of only 0.722, indicating once again the inadequacy of the correction term when it is large.

Both the K_1/K_2 ratio and the k_f value place 1,1-cyclopropanedicarboxylic acid in the same position within the series of substituted malonic acids previously studied. This finding reaffirms that the K_1/K_2 ratio and the k_f value are both reflections of the hydrogen bond strength in the monoanion, but suggests that the hydrogen bond strength is not necessarily related to the angle between the carboxyl groups.

Registry No.—1,1-Cyclopropanedicarboxylic acid, 598-10-7; monoanion of 1,1-cyclopropanedicarboxylic acid, 58325-50-1.

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Preparation of 9,10-Difluoroanthracene

Leon M. Stock* and Michael R. Wasielewski

Department of Chemistry, University of Chicago, Chicago, Illinois 60637

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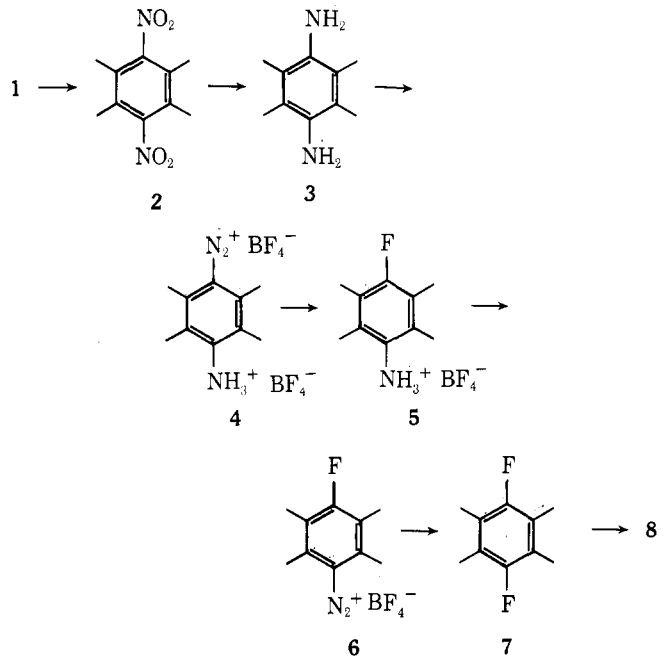
Fluoroanthracene and 9,10-difluoroanthracene are valuable molecules for investigations in magnetic resonance and photochemistry.[1,2,3] These aryl fluorides are not readily prepared by the Schiemann reaction or its modifications.[4] Thus, the first successful preparation of 9-fluoroanthracene from 9-aminoanthracene used nitric oxide as the diazotization reagent.[5] However, 9-aminoanthracene is readily oxidized and widely variable amounts of the desired diazonium salt are obtained.[6] Dewar and Michl circumvented this problem by the use of 9-amino-1,2,3,4,5,6,7,8-octahydroanthracene as the starting material for conversion to 9-fluoro-1,2,3,4,5,6,7,8-octahydroanthracene and thence to 9-fluoroanthracene by dehydrogenation.[2] However, a new difficulty arises in the application of their procedure for the synthesis of 9,10-difluoroanthracene because charged substituents in the 10 position greatly enhance the rate of hydrolysis of 1,2,3,4,5,6,7,8-octahydroanthracene-9-diazonium tetrafluoroborate.[7] We wish to report a route, Chart I, for the synthesis of 9,10-difluoroanthracene in which these hydrolysis reactions are minimized. This known compound was previously obtained in less than 1% yield as a by-product in the reaction of fluorobenzyne with furan[8] and in 5% yield by the reaction of sulfur tetrafluoride with anthraquinone to yield 9,9,10,10-tetrafluoro-9,10-dihydroanthracene followed by iron gauze catalyzed defluorination.[9]

Octahydroanthracene (1) was converted to the diamine 3 in good yield using known procedures.[10] Not unexpectedly,

Chart I



the treatment of 3 in aqueous media with nitrous acid prepared from either sulfuric, hydrochloric, or fluoroboric acid led to small yields of octahydroanthraquinone as the only isolable product. This reaction was incomplete because the salts of 3 are insoluble in the aqueous media. The use of tetrahydrofuran as a cosolvent provided the quinone in excellent yield. As noted, the diazonium ions of duridines are unstable in water;[7] this problem is compounded in the diazonium derivatives of 3 with their activating ammonium and diazo groups. We were able to circumvent this difficulty through a reduction in the polar character of the medium using ethanol as a solvent and isoamyl nitrite as the diazotization agent in the presence of excess 48% fluoroboric acid. Under these conditions, 3 was cleanly and rapidly converted to 4 which precipitated. This salt is stable and may be stored for several weeks. Salt 4 was decomposed thermally in vacuo to give 5, which is a useful intermediate for the preparation of many other fluoroanthracenes. Compound 5 was diazotized by the procedure used for 3. The product, 6, was precipitated by the addition of ether. Diazonium salt 6 is unstable and cannot be stored for more than 1 day without noticeable deterioration. Thermal decomposition of 6 in vacuo gave 7 in 90% yield. Dehydrogenation of 7 with dicyanodichloroquinone proceeded successfully to yield 57% of 9,10-difluoroanthracene.

Experimental Section

All melting points are corrected. Varian equipment was used to record the NMR spectra at 60 or 100 MHz with tetramethylsilane as an internal reference and fluorine NMR spectra at 56.4 or 94.1 MHz. Infrared and ultraviolet spectra were recorded with Beckman IR-10 and Cary 14 instruments, respectively. Octahydroanthracene (Columbia Organic Chemicals Co.) was used without further purification. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

9,10-Dinitro-1,2,3,4,5,6,7,8-octahydroanthracene (2). Chloroform (900 ml) and concentrated sulfuric acid (450 ml) were added to a flask fitted with a mechanical stirrer, thermometer, and addition funnel. The mixture was cooled to −20 °C and 100% nitric acid (27 ml) was added cautiously. A solution of octahydroanthracene (27.0 g, 0.145 mol) in chloroform (150 ml) was added dropwise to the stirred acid mixture over 30 min maintaining the temperature below −10 °C. The resulting dark red mixture was stirred for 15 min longer, poured onto ice, and extracted with chloroform (6 × 300 ml). The extracts were combined, washed to neutrality with saturated sodium bicarbonate solution, and dried over magnesium sulfate. The solvent was removed in vacuo. The residue was suspended in ethanol (500 ml) and

heated to reflux. After cooling the product was collected and washed repeatedly with cold ethanol. Air drying provided light tan crystals of **2** [29.2 g, 73%, mp 302–305 °C (lit.[10] mp 305 °C)]: NMR ($CDCl_3$) δ 1.73 (m, 8 H), 2.54 (m, 8 H); ir (KBr) 1540 (s, N–O), 1375 cm^{-1} (s, N–O).

9,10-Diamino-1,2,3,4,5,6,7,8-octahydroanthracene (3). A hot solution of stannous chloride dihydrate (143 g, 630 mmol) in concentrated hydrochloric acid (180 ml) was cautiously added to a refluxing solution of **2** (15.0 g, 54 mmol) in glacial acetic acid (635 ml). The mixture refluxed vigorously during the addition of the tin solution. The mixture was refluxed for 18 h. The tin salt was collected after the reaction mixture was cooled to ambient temperature. The crude solid was washed repeatedly with ether and air dried. The dry tin salt was taken up in 20% sodium hydroxide solution (400 ml). The liberated amine was extracted into methylene chloride (3 × 200 ml). The extracts were washed thoroughly with water and dried over magnesium sulfate. Removal of the solvent yielded golden crystals of **3** [9.3 g, 79%, mp 188–189 °C (lit.[10] 188–189 °C)]: NMR ($CDCl_3$) δ 1.82 (m, 8 H), 2.46 (m, 8 H), 3.13 (s, br, 4 H); ir (KBr) 3300, 3400 (m, N–H), 1640 cm^{-1} (s, N–H).

1,2,3,4,5,6,7,8-Octahydroanthracene-9-ammonium-10-diazonium Fluoroborate (4). A solution of **3** (10.8 g, 50 mmol) in ethanol (100 ml) and 48% fluoroboric acid (54.0 g) was cooled to −5 °C. The vigorously stirred purple solution was diazotized by the dropwise addition of isoamyl nitrite (14.0 g, 120 mmol) with the temperature kept below 0 °C. The mixture became greenish-yellow as a precipitate formed. Ten minutes after the addition was complete cold ether (250 ml) was added and the stirring maintained for 5 min longer. The bright yellow crystals were collected and washed thoroughly with cold ether. Air drying provided **4** (11.6 g, 58%, mp 160 °C dec); NMR ($CDCl_3$) δ 1.97 (m, 8 H), 2.58 (m, 8 H); ^{19}F NMR ($CDCl_3$) +148.2 ppm (s, br) relative to external $CFCl_3$; ir (KBr) 3360 (s, N–H), 2160 (s, $^+N{\equiv}N$), 1660 (s, N–H), 1570 (s, N–H), 1050 cm^{-1} (s, br, B–F).

9-Fluoro-1,2,3,4,5,6,7,8-octahydroanthracene-10-ammonium Fluoroborate (5). A mixture of **4** (11.7 g, 29 mmol) and sand (120 g) was decomposed in a sublimator at 1 Torr and 160 °C over 8 h to yield colorless crystals of **5** (6.9 g, 78%, mp 180–182 °C dec): NMR ($CDCl_3$) δ 1.81 (m, 8 H), 2.70 (m, 8 H), 6.42 (s, 3 H); ^{19}F NMR (Me_2SO) +120.4 (s), +146.2 ppm (s), relative to external $CFCl_3$; ir (KBr) 3230 (s, N–H), 1585 (s, N–H), 1510 (m, N–H), 1080 cm^{-1} (s, br, B–F).

The fluoro amine was liberated by the treatment of **5** with excess potassium hydroxide in ethanol. 9-Fluoro-10-amino-1,2,3,4,5,6,-7,8-octahydroanthracene (mp 107–109 °C) was obtained in quantitative yield: NMR ($CDCl_3$) δ 1.82 (m, 8 H), 2.58 (m, 8 H), 3.37 (s, br, 2 H); ^{19}F NMR ($CDCl_3$) +131.1 ppm (s), relative to external $CFCl_3$; ir (KBr) 3490, 3300 (s, N–H), 2960 (s, C–H), 1660 (s, N–H), 1070 cm^{-1} (s, C–F); mass spectrum *m/e* calcd for $C_{14}H_{18}NF$, 219.1422; found, 219.1429; *m/e* (rel intensity) 219 (100), 218 (13), 217 (12), 203 (6), 191 (24), 190 (7), 176 (10), 161 (7).

Anal. Calcd for $C_{14}H_{18}NF$: C, 76.68; H, 8.27; N, 6.38; F, 8.66. Found: C, 76.91; H, 8.34; N, 6.34; F, 8.59.

9-Fluoro-1,2,3,4,5,6,7,8-octahydroanthracene-10-diazonium Fluoroborate (6). A suspension of **5** (6.0 g, 19.5 mmol) in ether (55 ml) containing 48% fluoroboric acid (6.5 g) was cooled to −5 °C. The vigorously stirred mixture was diazotized by dropwise addition of isoamyl nitrite (6.5 g, 56 mmol) maintaining the temperature below 0 °C. Stirring and cooling were maintained for 30 min following the addition during which time the mixture became homogeneous. Cold ether (500 ml) was added and the mixture stirred vigorously for 5 min longer. The yellow precipitate was filtered, washed with cold ether, and quickly air dried to yield **6** (5.5 g, 89%, mp 100 °C dec): ir (KBr) 2240 (s, $^+N{\equiv}N$), 1060 cm^{-1} (s, br, B–F). Because it was unstable, this salt was promptly converted to **7**.

9,10-Difluoro-1,2,3,4,5,6,7,8-octahydroanthracene (7). A mixture of **6** (6.6 g, 21 mmol) and sand (66 g) was decomposed in a sublimator at 1 Torr and 100 °C for 12 h to give colorless crystals of **7** [4.16 g, 90%, mp 145–146 °C (sealed tube)]: NMR ($CDCl_3$) δ 1.73 (m, 8 H), 2.56 (m, 8 H); ^{19}F NMR ($CDCl_3$) +126.2 ppm (s), relative to external $CFCl_3$; ir (KBr) 1040 (s, C–F), 960, 835 cm^{-1} (s, C–H); mass spectrum *m/e* calcd for $C_{14}H_{16}F_2$, 222.1219; found, 222.1222; *m/e* (rel intensity) 222 (100), 221 (9), 220 (8), 194 (89), 193 (12), 181 (17), 180 (20), 179 (24), 178 (6), 177 (14), 167 (6), 165 (16), 164 (13), 151 (10), 146 (7), 133 (6).

Anal. Calcd for $C_{14}H_{16}F_2$: C, 75.65; H, 7.26; F, 17.10. Found: C, 75.81; H, 7.32; F, 17.00.

9,10-Difluoroanthracene (8). A solution of **7** (4.6 g, 19 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (18.4 g, 81 mmol) in toluene (184 ml) was refluxed under nitrogen for 8 h. The solution was cooled and filtered. The filtrate was concentrated prior to chromatography on neutral alumina (5 × 25 cm) with benzene. Removal of the solvent provided long yellow needles of **8** [2.58 g, 57%, mp 164–165 °C (lit.[8] 170–172 °C)]: NMR ($CDCl_3$) δ 7.51 (m, 4 H), 8.22 (m, 4 H); ^{19}F NMR ($CDCl_3$) +131.9 ppm (m), relative to external $CFCl_3$; ir (KBr) 1030 (s, , C–F), 1370, 745 cm^{-1} (s, C–H); mass spectrum *m/e* calcd for $C_{14}H_8F_2$, 214.0693; found, 214.0622; *m/e* (rel intensity) 214 (100), 107 (9), 94 (5). Recrystallization of the product from ethanol did not alter the melting point. Consequently, an analysis was obtained.

Anal. Calcd for $C_{14}H_8F_2$: C, 78.50; H, 3.76; F, 17.74. Found: C, 78.36; H, 3.82; F, 17.55.

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Registry No.—**1**, 1079-71-6; **2**, 23585-27-5; **3**, 23585-28-6; **4**, 58325-07-8; **5**, 58325-09-0; **5** free amine, 58325-08-9; **6**, 58325-11-4; **7**, 58325-12-5; **8**, 1545-69-3.

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Synthesis of 1-Azacycl[3.2.2]azine

Michael DePompei and William W. Paudler*

Department of Chemistry, The University of Alabama, University, Alabama 35486

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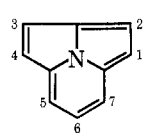
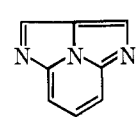
Some time ago,[1] we expanded the chemistry of Boekelheide's[2] cycl[3.2.2]azine (**1**) to include the synthesis of 1,4-diazacycl[3.2.2]azine (**2**). This compound, in strong contrast



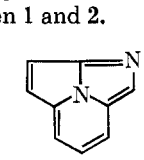
1



2

to the acid stability of **1**, is readily hydrolyzed to 5-aminoimidazo[1,2-*a*]pyridine-3-carboxaldehyde. In addition to this derivative, we recently described[3] the synthesis of 2-azacycl[3.2.2]azine (**3**) and established, among other chemical properties, that this ring system is stable to aqueous acid.

These hydrolytic results prompted us to prepare 1-azacycl[3.2.2]azine (**4**), a compound of "intermediate" structure between **1** and **2**.



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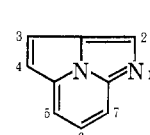

4

Results and Discussion

An application of the techniques developed for the synthesis of 2-azacycl[3.2.2]azine (**3**) to 5-methylimidazo[1,2-*a*]pyridine (**5**) afforded the desired compound as outlined in Scheme I.