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.

Acknowledgment. We are indebted to the National Science Foundation, the Block Fund of the University of Chicago, and the Fannie and John Hertz Foundation for the support of this work.

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

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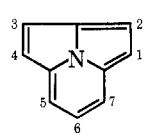
Some time ago,[1] we expanded the chemistry of Boekelheide's[2] cycl[3.2.2]azine (**1**) to include the synthesis of 1,4-diazacycl[3.2.2]azine (**2**). This compound, in strong contrast



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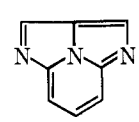

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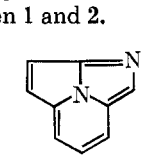
to the acid stability of **1**, is readily hydrolyzed to 5-aminoimidazo[1,2-*a*]pyridine-3-carboxaldehyde. In addition to this derivative, we recently described[3] the synthesis of 2-azacycl[3.2.2]azine (**3**) and established, among other chemical properties, that this ring system is stable to aqueous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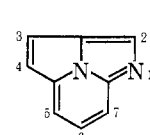

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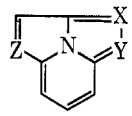
Results and Discussion

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.

Table I. ^{1}H NMR Spectral Parameters of Some Cycl[3.2.2]azines[a]



1, X = Y = Z = CH
2, X = CH; Y = Z = N
3, Y = Z = CH; X = N
4, X = Y = CH; Z = N

Compd	Chemical shifts, τ						
	H_1	H_2	H_3	H_4	H_5	H_6	H_7
1	2.81	2.50	2.50	2.81	2.14	2.41	2.14
2		1.30	1.30		1.88	1.88	1.88
3	1.55		2.35	2.70	2.04	2.49	2.18
4		1.42	2.34	2.54	2.06	2.02	1.91
6		0.90	2.14		1.06	1.40	1.30[b]
8		1.05	1.82	2.00	multiplet centered at 1.36[c]		
10		1.46	2.30		2.04	1.90	2.00

	Coupling constants, Hz
1	$J_{56} = 8.0, J_{1,2} = 4.2$
2	$J_{56} = 8.0$
3	$J_{56} = 7.8, J_{62} = 7.0, J_{34} = 4.7, J_{1,4} = 1.0$
4	$J_{56} = J_{67} = 8.0, J_{34} = 4.8$
6	$J_{56} = 8.0, J_{67} = 8.0$
10	$J_{56} = 8.0, J_{67} = 8.0$

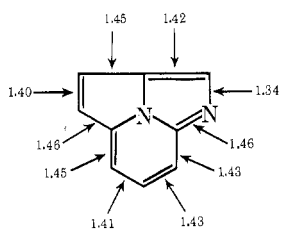
[a] Dilute solutions in $CDCl_3$. [b] TFAA solvent. [c] D_2O solvent.

The structures of compound **4** and its synthetic precursors (**6** and **7**) were established in the usual manner (synthetic sequence, elemental and mass spectral analyses).

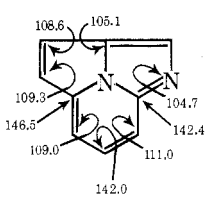
A comparison of the ^{1}H NMR spectrum of 1-azacycl[3.2.2]azine (**4**) with that of cycl[3.2.2]azine (**1**) demonstrates the anisotropic peri effect on N-1 upon the chemical shift of H-7 (0.23 ppm deshielding). This effect has been estimated to be about −0.15 to −0.20 ppm in quinolines, polyazaindenes, and related ring systems.[4]

The generally more deshielded chemical shifts of H-3 and H-4 simply reflect the "electron drift" into the imidazole portion of the 1-azacycl[3.2.2]azine (**4**) in comparison to the symmetrical cycl[3.2.2]azine (**1**). Another point of interest, implying more isolated double bond character for C_3–C_4, is the fact the J_{34} (4.8 Hz) is larger in compound **4** than in compound **1**. This coupling constant is consistent with an estimated bond order of 0.8.[6]

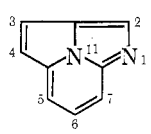
Geometry-optimized MINDO/2 calculations[5] gave the following ground-state parameters for compound **4**:



Bond lengths (Å)



Bond angles (deg)



MINDO/2 total electron densities[7] (exclusive of $1s^2$)

N-1 = 5.16
C-2 = 3.88
C-3 = 3.96
C-4 = 4.13
C-5 = 4.01
C-6 = 3.98
C-7 = 4.05
N-11 = 4.91

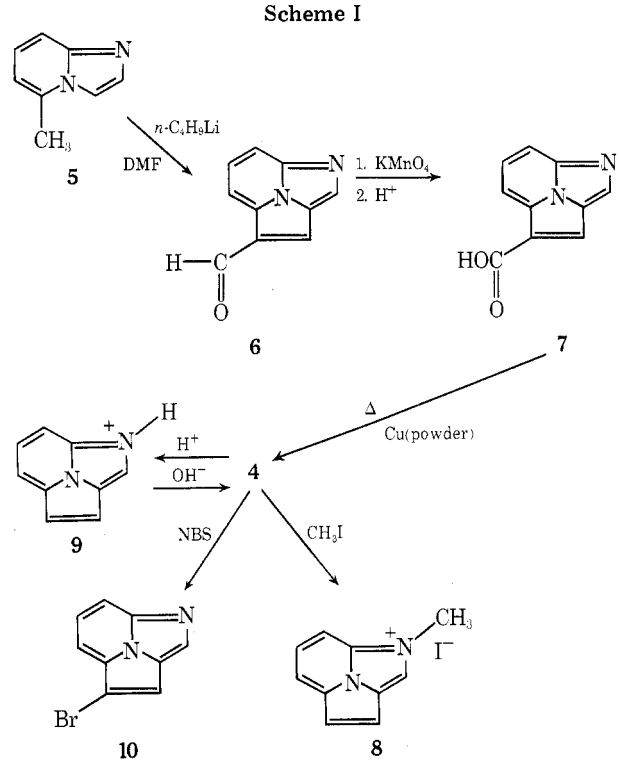
The most significant observations of these calculations, as applied to this work, are that C_3–C_4 is the shortest carbon–carbon double bond and that C-2 is the most electropositive carbon atom in the ring system. The former observation is consistent with our comments regarding the nature of C_3–C_4 in the 2-azacycl[3.2.2]azine—as a rather "isolated" double bond.

Thus, we suggest that the ground-state structure of 1-azacycl[3.2.2]azine is, perhaps, best represented by formulation **11**.

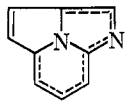
That the central nitrogen atom is not significantly involved in the delocalization is evident from the fact that its charge density is 4.91 (exclusive of the $1s^2$ electrons).

Bromination of compound **4** affords a monobromo deriva-

Scheme I



5 6 7 9 4 10 8

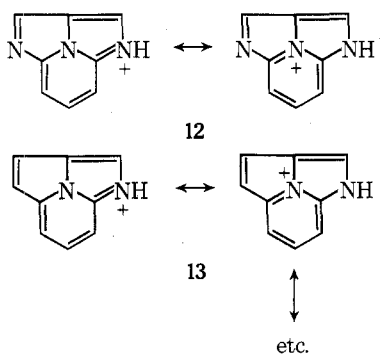


11

tive whose ^1H NMR spectrum (see Table I) clearly identifies it as the 4-bromo derivative (**10**). This is, of course, in agreement with the results of electrophilic substitution studies on cycl[3.2.2]azine and on its 2-aza derivative.[2]

Methylation of compound **4**, as expected, affords a *N*-methyl quaternary salt (**8**) (see Table I). The ^1H NMR spectrum of this compound is essentially superimposable upon that of the parent compound **4** in aqueous acid. The intriguing result is that the 1-azacyl[3.2.2]azine (**4**) is stable to aqueous acid, in contrast to the great acid lability of the 1,4-diaza analogue **2**.

If we consider the monoprotonated forms of compounds **2** and **4** (structures **12** and **13**), as being initially formed, the acid



12

13

etc.

lability of the HC=N– bond, an imine in **12**, as compared to the –CH=CH– bond in **13**, is understandable. Thus, the hydrolytic instability of the protonated diazacyl[3.2.2]azine (**12**) as compared to the monoazacycl[3.2.2]azine (**13**) is readily explained.

Experimental Section[8]

4-Formyl-1-azacycl[3.2.2]azine (6). To a stirred solution of 45 ml of 2 M BuLi (0.908 mol) in 20 ml of sodium-dried tetrahydrofuran (THF) was added tetramethylethylenediamine (TMEDA, 10.53 g, 0.0908 mol) under a N_2 atmosphere and at −15 °C. 5-Methylimidazo[1,2-*a*]pyridine (5.00 g, 0.0379 mol) in 30 ml of dried THF was then added to the solution. After 1 min, a solution of dry dimethylformamide (5.52 g, 0.0758 mol) in 30 ml of THF was added all at once. The resulting blue-green solution was stirred for an additional 30 min, after which time 100 ml of water was added to the reaction mixture. The mixture was extracted with $CHCl_3$ (3 × 150 ml), the combined extracts were dried over anhydrous Na_2CO_3 and filtered, and the solvent was evaporated in vacuo. The resulting brown solid was chromatographed over Al_2O_3 (grade III) and eluted with benzene. Evaporation of the solvent afforded a yellow solid which was recrystallized from chloroform to yield 0.580 g (9%), mp 210–212 °C. Anal. Calcd for $C_{10}H_6N_2O$: C, 70.59; H, 3.52; N, 16.47. Found: C, 70.35; H, 3.40; N, 16.22.

1-Azacycl[3.2.2]azine-4-carboxylic Acid (7). To a solution of 4-formyl-1-azacycl[3.2.2]azine (0.10 g, 0.588 mmol) in 10 ml of acetone was added 5 ml of water. Solid $KMnO_4$ (220 mg, 1.4 mmol) was added all at once, and the resulting solution was stirred for 1 h. The solution was treated with a small amount of solid $NaHSO_3$ and filtered through a Celite pad. The filtrate was evaporated in vacuo to approximately 5 ml and carefully acidified with 2 N HCl. The white precipitate was filtered and dried to yield 85 mg (75%) of 1-azacycl[3.2.2]azine-4-carboxylic acid, which decomposes at its melting point (318–320 °C).

1-Azacycl[3.2.2]azine (4). In a 10-ml distillation flask fitted with a short path condenser was placed a mixture of 1-azacycl[3.2.2]azine-4-carboxylic acid (0.350 g, 1.88 mmol) and Cu powder (400 mg). The flask and its contents were heated with a flame until a greenish liquid collected on the walls of the flask and condenser. The liquid was collected by dissolving it in $CHCl_3$. The $CHCl_3$ solution was placed on a short (5 cm) alumina column (grade III) and eluted with $CHCl_3$. Evaporation of the $CHCl_3$ eluent afforded 1-azacycl[3.2.2]azine (205 mg, 77%) as a low-melting solid. The picrate of compound **4** was obtained, mp 218–220 °C, and was analyzed. Anal. Calcd for $C_{15}H_9N_5O_7$: C, 48.52; H, 2.42; N, 18.87. Found: C, 48.42; H, 2.20; N, 18.35.

***N*$_1$-Methyl-1-azacycl[3.2.2]azinium Iodide (8).** To a solution of 1-azacycl[3.2.2]azine (50 mg, 0.35 mmol) in 10 ml of reagent-grade acetone was added 0.5 ml of CH_3I. The resulting solution was allowed to stand at room temperature for 15 h. The crystalline precipitate was collected and washed with 5 ml of cold reagent-grade acetone to yield *N*$_1$-methyl-1-azacycl[3.2.2]azinium iodide (85 mg, 84%) as a brick-red solid, mp 142–144 °C. Anal. Calcd for $C_{10}H_9N_2I$: C, 42.24; H, 3.16; N, 9.86. Found: C, 42.05; H, 2.89; N, 9.50.

4-Bromo-1-azacycl[3.2.2]azine (10). To a solution of 1-azacycl[3.2.2]azine (100 mg, 0.70 mmol) in 10 ml of $CHCl_3$ was added *N*-bromosuccinimide (0.310 mg, 1.75 mmol). The resulting solution was stirred for 5 h at room temperature and filtered, and the filtrate was evaporated to dryness. The residue was placed on a short (5 cm) alumina column (grade III) and eluted with benzene. Evaporation of the benzene afforded a yellow solid which was sublimed to yield 95 mg (62.1%) of 4-bromo-1-azacycl[3.2.2]azine, mp 81–82 °C. Anal. Calcd for $C_9H_5N_2Br$: C, 48.87; H, 2.26; N, 12.67. Found: C, 48.51; H, 2.05; N, 12.48.

Registry No.—**1**, 209-81-4; **2**, 10558-77-7; **3**, 54384-90-6; **4**, 209-83-6; **4** picrate, 58374-91-7; **5**, 933-69-7; **6**, 58374-92-8; **7**, 58374-93-9; **8**, 58374-94-0; **10**, 58374-95-1.

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(7) The electron densities given are exclusive of the $1s^2$ electrons.
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Reactions of Dichlorine Heptoxide with Olefins[1]

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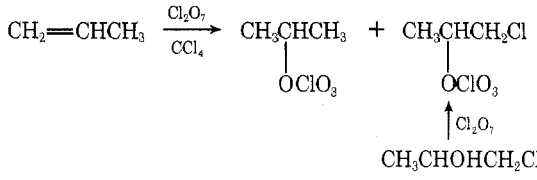
Received December 15, 1975

Dichlorine heptoxide in carbon tetrachloride is a conveniently accessible perchlorylation reagent, and its reactions with alcohols,[2] amines,[3] ethers,[4] and alkyl iodides[5] have been described. As a continuation of this study of the utility of the reagent the present investigation deals with its reactions with olefins.

Propene was found to react with dichlorine heptoxide in carbon tetrachloride to give isopropyl perchlorate (32%) and 1-chloro-2-propyl perchlorate (17%). The yields of these impact sensitive materials were determined by NMR using a quantitative internal standard. Isopropyl perchlorate was identified by spectral comparison with an authentic sample.[2] A sample of 1-chloro-2-propyl perchlorate was isolated and analyzed, and the compound was also synthesized independently from 1-chloro-2-propanol and dichlorine heptoxide.



cis-2-Butene reacted with dichlorine heptoxide to give 3-chloro-2-butyl perchlorate (30%), 3-keto-2-butyl perchlorate (2%), and 2,3-butane diperchlorate (5%). When the reaction