the two zones had become separated by a 5–6 cm. clear interzone, the column was extruded and the oily *cis*-II compound (a few mg.) isolated as described for *cis*-I; $E^{\text{mol.}}_{1\text{ cm.}}$ (max. hexane) 6.53×10^4 at 385 mμ, 7.05×10^4 at *370* mμ, 2.68×10^4 at 311–312 mμ (*cis*-peak).

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[CONTRIBUTION FROM HAVEMEYER LABORATORY, COLUMBIA UNIVERSITY]

Two-Step Synthesis of Azulene

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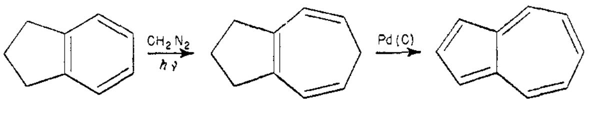
Azulene is prepared from indane by irradiating with diazomethane and dehydrogenating the resulting trimethylenetropilidene.

Among the various syntheses of azulene,[2] the most satisfactory is that of Plattner and St. Pfau[2a] as improved by Anderson and Nelson[2c] in which four steps and an over-all yield 5.8% of theory are involved. In this paper a shorter, more convenient synthesis is reported.

Application of the method of preparing tropilidenes from benzenes and diazomethane by irradiation[3] to indane yields a mixture of hydrocarbons from which crude trimethylenetropilidenes are separated by distillation. Catalytic dehydrogenation affords azulene in 18.3% of the theoretical yield or 6.7% over-all based on the amount of indane consumed. Purified with very small loss by solution in ice-cold 7.5 *M* sulfuric acid, precipitation and sublimation, the azulene had the same m.p.[2a] and absorption spectra[4,2a,5] as reported in the literature.



Experimental

Trimethylenetropilidene.—To a stirred mixture of 322 g. of indane, b.p. 72–74° at 20 mm., and 60 ml. of 50% aqueous potassium hydroxide in a 1-l. erlenmeyer flask surrounded by an ice-bath, 21 g. of nitrosomethylurea was added in several portions over the course of 1 hr. After being stirred for another hour, the yellow organic layer was separated, dried over potassium hydroxide, and transferred to a Pyrex, 500-ml., water-jacketed, round-bottom flask. The solution was then irradiated with two General Electric Reflector Sunlamps on opposite sides of the flask for 24 hr. by which time the initially rapid evolution of nitrogen had ceased and the solution was pale yellow. Distillation through a one-foot Widmer column yielded a higher boiling residue which was saved and 267 g. of indane, b.p. 72–75° at 20 mm., which was retreated with diazomethane. The second and third irradiations were performed using 267 g. and 235 g. of indane, respectively, and the same quantity of diazomethane. In each case, the higher boiling residue was separated from the recovered indane which was used for the subsequent irradiation. From the third irradiation there was recovered 189 g. of indane. The combined higher boiling residues were fractionated under nitrogen through a one-foot, helix-packed column at 20 mm. yielding 98 g. of indane, b.p. 70–75°, and 14.2 g. of a colorless liquid, b.p. 80–81°, $n^{25}\text{D}$ 1.5174.

Azulene.—The dehydrogenation apparatus was a Pyrex tube 25 cm. long and 18 mm. wide, fitted at the top with an addition funnel and at the bottom with a small side-arm flask. The tube was charged with *ca.* 5 g. of a catalyst consisting of 5% palladium-on-coconut charcoal prepared by procedure of Linstead and Thomas.[6] The column was heated electrically to 340°. The dehydrogenation was effected by adding trimethylenetropilidene dropwise at the top of the column at 20 mm. pressure. The addition was completed in about one hour. Slower addition did not affect the yield. The cooled column and the receiver were washed with pentane to dissolve all azulene. Analysis of this solution spectroscopically indicated the presence of 2.52 g. of azulene. The pentane solution was extracted with 100 ml. of ice-cold 7.5 *M* sulfuric acid and then with a 50-ml. portion of acid. The red acid solutions were extracted once with pentane and poured slowly into 200 ml. of ice-cold water in a separatory funnel. The pentane extract of the liberated azulene was dried over anhydrous potassium carbonate, concentrated in a sublimator tube by heating gently over a steam-bath, the last vapors of pentane being "poured" off. Sublimation at 0.5 mm. and about 40° yielded 2.27 g. of purple crystals, m.p. 98–99°; reported[2a] m.p. 98.5–99°. The absorption spectra of this sample in the ultraviolet, visible and infrared were identical with those reported.[4,2a,5]

Based on a total consumption of 35 g. of indane in the three irradiations, the yield of azulene (2.52 g.) was 6.7%.

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