Coupling constants were determined by standard side-banding techniques on a Varian A-60D nmr spectrometer with a Hewlett-Packard Model 200CD audio-oscillator and Model 522B electronic counter. The probe temperature was 38 ± 2°C. Recorded values are averages of at least five traces at a 50-cps sweep width (500 sec sweep time) and are believed accurate to within ±0.2 Hz. Solution concentrations were 30% (vol:vol or wt:vol) in all cases.

Solvents used were spectroquality $CHCl_3$ (shaken three times with alumina to remove ethanol), chemical grade C_6H_6 (dried over calcium hydride and distilled), chemical grade THF and $N(C_2H_5)_3$ (distilled and stored over molecular sieve), chemical grade $C_6H_5NO_2$ (stored over molecular sieve), and chemical grade CH_3OH and DMSO (dried over $CaSO_4$ and distilled).

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Synthesis of 1,3-Disubstituted Azulenes

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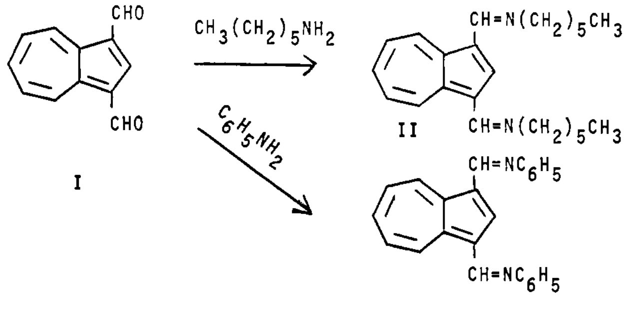
The syntheses and characterization of several 1,3-disubstituted azulene derivatives are described. Yields, melting points, elemental analysis, and infrared data are reported.

In a previous paper (*4*), we reported the preparation and thermal stabilities of poly-Schiff bases containing azulene. In connection with our investigation of azulene polymers, we now wish to report the syntheses of 1,3-substituted azulenes.

The imines II and III were prepared by the condensation of 1,3-azulenedicarboxaldehyde, I, with hexylamine and aniline, respectively. These derivatives have not been reported.

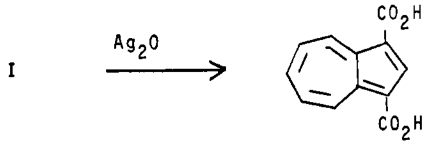


I

II

III

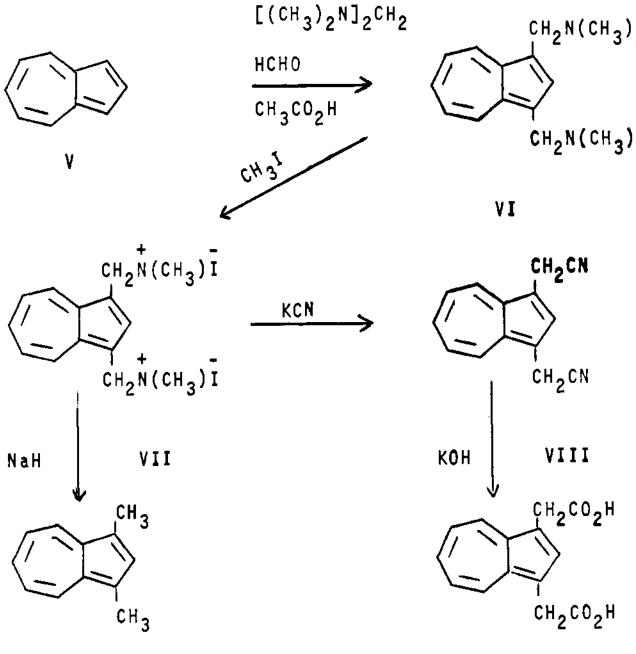
Muhlstadt and co-workers (*3*) reported a 30% yield of 1,3-azulenedicarboxylic acid, IV, by the permanganate oxidation of 1,3-azulenedicarboxaldehyde. The poor yield prompted us to investigate alternate oxidation procedures. When I was oxidized with silver oxide it gave a 90% yield of product:



IV

Azulene, V, was aminomethylated to 1,3-bis(dimethylaminomethyl)azulene, VI. The reaction was effected in glacial acetic acid with paraformaldehyde and *N*,*N*,*N*,*N*-tetramethyldiaminomethane. Treatment of the tertiary amine, VI, with excess methyl iodide gave 1,3-bis(methyltrimethylammonium iodide), VII.

The compounds 1,3-azulenediacetonitrile, VIII, and 1,3-dimethylazulene, X, were prepared by the reaction of VII with potassium cyanide and sodium hydride, respectively. Alkaline hydrolysis of VIII gave 1,3-azulenediacetic acid, IX. The azulene derivatives VIII and IX are reported for the first time.



V

VI

VII

VIII

X

IX

EXPERIMENTAL

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Model IR-9 spectrophotometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

1,3-Azulenedicarboxaldehyde, I. This compound was obtained by treating a solution of azulene in dimethylformamide with phosphorus oxychloride according to the procedure of Hafner and Bernhard (*2*).

Condensation of 1,3-Azulenedicarboxaldehyde and Hexylamine. A mixture of 1,3-azulenedicarboxaldehyde (0.9 gram, 0.005 mole), hexylamine (1.3 grams, 0.011 mole), and 25 ml of ethanol was refluxed with stirring for 8 hr. The solvent was removed under reduced pressure, and the residue was chromatographed on alumina. Elution with hexane gave 0.43 gram (24%) of azulene-1,3-bis(methyleneaminohexane), II, as a blue oil; ir (CCl_4) 1622 cm^{-1} (C=N).

Anal. Calcd for $C_{24}H_{34}N_2$: C, 82.73; H, 9.78; N, 7.99. Found: C, 82.48; H. 9.71; N. 7.78.

Condensation of 1,3-Azulenedicarboxaldehyde and Aniline. The reaction was carried out as described above using (1.0 gram, 0.011 mole) of aniline. After removal of the solvent, the residue was crystallized from hexane to give 1.1 grams (68%) of azulene-1,3-bis(methyleneaniline), III: mp 88–9°C, ir (KBr) 1615 cm^{-1} (C=N).

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.19; H, 5.43; N, 8.38. Found: C, 86.04; H, 5.58; N, 8.58.

1,3-Azulenedicarboxylic Acid, IV. To a stirred mixture of I (4.6 grams, 0.025 mole) in 300 ml of ethanol and silver nitrate (18.7 grams, 0.11 mole) in 300 ml of water was added (8.8 grams, 0.22 mole) of sodium hydroxide in 50 ml of water over a period of 15 min at 35–40°C. After 2.5 hr at this temperature, the mixture was filtered, concentrated under reduced pressure to about 300 ml, and extracted with three 50-ml portions of ether. The aqueous layer was acidified with concentrated HCl, and the precipitate was collected by filtration. The product was reprecipitated from a dilute alkaline solution using decolorizing charcoal to give 5.4 grams (90%) of IV as a red powder: mp 268°C (decomp), ir (KBr) 1643 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_8O_4$: C, 66.67; H, 3.73. Found: C, 66.74; H, 3.58.

1,3-Bis(methyltrimethylammoniumiodide)azulene, VII. 1,3-Bis(dimethylaminomethyl)azulene, VI, prepared according to the procedure of Anderson and co-workers (*1*) was treated with excess methyl iodide in ethanol and refrigerated overnight. The resultant precipitate was collected by filtration and crystallized from ethanol–ether to give a 75% yield of VII as violet needles, mp >300°C.

Anal. Calcd. for $C_{18}H_{28}I_2N_2$: C, 41.08; H, 5.36; N, 5.32. Found: C, 41.41; H. 5.68; N, 4.89.

1,3-Azulenediacetonitrile, VIII. A mixture of VII (5.3 grams, 0.01 mole), KCN (3.9 grams, 0.06 mole), and 200 ml of ethanol was refluxed for 2 hr. The solvent was removed under reduced pressure, diluted with 100 ml of water, and extracted with three 50-ml portions of methylene chloride. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated to dryness under reduced pressure. The residue was crystallized from acetonitrile–water to give 0.42 gram (20%) of VIII: mp 128–9°C; ir (Nujol) 2234 cm^{-1} (C≡N).

Anal. Calcd. for $C_{14}H_{10}N_2$: C, 81.52; H, 4.88; N, 13.60. Found: C, 81.28; H, 5.16; N, 13.77.

1,3-Azulenediacetic Acid, IX. A mixture of VII (0.41 gram, 0.002 mole), 25 ml of ethanol, and 25 ml of 2*N* KOH was refluxed for 5 hr. The reaction mixture was cooled, diluted with 100 ml of water, and extracted with methylene chloride. The aqueous layer was acidified with concentrated HCl; the precipitate was collected and crystallized from hexane to give 0.16 gram (33%) of IX: mp >300°C; ir (KBr) 1694 cm^{-1} (C=O).

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.96. Found: C, 68.74; H, 5.03.

1,3-Dimethylazulene, X. A mixture of VIII (0.53 gram, 0.001 mole), 25 ml dry benzene and an excess of a 53% oil dispersion of sodium hydride was refluxed for 3 hr. After cooling, the mixture was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was chromatographed on alumina. Elution with ligroin (30–60°C) gave 0.03 gram (20%) of X; mp 53–4.5°C.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.37; H, 7.84.

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