealed tube containing 9 mg. (0.041 millimole) of 1-benzylazulene and filled with nitrogen was immersed in a fused salt-bath at 310–320° for 30 minutes.[12] The tube was cooled, opened, and the contents extracted with small portions of hot benzene until the solvent remained colorless. After removal of the solvent and extraction of the soluble colored portion of the residue with 30–60° petroleum ether, the concentrate from the extracts was chromatographed on a small alumina column. Elution with petroleum ether developed three bands (violet-blue, blue, greenish-blue) which were collected. The absorption spectra from the first fraction (less than 1 mg.) showed the material to be azulene. From the second fraction was obtained 4 mg. (45% recovery) of 1-benzylazulene. The amount of material in the greenish-blue fraction was extremely small, but the visible absorption spectrum of the petroleum ether solution (λ_{max} in mμ at 560, 590, 622, 640, 660 and 685) corresponded more closely to that expected for 1,3-dibenzylazulene than for 2-benzylazulene.

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[9] A. F. Shepard, N. R. Winslow and J. R. Johnson, THIS JOURNAL, **52**, 2083 (1930).

[10] It has been found possible and convenient to quantitatively determine small amounts of azulene and many of its derivatives by colorimetric methods. For blue compounds a yellow filter of ten thicknesses of Du Pont yellow cellophane (for gift wrapping) between two cover glasses was prepared to fit a Fisher Electrophotometer, AC model. A colorimetric calibration curve was determined on a pure sample of the compound.

[11] R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940).

[12] These conditions correspond to those found best for the rearrangements of 1-phenylazulene by Pl. A. Plattner, *et al.*, reference 5a.