Monatshefte für Chemie 113, 1275—1282 (1982)

Monatshefte für Chemie
Chemical Monthly

Electron Transfer from Dibenzo[*b*,*f*]-1-azapentalene Dianion: Attempted Synthesis of Dibenzo[*b*,*f*]-1-azapentalene

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(Received 8 March 1982. Accepted 14 April 1982)

When dibenzo[*b*,*f*]-1-azapentalene dianion (**3**) was allowed to react with either iron (III) chloride or ethylene bromide, a one-electron transfer from **3** took place readily to give the radical anion **11**. Further electron transfer from **11** did not occur presumably due to the antiaromatic character of dibenzo[*b*,*f*]-1-azapentalene (**1**) that would have resulted. The radical anion **11** underwent further transformation by hydrogen abstraction from the solvent to give 5,10-dihydroindeno[1,2—*b*]indole (**2**) and by dimerization to the *meso* and (*R*, *S*) isomers of 5,5',10,10'-tetrahydro-10,10'-biindeno[1,2—*b*]indole (**4a** and **4b**) respectively.

(Keywords: Antiaromatic character; Dibenzo[b,f]-1-azapentalene dianion; Electron transfer; Lithiation)

Elektronentransfer von Dibenzo[b,f]-1-azapentalen-Dianion: Ein Versuch zur Synthese von Dibenzo[b,f]-1-azapentalen

Die Reaktion von Dibenzo[*b*,*f*]-1-azapentalen-Dianion (**3**) mit Eisen(III) oder Ethylenbromid ergab einen Ein-Elektronentransfer zum Radikalanion **11**. Ein weiterer Elektronentransfer fand nicht statt, vermutlich wegen des antiaromatischen Charakters von Dibenzo[*b*,*f*]-1-azapentalen (**1**), das dabei entstehen müßte. Das Radikalanion **11** ergab unter Wasserstoffentzug aus dem Lösungsmittel 5,10-Dihydroindeno[1,2—*b*]indol (**2**), das weiter zum *meso*- bzw. (*R*, *S*)-5,5',10,10'-tetrahydro-10,10'-biindeno[1,2—*b*]indol (**4a** bzw. **4b**) dimerisierte.

Introduction

In a continuation of the study of heterocyclic antiaromaticity as applied to dibenzo[*b*,*f*]-1-azapentalene (**1**)[1–4], attempts were made to obtain **1** by oxidation of dibenzo[*b*,*f*]-1-azapentalene dianion (**3**). This

0026-9247/82/0113/1275/$ 01.60

paper deals with the oxidation of **3** by iron(III) chloride and ethylene bromide. Preliminary results indicated that both these oxidation reactions yielded the dimeric product **4**[2].

Dianions that form aromatic compounds by two-electron transfer are readily oxidized by cadmium(II) chloride. For example, the dianion derived from 9,10-dihydroanthracene underwent smooth electron transfer to form anthracene in the presence of cadmium(II) chloride, the latter being reduced to metallic cadmium[5]. Perhaps an organocadmium intermediate was responsible for the change in color from red to green on the addition of cadmium(II) chloride to a tetramethylethylenediamine-cyclohexane solution of the red dianion (**3**). The reisolation of 5,10-dihydroindeno[1,2—*b*]indole (**2**) reflected the resistance to disruption of the aromaticity of the dianion **3**[2].

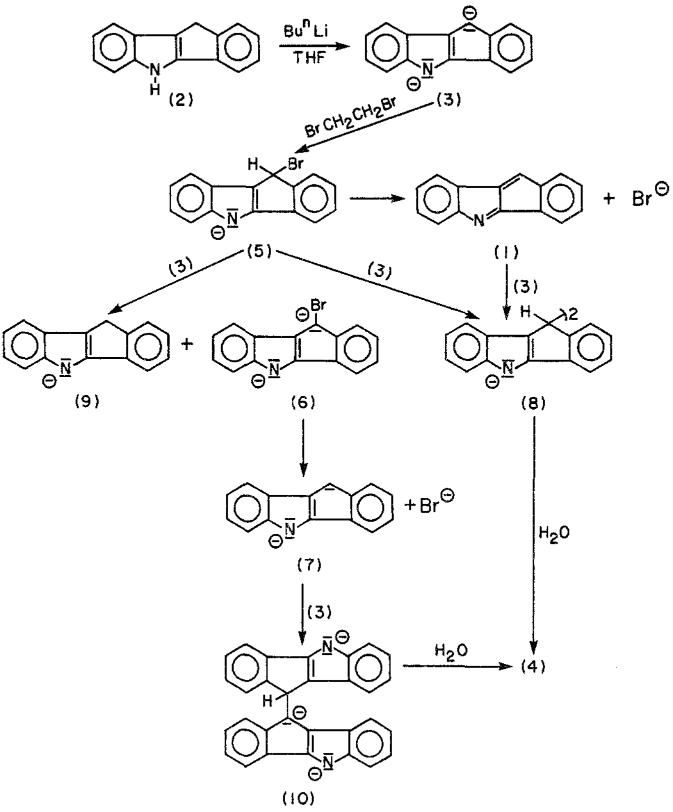
Results and Discussion

The proton magnetic resonance (pmr) spectrum of the crude product obtained from the iron(III) chloride oxidation of the dianion **3** indicated the presence of 5,10-dihydroindene[1,2—*b*]indole (**2**) [58 mole %] and a mixture of the *meso* and (*R*, *S*) isomers of 5,5′,10,10′-tetrahydro-10,10′-biindeno[1,2—*b*]indole (**4a** and **4b**) respectively [42 mole %]. The ratio of **4a**:**4b** was 33:67. The mole proportions were determined by comparison of the **10** protons of **2** (singlet, δ 3.70) with those of the 10,10′ protons of **4a** (singlet, 4.92) and **4b** (singlet, 5.02). Analysis of the crude product by high performance liquid chromatography (*HPLC*) substantiated these figures (Table 1). The aromatic region of the pmr spectrum had an area of 8% in excess of that required to account for **2** and **4**. Other components in the crude were presumably responsible for this discrepancy. HPLC data indicated the presence of seven trace components in the crude product, in addition to the five major components. Three of these were identified as **2**, **4a**, and **4b**. The two remaining components have not yet been identified (Table 1). By chemical ionization mass spectroscopy, molecular ion peaks corresponding to **2** and **4** were observed. Also, at least six other molecular ion peaks were observed (experimental section).

Dibenzo[*b*,*f*]-1-azapentalene (**1**) was expected to form by the reaction of the dianion **3** with ethylene bromide *via* elimination of lithium bromide from the bromo intermediate **5**. The outcome of this reaction was, however, similar to that of the iron(III) chloride oxidation of **3**. The major components were 5,10-dihydroindeno[1,2—*b*]indole (**2**) and the dimers **4a** and **4b** (Table 1). HPLC analysis showed seven other trace components in the crude reaction product.

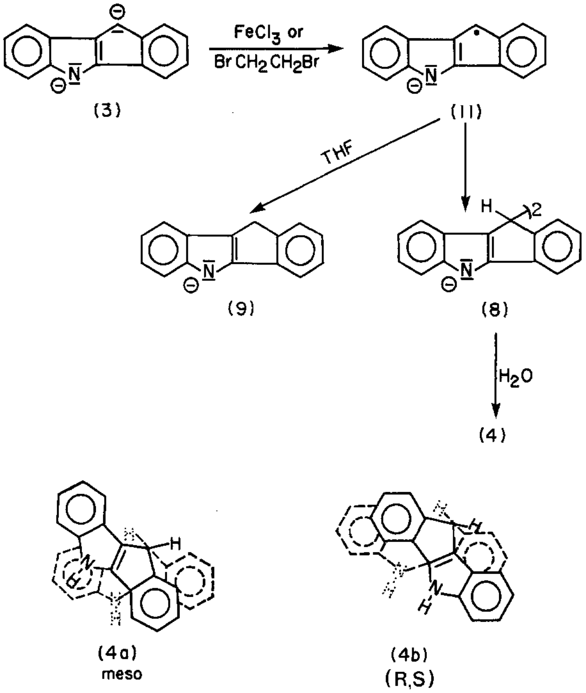
Studies of the reactions of 9-halofluorenes with *Grignard* reagents suggests that the dimer **4** could have formed by an S_N2 and/or electron transfer reaction[6] of the bromoindenoindole **5** with the dianion **3**. The red color of the dianion **3** was completely discharged by the addition of ethylene bromide, which seemed to imply that **2** in the crude did not result by the protonation of unreacted **3** during work-up. Compound **2** could also have arisen from **9** which would form along with the dianion **6** in the metalation of **5** by **3**. The dimer **4** could then result by the reaction of **3** with the carbene **7** formed from **6**. However, kinetic studies of the reaction of 9-halofluorenes with base are not in keeping with this reaction pathway[7]. The bromoindenoindole **5** could also have suffered the elimination of lithium bromide to yield **1** which could have undergone attack by the dianion **3** to yield **4** (Scheme 1).

Scheme 1



The outcome of the reactions of **3** with iron(III) chloride and ethylene bromide were similar. These reactions are best explained in terms of an electron transfer mechanism (Scheme 2). As observed previously[4], electron transfer takes place preferentially from the charged carbocyclic ring of **3**. The resultant radical anion **11** can abstract a hydrogen atom from the solvent to give **2** or dimerize to **4**.

Scheme 2



Some Comments on 5,5′,10,10′-Tetrahydro-10,10′-biindeno[1,2—b]indole (4)

The structural assignment to the product **4** was based on mass, pmr, and infrared spectral data. The precipitate that appeared in the methylene chloride extract during the work-up of the reaction of **3** with ethylene bromide consisted of two major components (**4a**, **4b**), a trace of **2**, and a trace of an unknown component. The mass spectrum of the precipitate indicated the presence of a parent ion corresponding to **4** in addition to other parent ions (experimental section). Due to the varying volatilities of these compounds it was not possible to relate intensities of the parent ion peaks with the relative amounts of the compounds in the crude mixture.

The proton magnetic resonance spectrum of the precipitate in *DMSO-*d_6 was as follows (δ values): 4.92 (s, 2), 5.02 (s, 2), 5.4 (br, 1), 5.55 (br, 1), 6.20–7.95 (m, 32), 8.00–8.60 (br, 4). The 10-protons of 5,10-dihydroindeno[1,2—*b*]indole (**2**) appeared as a singlet at δ 3.70. The singlets at δ 4.92, 5.02 were expected of the 10,10′ protons of the isomers of 5,5′,10,10′-tetrahydro-10,10′-biindeno[1,2—*b*]indole (**4**), as these molecules were probably in the gauche conformation which would bring the 10,10′ protons into the deshilding space of the aromatic rings. For example, the 9 protons of 9-*H*-fluorene appeared at δ 3.87[8], but the 9,9′-protons of 9,9′-bifluorenyl appeared at δ 4.71[9] due to the predominance of the gauche rotamer of this molecule. In solution, 9,9′-bifluorenyl equilibrated rapidly between two gauche rotamers either *via* the anti (9,9′-H's anti) or the eclipsed conformation. Low temperatures slowed down this process which resulted in the broadening of the pmr spectrum of the aromatic region and also caused an upfield shift of the 1,1′-H's absorptions due to their presence directly below the opposing aromatic rings[10].

Inspection of models showed that in *meso* (**4a**) interconversion of the two gauche rotamers *via* the eclipsed conformation (10,10′ H's eclipsed) by rotation about the 10,10′ C—C bond led to severe steric interactions between the indole rings. Interconvertion between the gauche forms *via* the anti position appeared to be less hindered. On the basis of models, the *meso* compound (**4a**) would be expected to display slow rotation between the two gauche forms in comparison with the racemate (*R*, *S*) (**4b**). This resulted in the observation of the pmr signals for the 1,9′ and 1′,9 H's of **4a** while these hydrogens were in the shielding regions of the opposing aromatic rings. Hence the broad signals at δ 5.4, 5.55 (1 H each) corresponded to the singlet at 4.92 (2 H, 10,10′ H's).

The racemic form (**4b**) probably interconverted between its gauche forms *via* the eclipsed position (10,10′ H's eclipsed). A study of a model of this compound revealed no severe steric barriers in the eclipsed conformation, the anti conformation being the most hindered. Thus **4b** was not expected to display any aromatic absorptions upfield and the aromatic absorptions appeared together as a multiplet. The 10,10′ H's appeared as a singlet at δ 5.02.

The major portion of the crude from the ethylene bromide oxidation of **3** contained more of the (*R*, *S*) isomer (**4b**) in comparison with the *meso* product (**4a**) (pmr, HPLC, Table 1). On dissolving this crude in dimethyl sulfoxide and reprecipitating it in water, the more soluble **4b** remained dissolved to a larger extent than **4a**, thus reducing the intensity of the absorption at δ 5.02 in comparison with that at δ 4.92.

The less soluble **4a** exhibited signals at δ4.92, 5.4 and 5.55 in the expected proportions. The relative ratio of **4a** to **4b** was further confirmed by HPLC analysis.

Two electrons could not be transferred from dibenzo[*b,f*]-1-azapentalene dianion to either iron(III) chloride or ethylene bromide under the conditions employed. After transfer of the first electron, further electron transfer to yield dibenzo[*b,f*]-1-azapentalene (**1**) was unsuccessful presumably due to the antiaromaticity of **1**. Instead, the radical anion **11** that formed was transformed by the abstraction of a hydrogen atom from the solvent to give **2** and by dimerization to **4**.

Table 1. HPLC *data*

	Compound	**2**	**12**[a]	?	?	*meso* **4a**	(*R*, *S*) **4b**	mol% **4a**:**4b**	mol%[b] **2**:(**4a** + **4b**)
	Retention Time (min)	2.48	2.79	4.13	4.44	4.72	5.03		
Relative Areas	Ppt[c] from ethylene bromide oxidation (11% by *wt* of crude)	0.1				9.1	2.3	80:20 (78:22)[d]	2:98 (—)[d]
	Crude from ethylene bromide oxidation	4.2	2.3			2.0	6.4	24:76 (30:70)[d]	50:50 (52:48)[d]
	Crude from iron(III) chloride oxidation	5.7		0.9	1.5	1.8	4.0	31:69 (33:67)[d]	66:34 (58:42)[d]

[a] See experimental section for structure of **12**.

[b] Calculated assuming that the response factor for **4** would be twice that for **2** on a mole to mole basis (absorbance detected at 254 nm).

[c] Some of the precipitate remained undissolved in tetrahydrofuran, the solvent used to introduce the sample into the chromatograph.

[d] Estimated from pmr spectra by comparison of the signal intensities of the 10 H's of **2** with those of the 10,10′ H's of **4**.

Acknowledgements

Preliminary results related to this work are reported in *T. Abraham*'s doctoral dissertation which was directed by Professor *John J. Eisch*.

Mr. *Charles Benner* of the University of Dayton Research Institute operated the liquid chromatograph. Dr. *Chi Yu* of Miami University, Oxford, Ohio, recorded the mass spectral data.

Experimental

Instruments Used

1. Varian EM 360 A 60 MHz ^{1}H-NMR spectrometer. Chemical shifts are given in parts per million from internal *TMS*.

2. Beckman IR-33 spectrophotometer.

3. DuPont 21-490 chemical ionization mass spectrometer. Data were recorded at an ionizing voltage of 70 eV (source temperature 200°, sample temperature given) with methane as the ionizing gas.

4. Water Associates Model 244 Liquid Chromatograph. Model 440 Absorbance Detector (240 nm). Column: μ Porasil P/N 27477 S/N; Solvent: 20 volume % tetrahydrofuran in hexane; Flow rate: 2 ml/min.

Tetrahydrofuran was dried by distillation under nitrogen from sodium benzophenone ketyl. Ethylene bromide was distilled under nitrogen from calcium hydride. Anhydrous iron(III) chloride (Pennwalt) was used as received. *n*-Butyllithium (Aldrich) was titrated before use.

Reaction of Dibenzo[b,f]-1-azapentalene Dianion with Ethylene Bromide

Under nitrogen, *n*-butyllithium (10.8 mmol, 6.4 ml of a 1.69 *M* solution in hexane) was added dropwise to a cold (ice-bath), stirred solution of 5,10-dihydro indeno[1,2—*b*]indole[4] (1.0 g, 4.87 mmol) in 50 ml of anhydrous tetrahydrofuran (*THF*). The red solution of the dibenzo[*b*,*f*]-1-azapentalene dianion thus formed was stirred for 45 min at room temperature. Ethylene bromide (0.5 ml, 5.85 mmol) in 10 ml of anhydrous *THF* was then added dropwise to the recooled (ice-bath) reaction mixture. The red color of the dianion was soon discharged and the contents of the reaction vessel was stirred overnight at room temperature.

The reaction solution was poured into 150 ml of methylene chloride and washed several times with water in order to remove most of the *THF*. During this procedure a white precipitate appeared at the interface of the water and organic layers. The precipitate was filtered off, washed with distilled water, and dried [overnight at 80°/0.1 mm Hg, 0.1 g, mp. 360-361° (vacuum sealed capillary)]. This material was shown to be a mixture of the *meso* and (*R*, *S*) isomers of 5,5′,10,10′-tetrahydro-10,10′-biindeno[1,2—*b*]indoles (**4 a**) and (**4 b**) respectively, and a trace of the starting material 5,10-dihydroindeno[1,2—*b*]indole (**2**) (HPLC data in Table 1, spectral data). In addition to the components in Table 1, a trace component (3.24 min) was also present.

IR (KBr): 3 405 (m), 3 055 (m), 1 605 (s), 1 522 (m), 1 502 (s), 1 482 (m), 1 453 (s), 1 441 (s), 1 382 (s), 1 360 (ω), 1 310 (s), 1 278 (s), 1 248 (s), 1 220 (ω), 1 150 (ω), 1 132 (s), 1 116 (ω), 1 100 (ω), 1 090 (ω), 1 033 (ω), 1 010 (s), 970 (ω), 938 (m), 926 (m), 885 (ω), 875 (ω), 856 (ω), 835 (ω), 820 (ω), 813 (ω), 785 (ω), 760 (s), 735 (s), 710 (s), 680 (ω), 670 (ω), 645 (ω), 635 (m), 620 (ω), 610 (ω).

PMR (*DMSO*-d_8): *meso* (**4 a**): 4.92 (s, 2), 5.40 (br, 1), 5.55 (br, 1), 6.20-7.95 (m, 16), 8.00-8.60 (br, 2). (*R*, *S*) (**4 b**): 5.02 (s, 2), 6.20-7.95 (m, 16), 8.80-8.6 (br, 2).

MS (200-400°): Molecular ion peaks corresponding to **4** and **2** were present. Parent ion peaks were also observed at *m*/e 433, 435 and 437 (containing two bromine atoms), in addition to seven other parent ions between 200-400.

The methylene chloride layer was dried ($MgSO_4$) and then evaporated to an off-white solid which was dried overnight (80°, 0.1 mm Hg, 0.8 g). This crude contained starting material (**2**), 5,10-dihydro-10-ethenylindeno[1,2—*b*]indole (**12**) or an isomer of **12**, and the biindoles **4 a** and **4 b** (HPLC, Table 1, spectral data). HPLC analysis of the small quantity of sublimate (ca. 0.01 g) that collected during the drying process indicated the major components to be **2**, and **12** or one of its isomers. The molecular ion peak for **12** was observed at *m*/e 231. In addition to those listed in Table 1, trace components were present at 1.81, 2.00, 5.39 and 5.66 min.

PMR (*DMSO-d*$_6$): **2**: 3.70 (s, 2), 6.15–8.56 (m, 9).

Meso-**4 a**: 4.93 (s, 2), 5.45 (br, 1), 5.60 (br, 1), 6.15–8.56 (m, 18). (*R*, *S*)-**4 b**: 5.05 (s, 2), 6.15–8.56 (m, 18).

MS (180°): *m*/e 205, 231, and 311, 313 (containing one bromine atom). MS (300°): *m*/e 408.

Reaction of Dibenzo[b,f]-1-azapentalene Dianion with Iron(III) Chloride

To a cold (ice bath) solution of the dianion **3** made from **2** (1.0 g, 4.87 mmol) was added anhydrous iron(III) chloride (2.37 g, 14.6 mmol) in one portion. Work-up of the reaction solution was performed as before. It was difficult to remove residual *THF* from the crude isolated. After drying as before (overnight, 80°/0.1 mm Hg), drying had to be continued (40 h, 100°, 0.1 mm Hg). The light brown crude material isolated weighed 0.95 g. In addition to those listed in Table 1, trace components were present at 2.00, 7.4, 8.07, 9.44, 10.31, 11.49 and 12.32 min.

MS (200–380°): Molecular ion corresponding to **2** and five other molecular ions between *m*/e 200–390. MS (400°): Molecular ion corresponding to **4** and a parent ion at *m*/e 483.

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