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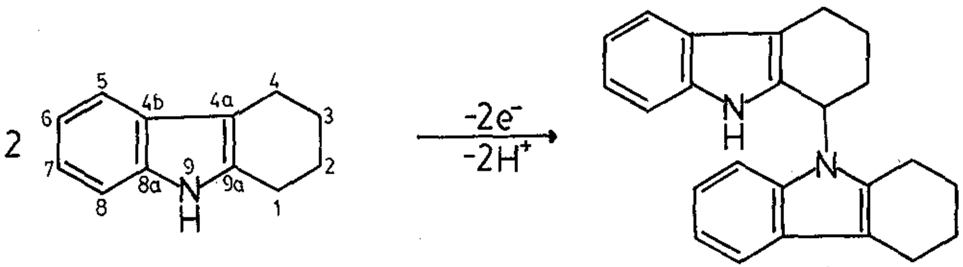
ANODIC DIMERIZATION OF 1,2,3,4-TETRAHYDROCARBAZOLE[1]

James M. Bobbitt* and John P. Willis

Department of Chemistry, The University of Connecticut
Storrs, Conn. 06268, U.S.A.

The oxidation of 1,2,3,4-tetrahydrocarbazole (1) in CH_3CN-H_2O (9:1) containing $LiClO_4$ (0.1N) at a graphite anode, in a two-compartment cell, and at +0.7 V (*vs*. SCE) gives a dehydro-dimer in 60-90% yield. The dimer has been identified as the 1,9' dimer (2).

For a number of years, we have been interested in the electrochemical dimerization of phenolic isoquinoline alkaloids.[2] We have now turned our attention to indole derivatives which are similar to phenols in many ways. Both phenols and indoles have similar electronic characters and electrochemical decomposition potentials, and both play roles in alkaloid biosynthesis. The dimeric *vinca* alkaloids in particular[3] are formed by an oxidative coupling reaction between two indole containing moieties. Tetrahydrocarbazole itself has been previously oxidized with Ni_2O_3 to the 4a-4a' dimer.[4]

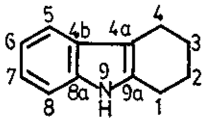


1 2

The anodic oxidation of 1 was carried out as follows: 120 ml of CH_3CN-H_2O (9:1), 0.1N in $LiClO_4$ was pre-electrolyzed for 20 minutes under N_2 at +0.70V vs. SCE in a two compartment cell. The electrodes were graphite felt[5] and were separated by a Nafion ion exchange membrane.[6] Compound 1 (250 mg) was added, and the electrolysis was allowed to proceed until no more starting material was visible by tlc (hexane-MeOH-EtOAC, 9:0.5:0.5). The time and current required for oxidation corresponded to the loss of 1e$^-$ per molecule.

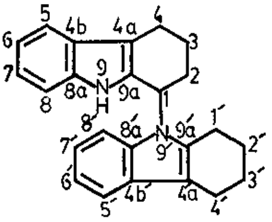
The reaction mixture was made strongly basic with NaOH and evaporated to near dryness under vacuum. The residue was partitioned between water and chloroform. The chloroform extract was dried over anhydrous Na_2SO_4. Rotary evaporation of the solvent yielded 244 mg (98%) of a light brown oil homogeneous by tlc. The oil was dissolved in 2-3 ml of acetone and cooled to about -10^0. After about 6 hours, 150 mg (60%) of a white crystalline product was obtained: m.p. 223-228^{0}d; ir (KBr) 3100 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.6-2.1 (m, 4H), 2.6-3.5 (m, 4H), 7.0-7.9 (m, 8H), 8.9 (s, 1H), ($CDCl_3$/DCl) δ 1.5-2.1 (m, 4H), 2.6-3.1 (m, 2H), 3.7 (t, 1H), 6.6-6.8 (m, 1H), 7.2-7.6 (m, 6H), 7.9-8.2 (m, 1H); mass spectrum m/e (rel. abundance) 340 ($M^{+\cdot}$, 100), 312 (10), 284 (10), 270 (5), 170 (18): Analysis, calculated for $C_{24}H_{24}N_2$: C, 84.76; H, 7.11; N, 8.23. Found: C, 84.49; H, 6.98; N, 7.99.

Table I. ^{13}C Chemical Shift Data for 1,2,3,4-Tetrahydrocarbazole.[a]



Carbon	Chemical Shift[b]
1	23.14
2	23.06
3	22.92
4	20.74
4a	109.79
4b	127.77
5	117.47
6	120.66
7	118.83
8	110.22
8a	135.67
9a	133.96

Table II. ^{13}C Chemical Shift Data for 1,9'-Tetrahydrocarbazole Dimer.[a]



Carbon	Chemical Shift[b]
1,1'	62.95, 29.00
2,2'	36.66, 22.98
3,3'	30.14, 22.98
4,4'	20.58, 21.59
4a, 4a'	107.83, 107.83
4b, 4b'	126.68, 126.76
5,5'	117.96, 119.84
6,6'	122.02, 124.77
7,7'	116.54, 134.47
8,8'	109.43, 130.33
8a, 8a'	136.22, 153.44
9a, 9a'	148.10, 176.11

[a] Spectrum taken in $CDCl_3$.

[b] 270 MHz, referenced to center of $CDCl_3$ triplet at 76.90 ppm downfield from TMS.

The structure proof of **2** rests upon analytical and spectroscopic evidence. The mass spectrum contains specific peaks at mass/charge ratios of 340 for the molecular ion and at 312 and 284 corresponding to the loss of two $CH_2=CH_2$ units from retro Diels-Alder reactions at positions 2 and 3 and 2' and 3' of **2**. Thus, there can be no substitution at these positions. The proton nmr spectrum ($CDCl_3$) of **2** is predictable and shows one NH at δ 8.9 (which can be exchanged by equilibration with DCl) and a one proton triplet ($CDCl_3$/DCl) at δ 3.7 corresponding to the hydrogen at either position 1 or 4. Therefore, the linkage must be between the nitrogen of one molecule and either position 1 or 4 of the other. Since the ir spectrum of 2 showed a hydrogen bonded NH at 3100 cm^{-1} (in contrast to **1** which does not), the linkage must be between positions 1 and 9' which allows for a five member intramolecular hydrogen bonded ring. The structure is also supported by ^{13}C nmr data as shown in Tables I and II for compounds **1** and **2** respectively.[5] The ^{13}C spectrum, besides showing the dimer to be unsymmetrical, reveals a striking change in the chemical shift of C-1 in **1** *vs.* **2**. A downfield shift of 39.8 ppm for C-1 of **2** (from **1**) is a consequence of the tertiary bonded nitrogen.

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1 This paper is dedicated with affection and respect to the late Professor Hans Schmid of the University of Zurich from whom I had the privilege of learning some chemistry--J.M.B.

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5 The WDF graphite felt was obtained from Carbon Products Division of Union Carbide Corp., New York, N.Y.

6 The Nafion membrane was graciously donated by the Plastics Division of the E. I. DuPont Co. of Wilmington, Delaware.

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