J = 2.5 Hz), 6.96-7.24 (m, 2 H), 7.44-7.67, 8.36-8.52 (each m, 1 H); mass spectrum, m/e 202 (M^+). Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.27; H, 8.98; N, 13.57.

Reaction of 2 with 26. A solution of **26** (1.27 g, 10 mmol) in THF (15 mL) was added to a solution of the lithio derivative, generated in situ from **2** (1.59 g, 10 mmol) and LDA in THF at -78 °C. The reaction conditions and workup of the reaction mixture were same as those in the reaction with **4**. The extract was chromatographed on silica gel with chloroform as an eluent to give 170 mg (11.5%) of isoxazolidinone compound **28**: colorless leaflets; mp 116-117 °C; IR (KBr) 3300, 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (s, 3 H), 0.88 (d, 3 H, J = 10.0 Hz), 0.92 (s, 3 H), 0.93 (d, 3 H, J = 10.0 Hz), 1.08, 1.32 (each s, 3 H), 1.44-2.50 (m, 6 H), 2.86 (dd, 1 H, J = 2.6, 1.0 Hz), 3.26 (ddd, 1 H, J = 9.2, 4.0, 2.6 Hz), 4.08 (ddd, 1 H, J = 8.0, 5.9, 1.0 Hz), 6.43 (br, 1 H, OH); ^{13}C NMR ($CDCl_3$) δ 12.1, 13.8, 14.5, 19.6, 22.5, 25.1 (each q), 32.3 (t), 37.8, 39.7 (each d), 39.9 (t), 55.7, 64.8 (each d), 66.0 (s), 66.9 (d), 71.9 (s), 175.8 (s); mass spectrum, m/e 296 (M^+). Anal. Calcd for $C_{16}H_{28}N_2O_3$: C, 64.83; H, 9.52; N, 9.45. Found: C, 64.79; H, 9.52; N, 9.40.

Registry No. 1, 17881-80-0; **2**, 23184-28-3; **3**, 4071-88-9; **4a**, 1137-96-8; **4b**, 3585-93-1; **4c**, 3585-90-8; **4d**, 19865-55-5; **5a**, 538-49-8; **5b**, 19036-99-8; **5c**, 24470-06-2; **6a**, 17431-39-9; **6b**, 21469-81-8; **6c**, 34912-68-0; **7a**, 4192-77-2; **7c**, 24393-61-1; **7d**, 24393-49-5; **8a**, 3376-23-6; **8b**, 16089-66-0; **8c**, 16089-63-7; **8d**, 3376-26-9; *cis*-**9a**, 83511-52-8; *trans*-**9a**, 83511-69-7; **9a** dipicrate, 83511-54-0; *cis*-**9b**, 83511-55-1; *trans*-**9b**, 83511-70-0; *cis*-**9c**, 83511-56-2; *trans*-**9c**, 83511-71-1; *cis*-**9d**, 83511-57-3; *trans*-**9d**, 83511-72-2; **10a**, 83511-58-4; **10d**, 83511-59-5; **11**, 83511-75-5; **12a**, 72552-74-0; **12b**, 58751-78-3; **13a**, 83511-60-8; **13a** dipicrate, 83511-61-9; **13b**, 83511-62-0; **13b** dipicrate, 83511-65-3; **14**, 83511-63-1; **14** dipicrate, 83511-64-2; **15**, 83511-73-3; **16**, 83511-66-4; **17**, 1552-92-7; **18**, 24423-87-8; **19**, 75997-55-6; **20**, 83511-67-5; **21**, 75997-58-9; **22**, 64890-49-9; **23**, 33934-42-8; **24**, 83511-68-6; **25**, 83511-77-7; **26**, 3146-84-7; **27**, 75997-57-8; **28**, 75997-59-0; DMAD, 762-42-5; benzaldehyde, 100-52-7; *p*-anisaldehyde, 123-11-5; *p*-tolualdehyde, 104-87-0; *N*-methylhydroxylamine hydrochloride, 4229-44-1; trimethylchlorosilane, 75-77-4; phenylhydroxylamine, 100-65-2; *N*-(trimethylsiloxy)aniline, 58751-79-4; azobenzene, 103-33-3; azoxybenzene, 495-48-7.

Directed Lithiation of 2-Phenyl- and 2-(*o*-Methylphenyl)imidazoline

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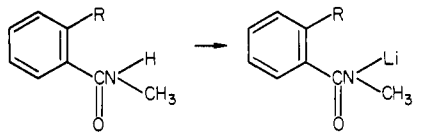
Received June 7, 1982

2-Phenyl- and 2-(*o*-methylphenyl)imidazoline have been converted into their ortho- and α-lithiated species, respectively, by treatment with *n*-BuLi–hexane in THF. Treatment of these reagents with a variety of nucleophiles gave ortho- and α-substituted products.

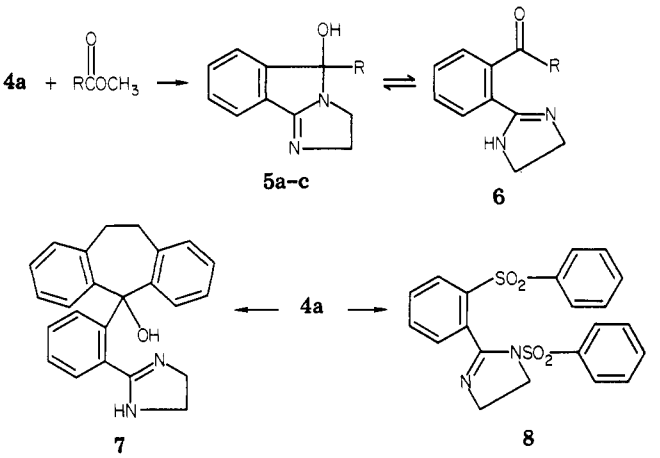
Hauser has reported that *N*-methylbenzamide[1] (**1a**) and *N*-methyl-*o*-toluamide[2] (**1b**) can undergo deprotonation



1a, R = H **2a**, R = Li
b, R = CH_3 **b**, R = CH_2Li

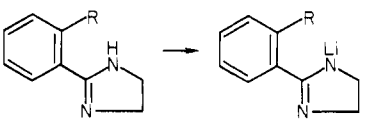
and ortho or benzylic lithiation,[3] respectively, when treated with *n*-BuLi in an inert ether solvent to form the dilithiated species **2a** or **2b**. Compounds that undergo dilithiation similar to that for **2a** have been reported for benzene derivatives with an ortho CSNHR,[4] SO_2NHR,[5] CH_2OH,[6] SO_3H,[7] or $NHCO_2$-*t*-Bu[8] group while toluene derivatives with an ortho CSNHR[4] or CO_2H[10] group give rise to dilithiated species similar to **2b**.

Scheme I



5a-c **6** **7** **8**

In the present work we report that the above lithiation reactions can be extended to 2-phenylimidazoline (**3a**) and



3a, R = H **4a**, R = Li
b, R = CH_3 **b**, R = CH_2Li

2-(*o*-methylphenyl)imidazoline (**3b**) to form the dilithiated **4a** and **4b** which can undergo reactions with a variety of nucleophiles.

The ortho lithiation of **3a** was maximized by studying the reaction of methyl *p*-chlorobenzoate to form the

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0022-3263/82/1947-5177$01.25/0

Table I. Compounds 5 and 9[a]

compd	R	reaction conditions: addn temp, °C	time, h	molar ratio ester/RLi	yield, %	mp, °C (recryst solv)[b]	^{1}H NMR (Me_2SO-d_6), δ: $ArCH_2$ and/or NCH_2CH_2N	OH	other
5a	4-ClC_6H_4	50	3	2:1	60	182–183 (A)[c]			
5b	2-furyl[d]	50	3	2:1	44	183 dec (B)	3.02 (m, 2 H), 4.18 (m, 2 H)	7.10 (s)	6.40–7.98 (m)
5c	t-C_4H_9	50	3	2:1	37	187–189 (C)	3.45 (m, 2 H), 3.98 (m, 2 H)	6.00 (s)	1.05 (s, 9 H, t-C_4H_9), 7.30–7.80 (m, 4 H)
9a	4-ClC_6H_4	−20	6	2:1	60	198–200 (B)	2.70–3.98 (m, 6 H)	6.25 (s)	
9b	2,4-$Cl_2C_6H_3$	−30	3	2:1	75	201 dec (D)	2.70–4.05 (m, 6 H)	6.50 (s)	
9c	$C_6H_5CH_2$[e]	−30	3	2:1	21	163–165 (C)	3.50–4.00 (m, 6 H)	5.72 (s)	2.95 and 3.13 (AB, J = 15, $CH_2C_6H_5$)
9d	C_6H_5CHOH	−50	3	0.5:1	61	172–174 dec (B)	3.10–4.00 (m, 6 H)	5.60 (s)	4.78 s, 1H, ArCH

[a] Satisfactory (±0.3) elemental analyses (C, H, N) were obtained for all new compounds. The IR spectra (KBr) of all compounds gave an OH signal at 2.93 ± 0.05 μm and broad saltlike absorption from 3.22 to 4.15 μm. [b] Recrystallization solvents: A, DMF; B, EtOH; C, CH_2Cl_2; D, CH_2Cl_2–EtOH; E, CH_2Cl_2–pentane. [c] Lit.[11] mp 184–185 °C. [d] UV (95% EtOH) max 200 nm (ε 13 680), 217 sh (7925), 278 (3240). [e] Mass spectrum, m/e 294 (M^+), 276 ($M - H_2O$), 257, 185, 169, 155, 141, 128, 116, 78.

Table II. ^{13}C NMR Data (ppm) for 5 and 9

compd	assignments[a]: NCCN	HOCN	C=N
5a	42.6, 50.6	93.1	157.8
5c	45.8, 58.6	92.6	152.4
9a	45.1, 52.3	84.5	160.1
9b	44.9, 52.6	83.2	158.5
9c[b]	44.1, 52.4	83.2	159.7
9d[c]	43.3, 52.3	84.9	159.7

[a] Chemical shifts are relative to Me_4Si as an internal standard. [b] Atom C-6; 34.3 ppm. [c] Atom C-6; 34.2 ppm; ArC(O)H, 75.3 ppm.

known[11] 5-(*p*-chlorophenyl)-2,3-dihydro-5*H*-imidazo[2,1-*a*]isoindol-5-ol (**5a**). The optimum yield (60%) of **5a** was obtained by treating a THF solution of **3a** with 3 equiv of *n*-BuLi in hexane at 50 °C for 3 h, adding 2 equiv of methyl *p*-chlorobenzoate, and maintaining the temperature at 50 °C for an additional 6 h (Scheme I). Application of these conditions to methyl 2-furoate and methyl pivalate gave **5b** and **5c** in 44% and 37% yields, respectively (Table I).[12] Since **5a** is known[13] to exist in the tautomeric form **6** under certain conditions, spectral studies of **5b** and **5c** were carried out to determine if they exist in the closed (**5**) or open (**6**) form. The ultraviolet spectrum[11] of **5b** gave strong end absorption at 200 nm characteristic of the closed form **5** while the ^{13}C NMR spectrum of **5c** (Table II) gave a signal at 92.6 ppm which is typical[13] for the C-5 atom of the closed form **5**.

Treatment of the dianion **4a** with dibenzosuberone gave **7** in 32% yield while benzenesulfonyl fluoride and **4a** resulted in the formation of a bis(phenylsulfonyl) product that was established as the N-ortho derivative **8** by IR, ^{1}H NMR, and ^{13}C NMR data.

When the dilithium derivative **4b** was formed from 2-(*o*-methylphenyl)imidazoline (**3b**) and *n*-BuLi and then reacted with methyl *p*-chlorobenzoate under the conditions used to form **5a**, none of the expected **9a** was obtained. Instead, a low yield of a compound that gave ^{1}H and ^{13}C NMR and mass spectral (M^+, m/e 419) data in agreement with structure **10** was obtained. The formation of **10** can be explained by the expected lithium enolate **11** obtained from **4b** and methyl *p*-chlorobenzoate reacting with a second equivalent of ester to form the ketoenolate **12** or its tautomeric equivalent **13**. Hydrolysis of **13** to the hydroxyketone **14** followed by loss of water gives rise to **10** (Scheme II). Satisfactory yields (60%) of **9a** could be obtained when the dilithium derivative **4b** was formed at 35 °C and then treated at −25 °C with 2 equiv of methyl *p*-chlorobenzoate. Extension of these conditions to methyl 2,4-dichlorobenzoate and methyl phenylacetate gave **9b** and **9c** in 75% and 21% yields, respectively. Treatment of methyl mandelate at −50 °C with an ester/**4b** ratio of 0.5:1 gave a good yield (61%) of **9d**.[14] The ^{13}C NMR spectrum (Table II) of compounds **9a–d** are in agreement with the imidazo[2,1-*a*]isoquinolin-5-ol system rather than the tautomeric ketone form **15**. The four compounds gave a chemical shift in the 83–85-ppm region that is typical

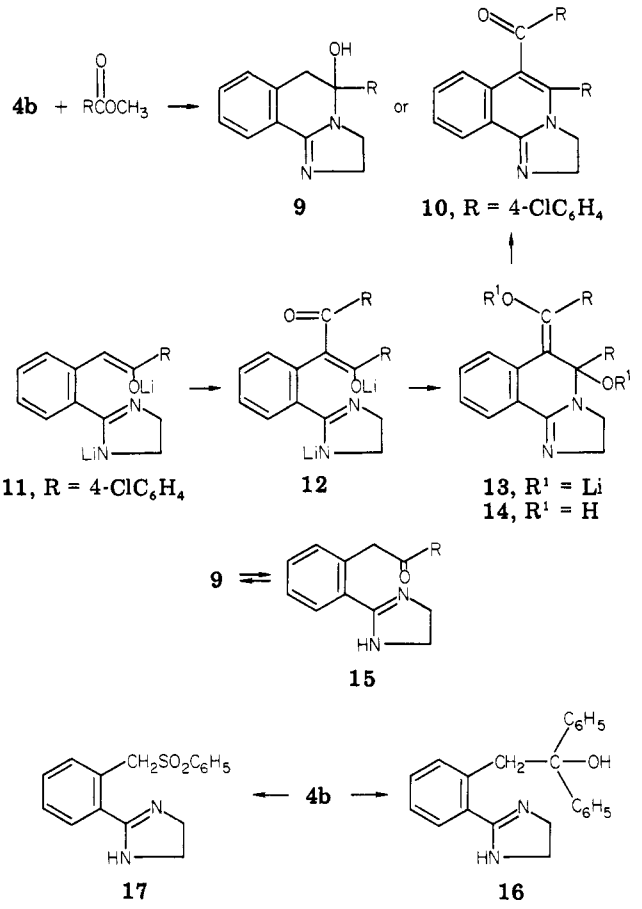
(11) The ultraviolet spectrum of analogues of **5b** are reported in: Aeberli, P.; Eden, P.; Gogerty, J. H.; Houlihan, W. J.; Penberthy, C. *J. Med. Chem.* **1975**, *18*, 177.

(12) Additional examples of the reaction of methyl *o*-halobenzoates with **4a** have recently been reported. Houlihan, W. J.; Parrino, V. A. *J. Heterocycl. Chem.* **1981**, *18*, 1549. Houlihan, W. J. U.S. Patent 3 932 450; *Chem. Abstr.* **1976**, *84*, 135662.

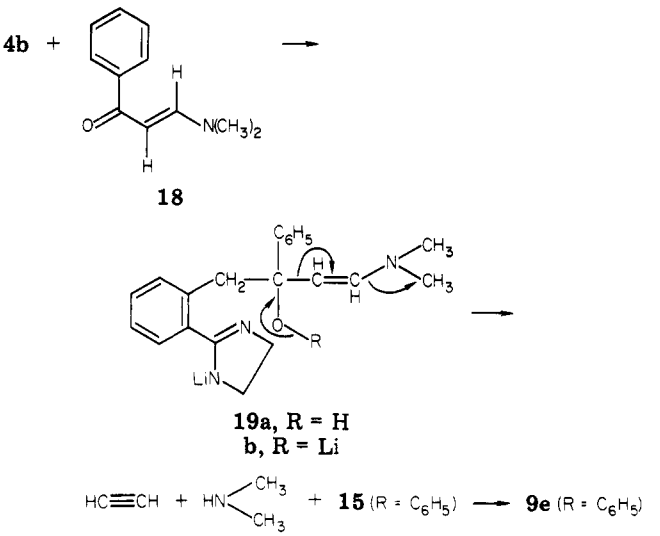
(13) Houlihan, W. J.; Barcza, S. *J. Pharm. Sci.* **1975**, *64*, 829.

(14) Additional examples of the formation of **9** from **4b** and various aryl and heteroaryl esters will be reported. Houlihan, W. J.; Gogerty, J. H.; Parrino, V. A.; Ryan, E. *J. Med. Chem.*, in press.

Scheme II



Scheme III



for the C-5 in structure **9**. No signals were observed in the carbonyl region of the spectra.

Reaction of **4b** with benzophenone gave the expected alcohol **16** in 66% yield and with benzenesulfonyl fluoride **4b** gave the sulfone **17** (28%). The structure of both compounds was confirmed by ^1H and ^{13}C NMR.

When **4b** was reacted with propenone **18** at −20 °C, compound **9e** (R = C_6H_5) was obtained rather than the expected alcohol **19a**. One probable pathway to explain the formation of **9e** is fragmentation of the lithium salt **19b** to acetylene, lithium dimethylamide, and the lithium salt of **15** (R = C_6H_5) followed by ring closure (Scheme III).

Experimental Section

Infrared (IR) spectra were recorded on Perkin-Elmer 257 and 457 grating infrared spectrometers, and ^1H nuclear magnetic resonance (NMR) spectra were recorded by using either a Varian T-60 or A-60A spectrometer. Chemical shifts are reported as δ values in parts per million relative to Me_4Si; coupling constants (J) are given in hertz. ^{13}C NMR spectra were obtained at 25.2 MHz on a Varian XL-100-12 spectrometer system equipped with a 620/L 16K computer in the Fourier transform mode with sample concentrations of ca. 0.5 M when possible. Chemical shifts are relative to Me_4Si as an internal standard. The mass spectra were obtained on a LKB 900 mass spectrometer. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Except where noted, solvents were reagent grade and were used as received. The organolithium reagents were obtained from Foote Mineral Co. and Lithium Corp. of America and were used without further purification. The tetrahydrofuran was dried by storage over 3-Å molecular sieves. Silica gel (0.063–0.2 mm) was used in preparing column chromatograms, and analytical thin-layer chromatography was conducted for all compounds on precoated 40 × 80 mm plastic sheets of silica gel G with fluorescent indicator.

(5*R*)-2,3-Dihydro-5*H*-imidazo[2,1-*a*]isoindol-5-ols (5). General Procedure. A stirred solution of 36.5 g (0.25 mol) of 2-phenylimidazoline (**3a**) in 250 mL of dry THF maintained under a N_2 atmosphere was treated with 320 mL (0.75 mol of *n*-BuLi) of 2.4 M *n*-BuLi in hexane over a 0.5-h period. The suspension was heated to 50 °C for 3 h and then treated dropwise with 0.55 mol of methyl ester in 250 mL of dry THF over ca. 15 min. The slurry was stirred at 50 °C for 6 h, cooled to 10 °C, and treated dropwise with 125 mL of saturated NH_4Cl solution. After standing overnight at room temperature, the resulting solid was filtered off, washed with 150 mL of H_2O, and then recrystallized from the appropriate solvent given in Table I.

5-[2-(4,5-Dihydro-1*H*-imidazol-2-yl)phenyl]-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptan-5-ol (7). The lithium reagent from 13.5 g (0.094 mol) of 2-phenylimidazoline, 150 mL of THF, and 200 mL (0.282 mol of *n*-BuLi) of 1.6 M *n*-BuLi in hexane was treated with 45 g (0.22 mol) of dibenzosuberone in 100 mL of THF and then heated to 50 °C for ca. 6 h. The mixture was cooled in an ice bath and treated with 54 mL of saturated NH_4Cl solution. The organic layer was separated and concentrated in vacuo. The residue was crystallized from CH_2Cl_2–petroleum ether to give 10.1 g (32%) of **7**: mp 179–180 °C; ^1H NMR ($CDCl_3$) δ 2.60 (4 H, br s, CH_2CH_2), 3.30 (4 H, br s, NCH_2CH_2N), 4.5 (2 H, s, NH, OH), 6.78–8.08 (12 H, m, aromatic); ^{13}C NMR (Me_2SO-d_6) δ 44.2 (NC—C—N), 77.42 (C—O), 166.66 (C=N). Anal. Calcd for $C_{24}H_{22}N_2O$; C, 81.3; H, 6.3; N, 7.9. Found: C, 81.2; H, 6.2; N, 7.7.

1-(Phenylsulfonyl)-2-[2-(phenylsulfonyl)phenyl]-4,5-dihydro-1*H*-imidazole (8). The lithium reagent from 14.6 g (0.10 mol) of 2-phenylimidazoline, 200 mL of THF, and 210 mL (0.30 mol *n*-BuLi) of 1.6 M *n*-BuLi was treated dropwise with a solution of 19.0 g (0.12 mol) of benzenesulfonyl fluoride in 100 mL of THF and then allowed to stand overnight at room temperature. The mixture was cooled in an ice bath and treated with 60 mL of saturated NH_4Cl solution. The THF layer was separated and the H_2O layer washed with ca. 100 mL of CH_2Cl_2. The combined CH_2Cl_2–THF layers were dried ($MgSO_4$), filtered, and then concentrated in vacuo to give the product: 7.1 g (28%); mp 182–184 °C (CH_3OH–ether); IR (KBr) 6.10 (C=N), 7.31, 7.63, 8.62 and 9.13 μm (SO_2N and SO_2Ar); ^1H NMR (Me_2SO-d_6) δ 3.94 (4 H, s, NCH_2CH_2N), 7.27–8.15 (14 H, m, C_6H_5, C_6H_5, C_6H_4); ^{13}C NMR (Me_2SO-d_6) δ 47.7 and 53.6 (NCCN), 126.9, 127.5, 129.0, 129.3, 130.1, 132.7, 133.3, 133.5, 138.2, 139.5, 141.5, 153.5 (C=N); mass spectrum, m/e 426 (M^+), 362 (M − SO_2), 297 (M − SO_2, SO_2), 285 (M − $C_6H_5SO_2$), 221 (M − SO_2, $C_6H_5SO_2$). Anal. Calcd for $C_{21}H_{18}N_2O_4S_2$; C, 59.1; H, 4.2; N, 6.6; S, 15.0. Found: C, 58.8; H, 4.3; N, 6.6; S, 14.7.

(5*R*)-2,3,5,6-Tetrahydroimidazo[2,1-*a*]isoquinolin-5-ol (9). General Procedure. A stirred solution of 8.0 g (0.05 mol) of 2-(*o*-methylphenyl)imidazoline in 200 mL of dry THF maintained under a N_2 atmosphere was treated dropwise with 105 mL (0.15 mol of *n*-BuLi) of 1.6 M BuLi in hexane and then heated at 35 °C for ca. 4 h. The mixture was then immersed in a dry ice/acetone bath, cooled to an internal temperature of −25 °C, and treated with 17.5 g (0.10 mol) of methyl ester in 100 mL of THF

at such a rate that the temperature did not exceed −20 °C. After an additional 3 h at −20 °C, the reaction mixture was allowed to warm to 0 °C and then treated with 30 mL of saturated NH_4Cl solution. After being allowed to stand overnight at room temperature, the mixture was concentrated in vacuo and then treated with 200 mL of CH_2Cl_2 and 100 mL of H_2O. The CH_2Cl_2 was separated, washed with H_2O, dried with anhydrous $MgSO_4$, filtered, and concentrated to give a solid that was recrystallized from the appropriate solvent given in Table I.

6-(*p*-Chlorobenzoyl)-5-(*p*-chlorophenyl)-2,3-dihydroimidazo[2,1-*a*]isoquinoline (10). A stirred solution of 8.0 g (0.05 mol) of 2-(*o*-methylphenyl)imidazoline in 100 mL of THF maintained under a N_2 atmosphere was treated dropwise with 105 mL (0.15 mol of *n*-BuLi) of 1.6 M *n*-BuLi in hexane and then heated at 35 °C for ca. 4 h. The mixture was then treated dropwise with a solution of 17.2 g (0.10 mol) of methyl *p*-chlorobenzoate in 50 mL of THF, heated at 50 °C for ca. 5 h, and then allowed to stand overnight at room temperature. The cooled mixture was treated with 30 mL of saturated NH_4Cl and stirred for ca. 2 h at room temperature. The organic layer was separated, dried with $MgSO_4$, filtered, and concentrated in vacuo to an oil (6.5 g). Chromatography on 200 g of silica gel with $CHCl_3/CH_3OH$ (90:10) as the eluant gave 2.7 g of **10**: mp 210–212 °C (CH_2Cl_2/pentane); R_f 0.3 ($CHCl_3$–CH_3OH, 90:10); IR ($CHCl_3$) 6.05 (C=N), 6.15 (C=O) μm; ^1H NMR ($CDCl_3$) δ 3.90 (4 H, octet, NCH_2CH_2N), 7.08–7.88 (11 H, m, aromatic), 8.23 (1 H, m, H-10); ^{13}C NMR ($CDCl_3$) δ 49.6 and 52.8 (NCH_2CH_2N), 156.8 (C=N), 194.9 (C=O); mass spectrum, *m/e* 419 (M^+), 308 ($M^+C_6H_4Cl$), 280 (M^+-OCC_6H_4Cl). Anal. Calcd for $C_{24}H_{16}Cl_2N_2O$: C, 68.7; H, 3.8; Cl, 16.9; N, 6.7. Found: C, 68.5; H, 3.8; Cl, 16.9; N, 7.0.

5-Phenyl-2,3,5,6-tetrahydroimidazo[2,1-*a*]isoquinolin-5-ol (9e) from 3-(Dimethylamino)-1-phenyl-2-propen-1-one and 18. The lithium reagent from 4.0 g (0.025 mol) of 2-(*o*-methylphenyl)imidazoline, 150 mL of THF, and 53 mL (0.075 mol) of 1.6 M *n*-BuLi in hexane was cooled to −20 °C and treated with 8.6 g (0.050 mol) of **18** in 100 mL of THF. After an additional 3 h at −20 °C, the mixture was treated with 15 mL of saturated NH_4Cl solution and allowed to stand overnight at room temperature. The mixture was evaporated in vacuo to a paste and treated with CH_2Cl_2 and H_2O. The CH_2Cl_2 was separated, dried with anhydrous $MgSO_4$, filtered, and concentrated to give 2.2 g (33%) of **9e**: mp 186–188 °C dec (CH_2Cl_2); R_f 0.40 ($CHCl_3$–CH_3OH, 1:1); NMR (Me_2SO-d_6) δ 2.75–3.80 (6 H, m, CH_2, NCH_2CH_2N), 6.05 (1 H, s, OH), 6.95–7.62 (8 H, m, aromatic), 7.86 (1 H, m, H-10); mass spectrum, *m/e* 264 (M^+), 246 (M^+-H_2O). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.2; H, 6.1; N, 10.6. Found: C, 77.5; H, 6.4; N, 10.4.

2-[2-[(Phenylsulfonyl)methyl]phenyl]-4,5-dihydro-1*H*-imidazole (17). The lithium reagent from 16.0 g (0.10 mol) of 2-(*o*-methylphenyl)imidazoline, 250 mL of THF, and 210 mL (0.30 mol of *n*-BuLi) of 1.6 M *n*-BuLi was cooled to −20 °C and treated dropwise with 19 g (0.12 mol) of benzenesulfonyl fluoride in 100 mL of THF. After an additional 3 h at −20 °C, the mixture was treated with 60 mL of saturated NH_4Cl solution. The resulting solid was filtered off and crystallized from CH_2Cl_2–petroleum ether to give 6.1 g (28%) of **17**: R_f 0.1 ($CHCl_3$–CH_3OH, 98:2); mp 193–195 °C; NMR (Me_2SO-d_6) δ 3.65 (4 H, m, CH_2CH_2), 5.53 (2 H, s, CH_2S), 6.42 (1 H, br, NH), 7.23–7.75 (9 H, m, C_6H_5, C_6H_4). Anal. Calcd for $C_{16}H_{16}N_2O_2S$: C, 64.0; H, 5.4; N, 9.3; S, 10.7. Found: C, 64.1; H, 5.7; N, 9.4; S, 10.4.

2-(4,5-Dihydro-1*H*-imidazol-2-yl)-α,α-diphenylbenzeneethanol (16). The lithium reagent from 3.2 g (0.02 mol) of 2-(*o*-methylphenyl)imidazoline, 50 mL of THF, and 42 mL (0.06 mol of *n*-BuLi) of 1.6 M *n*-BuLi in hexane was treated at room temperature with a solution of 8.4 g (0.046 mol) of benzophenone in 50 mL of THF. The mixture was held at 35 °C for 3 h, allowed to stand overnight at room temperature, cooled in an ice bath, and treated with 10.8 mL of saturated NH_4Cl solution. The two-phase system was separated, and the THF was treated with anhydrous $MgSO_4$ and activated charcoal and filtered through Celite. The filtrate was concentrated and the residue crystallized from Et_2O–pentane to give 4.5 g (66%) of **16**: mp 148–150 °C; R_f 0.10 ($CHCl_3$–CH_3OH, 95:15); NMR (Me_2SO-d_6) δ 3.70 (4 H, s, CH_2CH_2), 3.85 (2 H, s, CH_2), 6.25 (1 H, dd, J = 8 Hz, J' = 2 Hz, HC), 6.80–7.60 (14 H, m, 12 aromatic, NH, OH); ^{13}C NMR (Me_2SO-d_6) 44.13 (NCCN) 76.70 (C—O), 165.81 (C=N); mass spectrum, *m/e* 342 (M^+), 324 ($M^+\cdot H_2O$), 314 ($M^+CH_2CH_2$). Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.7; H, 6.5; N, 8.2. Found: C, 80.5; H, 6.8; N, 8.3.

Acknowledgment. We are grateful to W. Bonkoski and his associates for microanalyses, S. DiCataldo and A. Kahle for NMR spectra, and B. Owens for mass spectral measurements.

Registry No. **3a**, 936-49-2; **3b**, 57327-93-2; **4a**, 38385-75-0; **4b**, 83633-99-2; **5a**, 22232-71-9; **5b**, 83634-00-8; **5c**, 83634-01-9; **7**, 83634-02-0; **8**, 83634-03-1; **9a**, 56882-42-9; **9b**, 56882-51-0; **9c**, 83634-04-2; **9d**, 83634-05-3; **9e**, 56882-45-2; **10**, 83634-06-4; **16**, 83634-07-5; **17**, 83634-08-6; **18**, 1201-93-0; methyl *p*-chlorobenzoate, 1126-46-1; dibenzosuberone, 1210-35-1; benzenesulfonyl fluoride, 368-43-4; methyl 2,4-dichlorobenzoate, 35112-28-8; methyl phenylacetate, 101-41-7; benzophenone, 119-61-9; methyl mandelate, 771-90-4; methyl 2-furoate, 611-13-2; methyl pivalate, 598-98-1.

Naphthoannelated Cycloheptatrienylidene and Cycloheptatetraene: Generation and Properties

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Received April 22, 1982

A naphthoannelated cycloheptatrienylidene–cycloheptatetraene intermediate has been generated from both the corresponding tropone tosylhydrazone and a mixture of bromocycloheptatrienes. Thermolysis of the tosylhydrazone salt in cyclohexene or benzene gave only a mixture of naphthoannelated heptafulvalenes. Thermolysis of the tosylhydrazone salt in dimethyl fumarate gave the same two dimers along with the expected spirocyclopropane adduct. Thermolysis of the tosylhydrazone salt or dehydrobromination of the mixture of bromocycloheptatrienes (**21** and **22**) with potassium *tert*-butoxide in the presence of diphenylisobenzofuran gave, in addition to the heptafulvalene dimers, an adduct that is believed to have arisen from rearrangement of an initially formed allene adduct. On the basis of the chemistry reported here as well as INDO calculations on a number of cycloheptatrienylidene–cycloheptatetraene pairs (and the triplets of the carbenes) it is suggested that initially formed singlet carbenes either intersystem cross to their triplet forms and show triplet chemistry (carbenes **12**, **32**, and **34**) or drop to allene ground states to show at least some allene chemistry. The principal unanswered question is whether any bimolecular chemistry originates from any of the singlet carbenes. Calculations of Waali argue for all chemistry coming from the allene while some of the experimental observations are consistent with a carbene.

The chemical properties of seven-membered cyclic conjugated carbenes (most originating from tosylhydrazone salts) have been found to be highly sensitive to monoannelation by aromatic rings.[1] Prior to the recent report of

0022-3263/82/1947-5180$01.25/0