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Action of Potassium Fluoride on 5-Benzensulfonyl-5,10-dihydro-10-trimethylsilylindeno[1,2-b]indole. Attempted Synthesis of Dibenzo[b,f-1]azapentalene

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Summary. Mild and neutral experimental conditions were employed in order to maximize the chance of success in the isolation of dibenzo[b,f-1]azapentalene (**3**), a compound expected to exhibit antiaromatic character, from a precursor. Thus, 5-benzensulfonyl-5,10-dihydro-10-trimethylsilylindeno[1,2-b]indole (**7**) was allowed to react with potassium fluoride at room temperature. The outcome of the reaction was complex, but the major product was identified as 5,5′,10,10′-tetrahydro-10,10′-biindeno[1,2-b]indolylidene (**15**). Apparently, the anion **8** that was generated by the action of potassium fluoride on **7**, did not suffer direct elimination of the benzensulfenate anion. Instead, presumably due to the antiaromacitity of **3**, the benzensulfenate anion was eliminated only after a series of electron transfer reactions, resulting in **15**. Also, unexpectedly, dibenzo[b,f-1]azapentalene dianion (**5**) was silylated exclusively at the 10-carbon in preference to silylation at nitrogen. Experimental data indicated that the 10-carbon of **5** was silylated directly with chlorotrimethylsilane.

Keywords. Antiaromatic character; Dibenzo[b,f-1]azapentalene anions; Electron transfer; Elimination; Lithiation; Silylation.

Zur Einwirkung von Kaliumfluorid auf 5-Benzolsulfonyl-5,10-dihydro-10-trimethylsilylindeno-[1,2-b]indol. Versuchte Synthese von Dibenzo[b,f-1]azapentalen

Zusammenfassung. Um maximale Chancen zur Isolierung von Dibenzo[b,f-1]azapentalen (**3**), das antiaromatischen Charakter besitzen sollte, zu gewährleisten, wurden bei der versuchten Synthese möglichst schonende und neutrale Reaktionsbedingungen angewendet. 5-Benzolsulfonyl-5,10-dihydro-10-trimethylsilylindeno[1,2-b]indol (**7**) wurde dabei mit Kaliumfluorid bei Raumtemperatur umgesetzt. Die Reaktionsprodukte hatten eine komplexe Zusammensetzung, das Hauptprodukt wurde als 5,5′,10,10′-Tetrahydro-biindeno[1,2-b]indolyliden (**15**) identifiziert. Offensichtlich ging das bei der Einwirkung von Kaliumfluorid auf **7** gebildete Anion **8** keine direkte Eliminierung des Benzolsulfonat-Anions ein. Das Benzolsulfonat-Anion wurde stattdessen nach einer Serie von Elektronentransferschritten eliminiert, wobei Verbindung **15** resultierte. Ebenso unerwarteterweise wurde das Dibenzo[b,f-1]azapentalen-Dianion (**5**) ausschließlich am C-10 und nicht am Stickstoff silyliert. Die experimentellen Befunde zeigten an, daß die Silylierung am C-10 direkt mit Chlortrimethylsilan erfolgt war.

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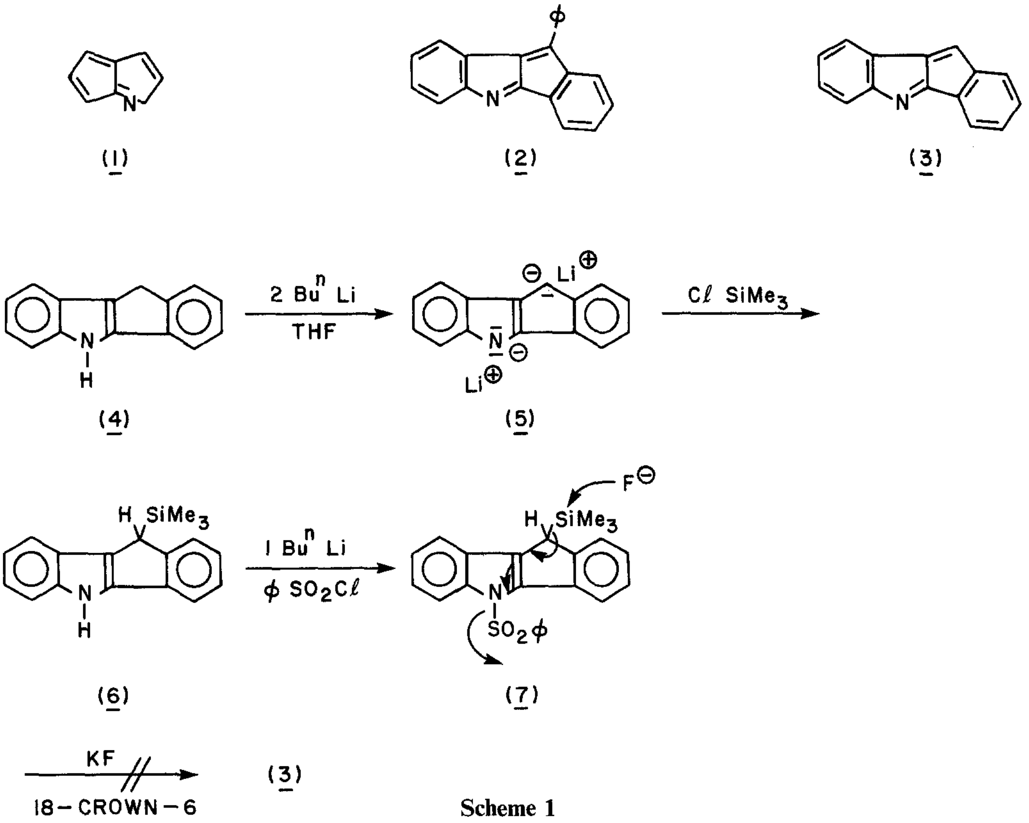
Introduction

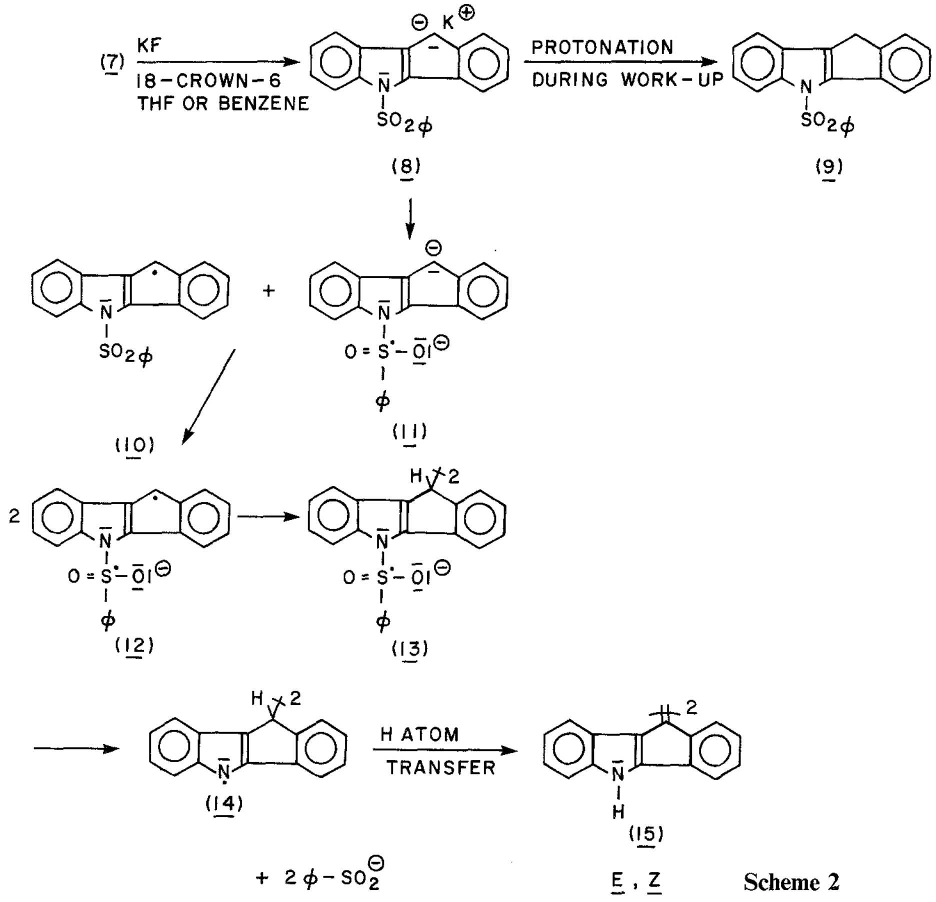
In connection with the concept of heterocyclic antiaromaticity, the first stable derivative of 1-azapentalene (**1**), namely, 10-phenyldibenzo[b,f-1]azapentalene (**2**), was synthesized [1, 2]. The unusual physical and chemical properties displayed by **2** prompted attempts to obtain the less substituted dibenzo[b,f-1]azapentalene (**3**), so far in vain [1–4]. The synthesis of benzo and dibenzo derivatives of **1** have been documented [5–8], but the published claims could not be substantiated [1, 2, 6, 9]. Since **3** is expected to be obtainable under mild and neutral conditions [2], a concerted elimination of the trimethylsilyl and benzensulfonyl groups from 5-benzensulfonyl-5,10-dihydro-10-trimethylsilylindeno[1,2-b]indole (**7**), by the action of fluoride ion, was attempted. The leaving groups, were, however, removed in a stepwise manner. The initial cleavage of the trimethylsilyl moiety by fluoride ion gave rise to the anion **8**. The ensuing electron transfer reactions resulted in the formation of (*E*)- and (*Z*)-5,5′,10,10′-tetrahydro-10,10′-biindeno[1,2-b]-indolylidene (**15**) as the major product. None of the desired **3** was observed. Also, an unexpected preference for silylation at the 10-carbon of dianion **5** (derived from 5,10-dihydroindeno[1,2-b]indole, **4**) over that of the nitrogen atom was noted when **5** was allowed to react with chlorotrimethylsilane.

Results and Discussion

Carbon-nitrogen double bonds can be formed by the base promoted elimination of the elements of arylsulfenic acid from N-arylsulfonamides [10]. When 5-ben-



Scheme 1



Scheme 2

zensulfonyl-5,10-dihydroindeno[1,2-b]indole (**9**) was allowed to react with potassium *t*-butoxide, the anion **8** that formed presumably underwent rapid elimination of the benzensulfenate anion to yield **3**, which was then rapidly attacked by unreacted **8** [2]. The dimeric product that formed suffered elimination of the benzensulfenate anion again, and, after a proton shift, yielded **15** [2]. Based on new evidence, it appears that in all probability, **3** was never formed *in situ*. It is more likely that the product **15** arose by a series of electron transfer reactions.

Since allyl anions can be generated by cleavage of the silicon-allylic carbon bond in allyltrimethylsilane [11], induced by fluoride ion, compound **7** was deemed suitable for the elimination process indicated in Scheme 1. The use of a catalytic amount of 18-crown-6 to solubilize the potassium fluoride, and an excess of solvent, should result in low concentrations of the anion **8**, thus reducing formation of the dimer **15**, and permitting the isolation of **3**. Indeed, when **7** was exposed to anhydrous potassium fluoride and 18-crown-6 in dry tetrahydrofuran, the removal of the trimethylsilyl and the benzensulfonyl groups were observed. However, the major components in the crude product were identified as the dimer **15** and compound **9** (Scheme 2). Dibenzo[b,f-1]azapentalene (**3**) could not be detected. HPLC-analysis of the crude product indicated the presence of at least eight compounds. Four the major components were identified (Table 1) by comparison of their HPLC

Table 1. HPLC data; reaction of **7** with KF in *THF*. Samples of compounds **6**, **7**, and **4** had the same retention time of 1.15 min. See text for structures of **9** and **16**

Retention time (min)	Area (%)	Assignment
Crude product		
0.83	0.273	
1.09	0.322	
1.30	18.009	**9**
1.55	8.349	
1.73	0.358	
2.20	45.818	(*E*)-**15**?
2.44	13.166	**16**?
2.95	13.704	(*Z*)-**15**?
Crystalline product (m.p. 206–225° dec.)		
0.76	1.767	
1.23	0.379	**9**
2.13	78.318	(*E*)-**15**?
2.90	19.537	(*Z*)-**15**?
Crystalline product (m.p. 178–195° dec.)		
0.83	1.300	
1.30	0.747	**9**
2.21	74.116	(*E*)-**15**?
2.97	23.837	(*Z*)-**15**?

retention times with those of authentic samples, and by mass spectrometry (Experimental). The steric effects arising from the opposing indole moieties in (*Z*)-**15** would create more of a twist in the 10,10′ carbon-carbon double bond than that in (*E*)-**15**. Therefore the crude reaction product is expected to contain (*E*)-**15** in a larger amount. This result has been assumed in the assignment of retention times for (*E*)- and (*Z*)-**15** (HPLC). Protonation of the unreacted anion **8** during the hydrolytic work up would explain the observation of **9**. One of the components appeared to be 5,10-dihydroindeno[1,2-b]indol-10-one (**16**). An authentic sample of **16** was not available, but the assignment of retention time was made from its known [1] solubility characteristics which was similar to those of **15**. The parent ion, and a fragmentation pattern characteristic of **16** [1] was observed in the mass spectrum of the crude product. The origin of **16** is not clear. The materials obtained on recrystallization of the crude product showed no signal corresponding to **16** in the HPLC and mass spectral traces. Compound **9** and the isomers **15** were detected. Even if dibenzo[b,f-1]azapentalene (**3**) were present in the crude product, it would have been a minor component, undetectable by mass and infrared (C=N) spectrometry.

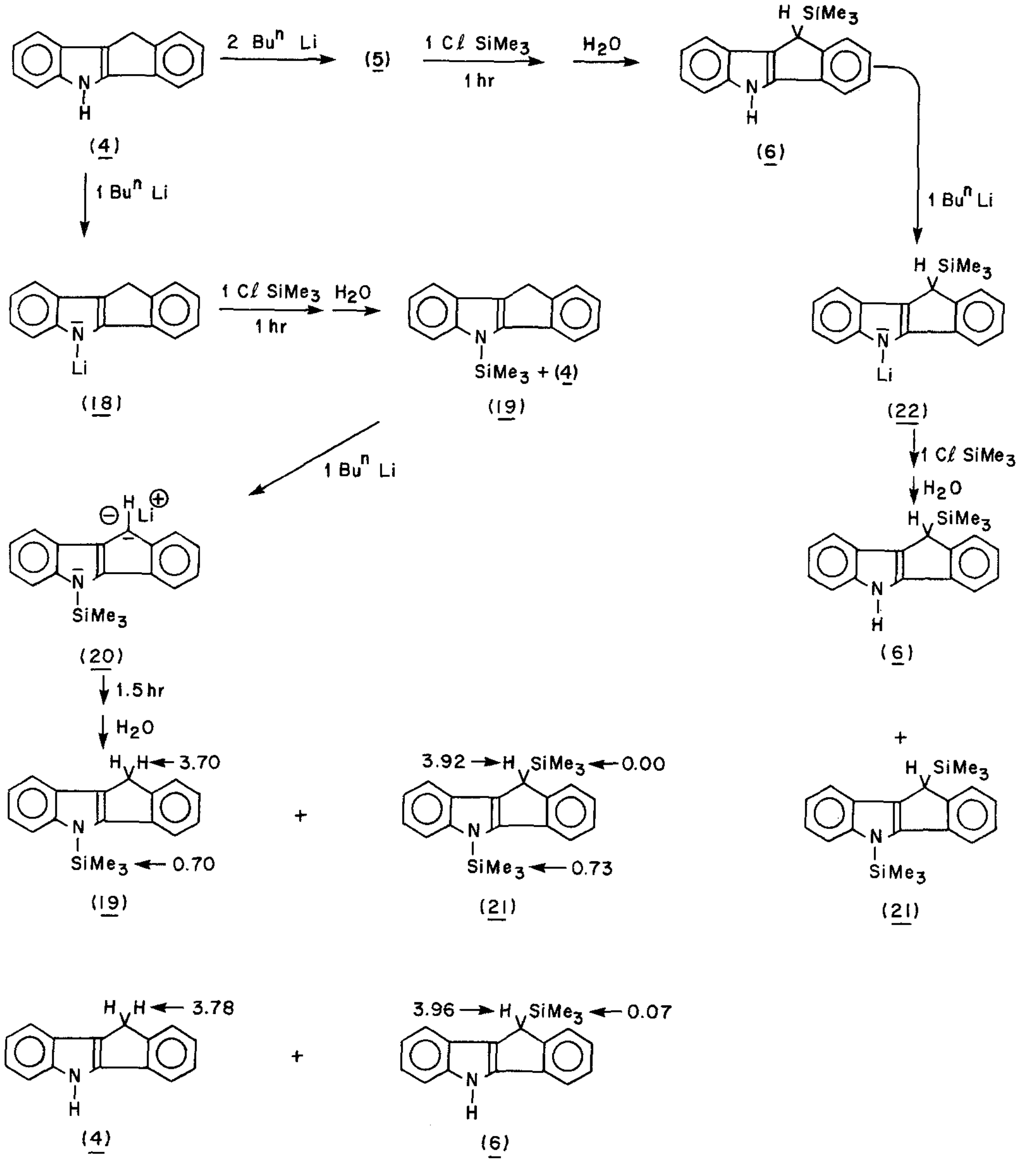
An attempt was made to trap **3** as its addition products with phenyllithium. A solution of 5-benzensulfonyl-5,10-dihydroindeno[1,2-b]indole (**9**) in anhydrous tetrahydrofuran was added to a large excess of phenyllithium. Dibenzo[b,f-1]azapentalene (**3**) was expected to form by metalation

Table 2. HPLC data; reaction of **7** with KF in benzene. Samples of compounds **6**, **7**, and **4** had the same retention time of 1.15 min

Retention time (min)	Area (%)	Assignment
Precipitated product		
0.91	6.204	
1.09	1.144	
1.23	0.888	
1.34	0.722	**9**
2.22	81.682	(*E*)-**15**?
2.71	0.669	
3.13	4.389	(*Z*)-**15**?
3.18	0.966	
3.23	3.335	
Crude product		
0.90	5.621	
1.17	5.296	
1.34	57.468	**9**
1.58	0.788	
1.87	0.288	
1.98	0.618	
2.23	21.285	(*E*)-**15**?
2.68	0.280	
2.93	1.884	(*Z*)-**15**?
3.09	1.149	
3.22	4.248	
4.09	0.225	
4.15	0.254	
4.28	0.215	
4.55	0.188	
4.68	0.164	

of a 10-H of **9** followed by the elimination of lithium benzensulfenate. However, no products corresponding to the addition of phenyllithium to **3** could be detected by mass and ^{1}H-NMR-spectrometry. 5,5′,10,10′-Tetrahydro-10,10′-biindeno[1,2-b]indoles (**17**) (presumed to be a mixture of *meso*- and *R,S*-isomers), 5,5′,10,10′-tetrahydro-10,10′-biindeno[1,2-b]indolylidenes (**15**), 5,10-dihydroindeno[1,2-b]indole (**4**), and diphenyl sulfone were detected by mass spectrometry and thin layer chromatography (unpublished results).

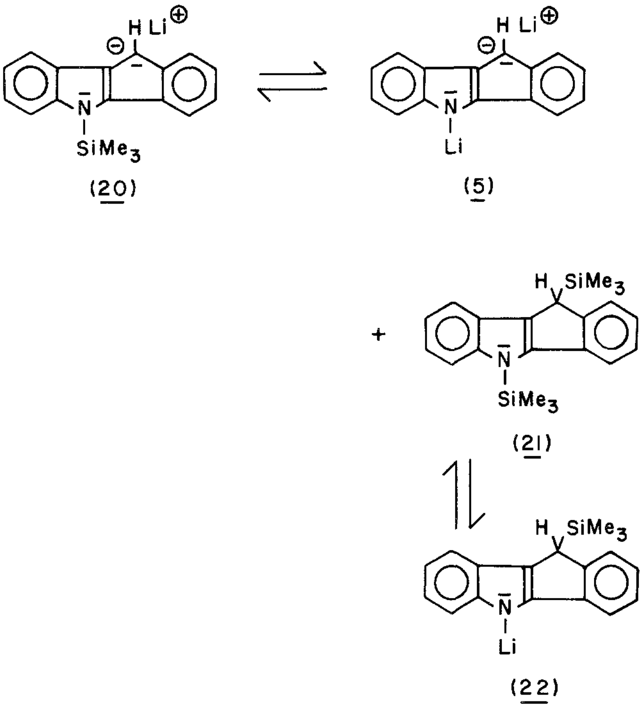
Perhaps due to its antiaromatic character [2], **3** is not formed. It seems reasonable to propose an electron transfer mechanism for these reactions, as illustrated for the reaction of **7** with fluoride ion (Scheme 2). The anion **8** that is expected to result from the cleavage of the trimethylsilyl group could undergo intermolecular electron transfer to the benzensulfonyl group instead of the conventional elimination process (Scheme 1). Coupling of the carbon radicals thus formed, homolysis of the nitrogen-sulfur bond to liberate the benzensulfenate anion, followed by hydrogen atom transfer would result in the observed product.



δ (ppm) PMR VALUES GIVEN. δ = 0.00 FOR C–SiMe$_3$ OF (21)

Scheme 3

In order to foster elimination over intermolecular electron transfer, **7** was allowed to react with potassium fluoride and 18-crown-6 in benzene. Anion **8** is expected to exist as a tight ion pair in this non polar solvent (when compared with *THF*), thus creating a barrier to the electron transfer processes and offering the possibility of isolating **3**. In benzene, the outcome of the reaction (Table 2) was similar to that observed in *THF*. The reactivity of **8**, as expected was lower in benzene when compared with *THF*. Thus a large quantity of **9** resulted from protonation of unreacted **8** during the work up of the reaction mixture. Compound

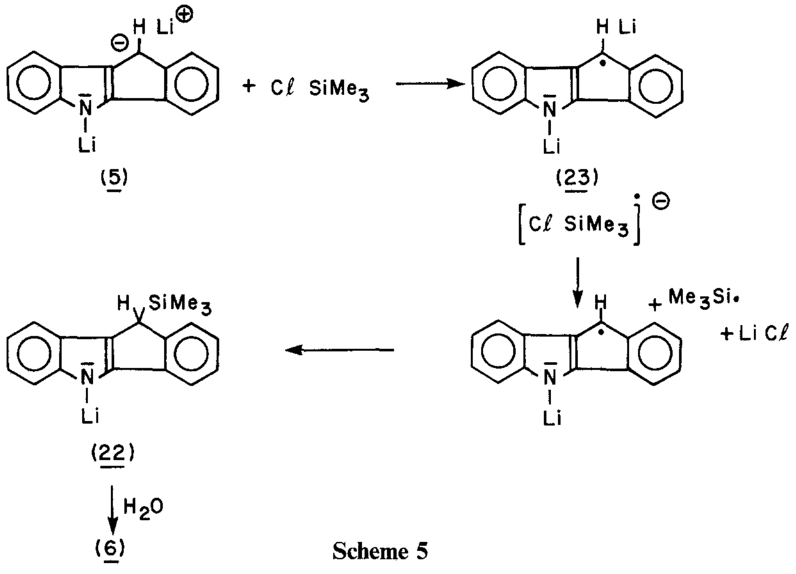


Scheme 4

9 was identified by HPLC, ^{1}H-NMR and mass spectrometry (Table 2, Experimental). Apparently the benzensulfenate anion was not eliminated in the expected manner.

Dibenzo[b,f-1]azapentalene has, so far, defied synthesis.

An unusual observation was made in the derivatization of the red dianion **5** with one equivalent of chlorotrimethylsilane to yield the C-10 silylated product **6** (Schemes 1 and 3). Due to the much higher silicon-nitrogen bond energy when compared with that of silicon-carbon bonds [12], the N-silylated derivative was expected to be formed. ^{1}H-NMR-signals other than those of **6** were barely discernable. Further, experimental evidence indicated that the 10-carbon of **5** was silylated directly, and that **6** was not the result of a nitrogen to carbon rearrangement of the trimethylsilyl group. Of course, in the absence of any charge in the carbocyclic ring, the charged heterocyclic ring is silylated. For example, **19** is formed when the colorless monoanion derived from **4**, namely **18**, is allowed to react with one equivalent of chlorotrimethylsilane. The only other component detectable by NMR was **4**, which could have arisen by incomplete reaction or by the partial hydrolysis of **19** during the aqueous work up. By ^{1}H-NMR, the ratio of the 10 H's of **4** to those of **19** was 1 : 3.2. When **19** was metalated at 0° with one equivalent of *n*-butyllithium, the red anion **20** was formed. After 1.5 h, the crude product obtained after hydrolytic work up was analyzed by NMR spectrometry. Three times as much of compound **6** was present when compared with either **19** or **21**, the latter compounds being present in approximately equal amounts (areas of the trimethylsilyl groups in the NMR spectra). A large amount of **4** was observed. The ratio of the 10-H's of **4** to those of **19** was 6.4 : 1. These observations can be explained if **20**



Scheme 5

reacts with itself to give **5** and **21**, which then could react to give **6** (Scheme 4). The presence of a large quantity of **4** on aqueous work up implicates the intermediacy of **5** in the formation of **6**. When the anion **20** was allowed to remain overnight before work up, the quantities of **19** and **4** decreased, and that of **21** increased. The ratio of **21** to **6** was 1 : 2. These reactions are best viewed as a series of equilibria (Scheme 4) involving nucleophilic displacements of the trimethylsilyl groups. It also seems reasonable to conclude that **6** arose by direct silylation of the charged carbocyclic ring of the red dianion **5**. Since chlorotrimethylsilane is a good electron acceptor [13], and since the charged carbocyclic ring of **5** is a better electron donor than the heterocyclic ring [3, 4], the electron transfer processes of Scheme 5 would explain the formation of **6**. The radical anion **23** that formed after electron transfer from **5** to chlorotrimethylsilane couples with the trimethylsilyl radical generated by the ejection of chloride ion from the chlorotrimethylsilane radical anion.

Acknowledgements

The synthesis of 5,10-dihydro-10-trimethylsilylindeno[1,2-b]indole was first reported in T. Abraham's doctoral dissertation which was directed by Professor John J. Eisch. Mr. Charles Benner provided the HPLC data, and Dr. Chi Yu the mass spectral data.

Experimental

Instruments Used

1. Varian EM360A 60 MHz ^{1}H-NMR spectrometer. Chemical shifts are given in parts per million from internal *TMS*. 2. Beckman IR-33 spectrophotometer. 3. Finnigan 4021 electron impact mass spectrometer. Data was recorded at an ionizing voltage of 70 eV. 4. Waters Associates Model 244 Liquid Chromatograph. Model 440 Absorbance Detector (254 nm). Column: 5 micron Resolve silica; Solvent: 25 volume% tetrahydrofuran in hexane; Flow rate: 2 ml/min.

Tetrahydrofuran and benzene were dried by distillation under nitrogen from sodium benzophenone ketyl and calcium hydride respectively. *n*-Butyllithium (Aldrich) was titrated before use.

5,10-Dihydro-10-trimethylsilylindeno[1,2-b]indole (**6**) [1]

n-Butyllithium [107.2 mmol, 1.6 *M* (hexane)] was added dropwise, under nitrogen, to a stirred (magnetic bar) solution of 5,10-dihydroindeno[1,2-b]indole (10.0 g, 48.8 mmol) in 100 ml of anhydrous tetrahydrofuran (*THF*). During the addition, the reaction flask was maintained at 0°, after which stirring was continued at room temperature for 1 h. Chlorotrimethylsilane (6.8 ml, 53.7 mmol; distilled from calcium hydride under nitrogen) in 10 ml of anhydrous *THF* was then added dropwise to the cooled (ice bath) solution of the blood red dianion derived from the indenoindole. The red color was discharged as soon as the addition of chlorotrimethylsilane was completed. After stirring overnight at room temperature, 12.6 g of an off-white crude was isolated after the addition of water and extraction with methylene chloride. Two recrystallizations from methylene chloride/hexane mixtures gave 7.0 g of the desired product, m.p. 177–178° (52%).

5-Benzensulfonyl-5,10-dihydro-10-trimethylsilylindeno[1,2-b]indole (**7**)

n-Butyllithium [16 mmol, 1.6 *M* (hexane)] was added dropwise under nitrogen to a stirred and cooled (ice bath) solution of 5,10-dihydro-10-trimethylsilylindeno[1,2-b]indole (4.35 g, 15.7 mmol) in 50 ml of anhydrous *THF*. The solution thus obtained was stirred at room temperature for 0.5 h and then added dropwise under nitrogen to a stirred and cooled (ice bath) solution of benzensulfonyl chloride (4.0 ml, 31.3 mmol) in 25 ml of anhydrous *THF*. After stirring for 3 h at room temperature, methylene chloride was added to the reaction solution. The organic layer was washed well with water and dried ($MgSO_4$).

Silica gel (25.0 g) was added to this solution of the crude product and the solvents were removed by rotary evaporator (bath temperature 50°). The silica gel containing the adsorbed crude was placed in a column containing 150 g of the adsorbent. Elution was started with hexane; the polarity of the solvent was then gradually increased to 25% methylene chloride in hexane. A white solid (3.7 g, discolored yellow) was eluted. Recrystallization from a methylene chloride/hexane mixture gave the desired product as white crystals [2.4 g (36%), m.p. 128–152° dec.]. Calculated for $C_{24}H_{23}NO_2SSi$: C 69.02, H 5.55, N 3.35, S 7.67, Si 6.72. Found: C 70.73, H 5.46, N 3.47, S 7.71, Si 6.22. IR (KBr, cm^{-1}): 3 065 (w), 2 982 (w), 1 450 (s), 1 373 (s), 1 252 (s), 1 180 (s), 845 (s), 750 (s), 725 (s). NMR ($CDCl_3$, δ): 0.00 (s, 9 H), 0.23 (*TMS*), 3.95 (s, 1 H), 7.24–8.16 (m, 11 H), 8.46–8.97 (m, 2 H). MS (M^+, intensity): 417 (2.28), 344 (0.49), 276 (16.17), 205 (1.86), 204 (19.38), 203 (100), 202 (4.93), 201 (2.21).

Action of Potassium Fluoride on 5-Benzensulfonyl-5,10-dihydro-10-trimethylsilylindeno[1,2-b]indole (**7**) *in THF*

0.8 g **7** (1.91 mmol) in 25 ml of anhydrous *THF* was added dropwise, under nitrogen, at room temperature, to a suspension of potassium fluoride (5.2 g) in 50 ml of anhydrous *THF* containing 18-crown-6 (0.13 g). The solution became light green, then purple as the addition progressed. After stirring 4 h at room temperature, the reaction mixture was poured into water. The permanganate colored precipitate thus obtained was filtered off and dried overnight in air (0.53 g, m.p. 140° dec.). IR KBr, cm^{-1}): 3 405. Recrystallization from a *THF*/hexane mixture gave 0.13 g of permanganate colored crystals, m.p. 206–225° dec., and 0.3 g of crystals from the filtrate, m.p. 178–197° dec.

Data obtained on these materials by high performance liquid chromatography is given in the main body of the paper. Mass spectral data was recorded as the samples were gradually heated from room temperature to 400°. The data is recorded in the order of appearance of the parent ion peaks. As the temperature of the sample was increased, peaks due to the more volatile compounds disappeared, while those of the less volatile ones appeared. MS (M^+, intensity):

5-Benzensulfonyl-5,10-dihydroindeno[1,2-b]indole (**9**). 346 (6.97), 345 (27.86), 205 (17.42), 204 (100), 203 (25.87), 202 (6.69), 201 (4.33).

5,10-Dihydroindeno[1,2-b]indol-10-one (**16**). 220 (20.12), 219 (100), 218 (42.60), 205 (5.70), 204 (25.43), 203 (16.50), 202 (12.91), 200 (10.75), 191 (6.84), 190 (33.46), 109 (58.11).

(*E*)- and (*Z*)-5,5′,10,10′-Tetrahydro-10,10′-biindeno[1,2-b]indolylidenes (**15**). 408 (2.48), 407 (13.84), 406 (43.44), 405 (7.98), 404 (8.69), 403 (4.38), 402 (2.07), 401 (1.89), 205 (1.23), 204 (6.05), 203 (15.72), 202 (18.44), 201 (19.56).

Action of Potassium Fluoride on 5-Benzensulfonyl-5,10-dihydro-10-trimethylsilylindeno[1,2-b]indole (7) *in Benzene*

Compound **7** (1.29 g, 3.08 mmol) in 20 ml of anhydrous benzene was added dropwise under nitrogen to a suspension of 9.0 g potassium fluoride in 150 ml of anhydrous benzene containing 18-crown-6 (0.2 g). The benzene solution turned green and then to a permanganate color. After stirring for 4 h at room temperature, the benzene solution was washed with water. During the work up, a permanganate precipitate that appeared in the benzene solution was filtered off and dried in air (0.05 g). After drying ($MgSO_4$), 0.65 g of a permanganate colored solid was recovered from the benzene solution. NMR ($CDCl_3$, δ, benzene soluble fraction, external *TMS*): − 0.22, 0.00 (*TMS*), 0.02, 0.06, 0.15, 0.2–0.6 (trace), 0.94 (trace), 3.67 (s) (10 H's of **9**), 6.60–8.07 (m), 8.20–8.80 (m).

Reactions of the Mono and Dianions of 5,10-Dihydroindeno[1,2-b]indole (**4**) *and of the Monoanion of 5,10-Dihydro-10-trimethylsilylindeno[1,2-b]indole* (**6**) *with Chlorotrimethylsilane*

n-Butyllithium (1 or 2 equivalents, 2.6 *M* in hexane) was added dropwise *via* syringe, under nitrogen, to a cooled (ice bath) solution of the indole (0.5 g) in 10 ml of anhydrous *THF*. After stirring at room temperature for 1 h, chlorotrimethylsilane (1 equivalent) was introduced dropwise by syringe to the cooled (ice bath) *THF* solution. Stirring was continued at room temperature for the periods specified elsewhere in the text.

Methylene chloride was then added and the organic layer extracted twice with equal volumes of water. After drying ($MgSO_4$), the organic layer was evaporated to a crude solid and dried overnight (40°/0.1 mm Hg). ^{1}H-NMR spectra of the crude solids were recorded in pyridine (0.1 g/ml). Pyridine proved useful as solvent when compared with dimethyl sulfoxide-d_6 or acetone-d_6 where the solvent d_5 and water absorptions appeared in the region of interest (0–4 ppm from *TMS*). Chemical shifts are documented in Scheme 3.

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