ANODIC DIMERIZATION OF 1,2,3,4-TETRAHYDROCARBAZOLE AND SOME OF ITS DERIVATIVES[1]

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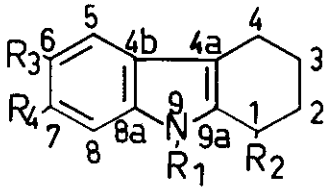
Abstract – The anodic oxidation of 1,2,3,4-tetrahydrocarbazole and two of its derivatives in aqueous acetonitrile at about +0.7 V (vs a standard calomel electrode and using a graphite felt anode) gave dimers having a linkage between carbon 4a of one unit and carbon 7 of the other. The oxidation of 5-methyl-5,6,7,8,9,10-hexahydrocyclohept[b]indole gave a corresponding dimer with a 5a-8' linkage. This is a correction and an extension of our earlier work.

The amino acid, tryptophan, is the biological precursor of the indole alkaloids, and a number of the biogenetic reactions involve oxidations. Furthermore, it has been noted frequently, most recently by Guengerich and MacDonald,[5] that there is a strong similarity between biological and electrochemical oxidations. For several years, we have been studying the electrooxidation of simple indole derivatives in order to gain insight into biological oxidation as well as to find new synthetic paths to the alkaloids themselves.[6,7]

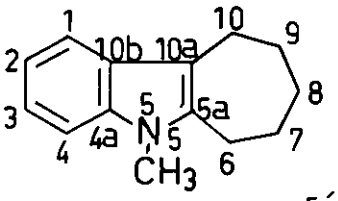
In 1980[6] we proposed structure 15 for the dimer obtained from the oxidation of tetrahydrocarbazole, 1 (1-H-2,3,4,9-tetrahydrocarbazole). On the basis of ^{13}C N.M.R. spectra (Table I) and the oxidation of suitably deuterated compounds, we now believe the structure to be 8. We have recently extended the work to N-methyltetrahydrocarbazole, 2, N-methyl-1-carbomethoxy-1,2,3,4-tetrahydrocarbazole, 3, and 5-methyl-5,6,7,8,9,10-hexahydrocyclohept[b]indole, 7, which gave similar dimers.

PREPARATION OF COMPOUNDS

Compounds 2 and 3 were prepared by methylation[8] of 1 and 1-carbomethoxy-1,2,3,4-tetrahydrocarbazole.[9] 7-Deutero-1,2,3,4-tetrahydrocarbazole, 4, was prepared by catalytic deuteration[10] of 7-chloro-1,2,3,4-tetrahydrocarbazole.[11] Compound 5 was prepared from 4 by methylation. In addition, 5 was prepared from 7-amino-N-methyl-1,2,3,4-tetrahydrocarbazole[12] by diazotization in D_2O-DCl followed by reduction with D_3PO_2.[13] In a similar manner, 6 was obtained from 6-amino-



1 R_1, R_2, R_3, R_4=H
2 R_1=CH_3, R_2, R_3, R_4=H
3 R_1=CH_3, R_2=CO_2Me, R_3, R_4=H
4 R_1, R_2, R_3=H, R_4=D
5 R_1=CH_3, R_2, R_3=H, R_4=D
6 R_1=CH_3, R_2, R_4=H, R_3=D



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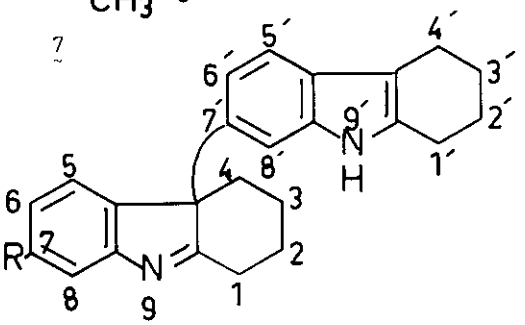
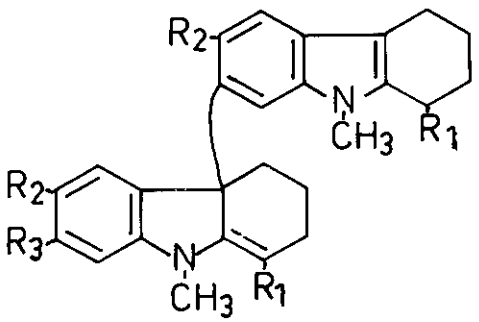
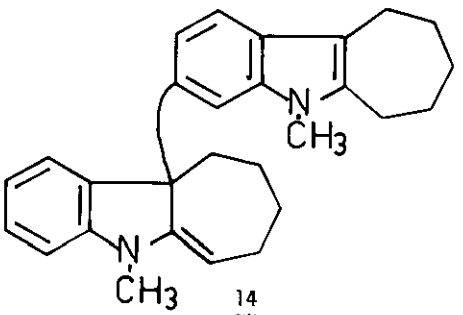


8 R=H
9 R=D



10 R_1, R_2, R_3=H
11 R_1, R_2=H, R_3=D
12 R_1=CO_2Me, R_2, R_3=H
13 R_1, R_3=H, R_2=D



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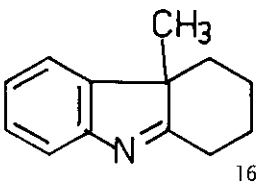

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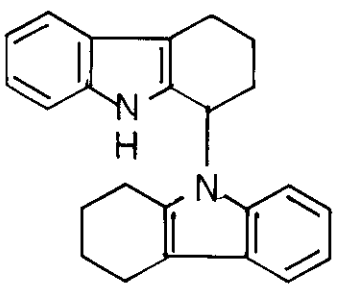

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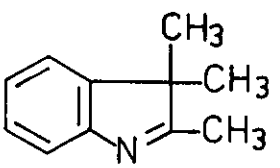

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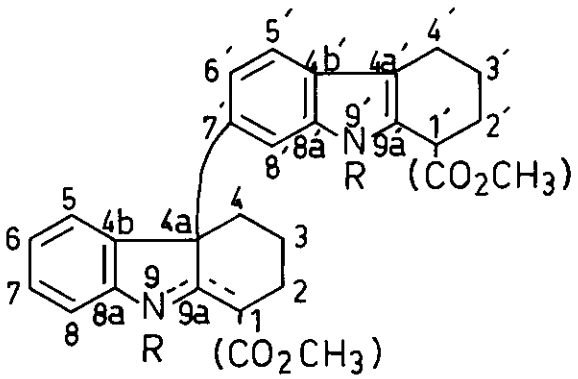
Table I. ^{13}C Spectra of Tetrahydrocarbazoles and Dimers[a]



Compound \ Carbon	1	2	3	4	4a	4b	5
1, 4	23.1(c)	23.1(c)	22.9(c)	20.7	109.8	127.8	117.6
2, 5, 6	23.3(d)	23.2(d)	23.2(d)	21.0	109.3	127.3	117.7
3	39.0	27.7	20.6(e)	20.8(e)	111.2	126.6	118.3(f)
8, 9	36.9	30.5(g)	29.3(g)	23.2(h)	63.2	148.2	122.3
10, 11, 13	92.4	33.3	17.8	23.2(i)	51.3	137.6	117.2
12 high mp	95.4	31.2	16.6(j)	23.6(j)	55.9	131.8	120.6
12 low mp	95.3	31.2	16.6(m)	23.6(m)	55.9	131.7	120.6

	6	7	8	8a	9a	R(CH_3)	C=O(p)	OCH_3(p)
1, 4	118.9	120.6(b)	110.2	135.6	134.0			
2, 5, 6	118.6(b)	120.6(b)	108.5	136.9	135.6	28.9		
3	118.7(f)	121.4	108.7	131.5	137.2	29.5	173.7	52.2
8, 9	125.1	127.1(b)	120.2	153.6	189.9			
10, 11, 13	122.4	127.1(b)	105.8	147.6	152.1	29.7		
12 high mp	122.7	127.4	107.9(k)	137.3(l)	163.1	35.8	168.2	50.8
12 low mp	122.7	127.4	107.9	(o)	(o)	35.8	(o)	50.8

	1'	2'	3'	4'	4a'	4b'	5'
8, 9	23.2(h)	23.2(h)	21.9(h)	20.9	109.9	127.0	117.1
10, 11, 13	23.2(i)	22.4(i)	22.1(i)	21.0	108.9	125.3	117.2
12, high mp	39.0	27.6	20.5(j)	20.8(j)	111.0	125.2	116.6
12, low mp	39.0	27.6	20.5(m)	20.8(m)	111.0	(o)	116.6

(continued)

Table I. (Continued)

Compound \ Carbon	6'	7'	8'	8a'	9a'	R'(CH_3)	C=O (p)	OCH_3 (p)
8, 9	118.4	130.7	108.0	136.2	134.6			
10, 11, 13	118.1	137.6	106.7	136.7	135.4	28.9		
12, high mp	118.5	147.0	105.8(k)	137.5(l)	136.3(l)	29.5	173.6	52.2
12, low mp	118.5	147.0	105.8	137.5(n)	136.3(n)	29.5	174.9	52.2

(a) Measured on a Brucker Ha-90 instrument in deuterochloroform.
(b) This signal disappeared when the sample contained deuterium on this carbon.
(c-n) Interchangable signals.
(o) Peak was very weak.
(p) For compounds 3 and 12 only.

1,2,3,4-tetrahydrocarbazole.[14] Compound 7 is known.[15]

The preparation of the deuterated compounds and their ^{13}C N.M.R. spectra are especially meaningful in two ways. There has been some question about the ^{13}C shift values of carbons 5 and 6 of indole (6 and 7 in the 1,2,3,4-tetrahydrocarbazole series). Originally,[16] carbon 5 was assigned the higher value (typically δ 122 for C-5 and 120 for C-6). These assignments were reversed by Gribble in 1975 in a footnote.[17] Our data on 6- and 7-deutero-1,2,3,4-tetrahydrocarbazole are in agreement with Gribble, as are our similar data on 2,3-diphenylindole.[18]

Secondly, there has been some doubt about whether catalytic deuteration of halides in base is a reliable method for introducing deuterium.[10] Our data, especially the preparation of 5 by an alternate method, would indicate that the deuteration is reliable, in this case at least. The strong C-H singlet in the decoupled ^{13}C spectra was replaced in each case by the small C-D triplet. No other peaks were changed. The ^{13}C N.M.R. data for compounds 1-6 and 8-13 are given in Table I. Data for 7 and 14 are given in the experimental section.

RESULTS AND DISCUSSION

The 4a linkage in 8 is substantiated by the ^{13}C resonances at δ 189.9 and 63.2 for carbons 9a and 4a as compared to δ 189.9 and 53.8 for 4a-methyl-1,2,3,4,4a-pentahydrocarbazole, 16.[20] Carbon 4a is shifted slightly downfield by the aromatic ring in 8 as compared to 16. The comparable carbon to 9a in 2,3,3-trimethylindolenine, 17,[21] (C-7a) resonates at δ 189. The 7' linkage in 8 is substantiated by deuterium studies. Thus, when 4 was oxidized, the product, 9, contained only one deuterium. Carbon 7 in 8 resonated at δ 130.7 as compared to 127.4 for 16 and 129.2 for 17. It

was not present in the spectrum of 9, but was replaced by a small triplet at 126.8 with a coupling constant of 1.05 ppm (C-D).

The structure of 10 was derived in a similar manner. The 4a linkage is supported by ^{13}C resonances at δ 51.3 and 152.1 for carbons 4a and 9a, respectively. In lochnericine,[22] the corresponding carbons appear at δ 54.8 and 167.4. The resonance from C-1 appeared at δ 92.4 and contained one hydrogen as shown on a partially decoupled spectrum. The 7' linkage was proved by the oxidation of 6 and 5 containing deuterium on C-6 and C-7, respectively. Oxidation of 6 gave 13 with two deuteriums, while 5 yielded 11 with only one deuterium. In all cases, the presence of deuterium on specific carbons was confirmed by the absence of a strong ^{13}C resonance for that carbon, as compared with the hydrogen form.

Compound 3 was investigated as a model for the preparation of the indole alkaloids, vinblastine and vincristine, which contain a linkage corresponding to a 1-6' bond. Actually, 3 without the N-methyl would have been a better model, but its oxidation[23] gave only a monomer, 1-hydroxy-1-carbomethoxy-1,2,3,4-tetrahydrocarbazole. Unfortunately, oxidation of 3 produced only the 4a-7' dimer, 12, in a fair yield. Compound 12 contains two chiral centers and should exist as two diastereomeric pairs. The pairs were separated into low-melting and high-melting racemates which had virtually identical ^{13}C spectra (Table I). The structures are based upon a comparison of the ^{13}C spectrum with that of 10. Significant points are, (1) C-1 appears at δ 95.4 and does not contain a hydrogen (2) C-4a is at 55.9 and is quaternary and (3) C-9a appears at 168.2 (compared to 167.4 in lochnericine[22]). Although no deuterium studies were done, the linkage at C-7' seems reasonable since the ^{13}C spectrum of 12 is quite similar to that of 10 in region, δ 105-128.

Compound 7 yielded the dimer, 14, in fair yield. Except for the aliphatic region, the ^{13}C spectrum of 14 is almost identical with that of 10. The aliphatic carbons of 14 appear at about 4δ units downfield from those of 10, as would be expected from a comparison of 2 and 7 (Experimental). Compound 7, without the N-methyl, does not give dimers and is still under study.

Kinetic studies of the electrooxidation of 1 and 2 have been carried out in detail,[24] but it is not yet possible to propose a plausible mechanism for this unique reaction.

EXPERIMENTAL

General. Melting points were taken on a Kofler hot stage apparatus and are corrected. Mass spectra were measured on an AEI MS-9 instrument. Evaporations were carried out on a rotary vacuum evaporator.

The Electrochemical Cell. Electrooxidations were carried out in a 250 ml beaker closed with a large Neoprene stopper containing holes for the electrode contacts and a nitrogen stream.[25] The cathode was platinum (1 x 1.5 cm), and the anode was graphite felt (4.5 x 6.5 cm, obtained as WDF felt from Union Carbide Corp., Carbon Products Div., New York). The cathode was segregated by a sack made of duPont Nafion (E. I. duPont, Wilmington, Del.). A standard calomel electrode was placed as close as possible to the anode. The anode potential was measured and controlled against the standard with a PAR Model 363 potentiostat (EG + G, Princeton Applied Research, Princeton, N.J.). The cell was further sealed with a soft rubber film and magnetically stirred.

6-Deutero-1,2,3,4-tetrahydrocarbazole, 4. 7-Chloro-1,2,3,4-tetrahydrocarbazole, mp 178-180°C, lit.[11] 179-180°C (5.5 g, 0.027 moles) was dissolved in 100 ml of dry ether and allowed to equilibrate for 4 h with 20 ml of D_2O, in order to replace N-H with N-D. The ether layer was separated, dried ($MgSO_4$) and evaporated to a gum. This was dissolved in 30 ml of CH_3OD containing $KOCH_3$ (from 2.2 g of K) and deuterated in a Parr, low-pressure hydrogenator apparatus over 2.5 g of 5% Pd/C. After deuteration at 10 psi for 39 h, the catalyst was removed by filtration; the solvent was evaporated; and the residue was partitioned between ether and water (to replace N-D with N-H). The ether layer was separated, dried (sat NaCl, $MgSO_4$) and evaporated to yield 4.4 g (96%) of 4, mp 118-120°C. m.s. m/e: M^+, 172.1113; calc. for $C_{12}H_{12}ND$, 172.1111. It showed one spot on T.L.C. using hexane-benzene, (5:3) on silica gel GF.

9-Methyl-6-deutero-1,2,3,4-tetrahydrocarbazole, 5, by Methylation of 4. Compound 4 (3.88 g, 0.023 moles) was dissolved in 25 ml of dry acetone and 25 ml of 66% aqueous KOH was added with stirring. Dimethyl sulfate (33 g, 0.26 moles) was added over 6 min while keeping the temperature at 30-33°C. After 30 min more, the reaction was complete (T.L.C. using hexane-EtOAc, 8:2 on silica gel GF). The mixture was poured into ice-water and extracted several times with ether. The combined ether layers were dried (sat NaCl, $MgSO_4$) and evaporated to a yellow oil which crystallized to give 1.67 g (40%) of 5, mp 50°. m.s. m/e: M^+, 186.1261; calcd for $C_{13}H_{14}ND$, 186.1268.

Compound 5 by Diazotization. 6-Amino-N-methyl-1,2,3,4-tetrahydrocarbazole[26] (1.5 g, 7.5 mmole, mp 83-85°C, lit[12] 87-89°C) was stirred with 4 ml of D_2O at 80-85° (to replace N-H with N-D). The D_2O was decanted and replaced with fresh D_2O and cooled until the organic compound solidified. The solid was collected by filtration and dissolved in 4.5 ml of 50% D_3PO_2 in D_2O and 3 ml of D_2O. The solution was cooled to 0-2°C and treated with 0.6 g of $NaNO_2$ in 1 ml of D_2O. After two days at 5°C (refrigerator), the dark mixture was diluted with D_2O and filtered. The precipitate was dried, dissolved in $CHCl_3$-acetone (2:1) and passed through a short column of 10 g of silica gel. The first 100 ml of eluant was evaporated to a tar and extracted with hot EtOH. The EtOH solution

was treated with carbon, filtered and concentrated to give 0.127 g (9%) of 5, identical in all respects to the compound obtained by methylation of 4.

6-Deutero-N-methyl-1,2,3,4-tetrahydrocarbazole, 6. This compound was prepared in 18% yield from 6-amino-N-methyl-1,2,3,4-tetrahydrocarbazole[14,26] by the same procedure used for 5. The product did not crystallize and gave the predicted ^{13}C spectrum (Table I).

1-Carbomethoxy-N-methyl-1,2,3,4-tetrahydrocarbazole, 3. This compound was prepared in 61% yield by methylation of 1-carbomethoxy-1,2,3,4-tetrahydrocarbazole[23] by the same procedure used for 5. It was distilled at 160-163°C/0.65-0.75 mm. Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.04; H, 7.04; N, 5.76. Found: C, 73.91; H, 6.89; N, 5.58.

Oxidations of 1 and 4. A solution of 2.4 g of $LiClO_4$ in 150 ml of CH_3CN-H_2O, 9:1 was preelectrolyzed at +0.7 V for 30 min, while being sparged with deoxygenated N_2. The potential was reduced to 0.0 V, and 300 mg (1.76 mmole) of 1 was added. The potential was raised to +0.7 V, giving an initial current of 25 mA. After 2 h and the passage of 0.0016 F of electricity, T.L.C. using benzene-EtOAc (7:3) showed only a trace of 1. The mixture was filtered, evaporated, and partitioned between ether and saturated aqueous $NaHCO_3$. The ether layer was separated, dried (sat NaCl, $MgSO_4$) and evaporated to a residue. About 2 ml of acetone was added, and, on cooling, 127 mg of 8 precipitated, mp 221-223°C, lit[6] 223-228°C. Preparative T.L.C. of the mother liquor provided 25 mg of 1, 43 more of 8 (total yield of 62% after correction for recovered 1) and 20 mg of a compound containing extra oxygen which was not characterized.

A similar oxidation of 4 gave a 60% yield of 9, mp 224-227°C. m.s. m/e: M^+, 341.2004; calcd for $C_{24}H_{21}N_2D$, 341.2004.

Oxidations of 2, 5, and 6. Compound 2[8b] (950 mg, 5.1 mmole) was oxidized at +0.7 V (initial current 25 mA, 0.0051 F of electricity) in a manner analogous to 1 to yield 300 mg of 10 as a precipitate from acetone. An additional 70 mg (total 370 mg, 40%) was obtained when the residue from the acetone filtrate was recrystallized from EtOH-$CHCl_3$. The compound melted at 185-186°C. m.s., m/e: M^+, 368; calcd for $C_{26}H_{28}N_2$, 368. Anal. Calcd: C, 84.78; H, 7.60; N, 7.60. Found: C, 84.60; H, 7.51; N, 7.40.

A similar oxidation of 5 yielded 11, mp 184-185°C in a yield of 42%. m.s. m/e: M^+ 369.2313; calcd for $C_{26}H_{27}N_2D$, 369.2317.

A similar oxidation of 6 yielded 13, mp 184-185°C in a 29% yield. m.s. m/e: M^+, 370; calcd for $C_{26}H_{26}N_2D_2$, 370.

Oxidation of 3. Compound 3 (940 mg, 3.87 mmole) was oxidized in a manner similar to that used for 1 except that the electrolysis mixture was kept at 4-6°C. The potential was +0.66 V giving an initial current of 25 mA, and reaction was stopped after passage of 0.0038 F of electricity. The pH was adjusted to 7 with NH_4OH, and the CH_3CN portion was evaporated under vacuum. The aqueous residue was suspended between ether and water, but an appreciable amount of tar was not soluble. The ether layer (no tar) was dried (sat NaCl, $MgSO_4$) and evaporated to give 0.9 g of gum. This was separated by preparative T.L.C.[27] (9 layers of silica gel GF_{254}, 10 x 10 x 0.2 cm, using EtOAc-MeOH, 3:1). The bands were eluted from the adsorbent with EtOAc-MeOH (4:1). The second band from the top yielded 260 mg of 3. The fourth band was eleuted and evaporated to a small volume, and the high-melting isomer of 12, 75 mg (11%, corrected for recovered 3) precipitated. This melted at 202-204°C. Recrystallization from MeOH-$CHCl_3$ did not raise the mp. Anal. calcd for $C_{30}H_{32}N_2O_4$: C, 74,36; H, 6.66; N, 5.78. Found: C, 74.99; H, 6.60; N, 5.70. m.s. m/e: M^+, 484.2357; calcd, 484.2364.

The mother liquor of the above crystallization was evaporated to dryness and dissolved in a small amount of MeOH. After several days, 73 mg of white crystals, mp 141-145°C, precipitated. Further reworking of this mother liquor gave an additional 51 mg (total, 124 mg, 18%). Recrystallization from MeOH raised the mp to 143-147°C. m.s. m/e: M^+, 484.2367; calcd 484.2364.

Oxidation of 7. Compound 7 (^{13}C N.M.R., $CDCl_3$, δ: C-6, 31.6; C-7, C-8, C-9, 3 peaks, 24.3, 26.2, 27.1; C-10, 28.4; C-1, 117.4; C-2, 118.5; C-3, 120.2; C-4, 108.6; C-10a, 113.0; C-10b, 127.6; C-4a, 138.8; C-5a, 135.8) (0.295 g, 1.5 mmole) was oxidized in a manner similar to that used for 2. The potential was +0.7 V, and the initial current was 47 mA. After the passage of 0.00175 F of electricity, the reaction mixture was treated as in the oxidation of 2. From acetone, 0.241 g of 14, mp 145-148°C, was obtained. Recrystallization from acetone-MeOH yielded 0.129 g (44%) of pure 14, mp 158-161°C: m.s., m/e, 396.2575, calcd. for $C_{28}H_{32}N_2$, 396.2558; ^{13}C N.M.R., $CDCl_3$, δ: C-6, 95.8; C-7, 37.1; C-8, C-9, C-10, C-6', C-7', C-8', C-9', C-10', 8 peaks 24,4-31.5; C-1, 117.6; C-2, 122.5; C-3, 127.1; C-4, 106.9; N-CH_3, 29.0; C-10a, 57.3; C-10b, 137.6; C-4a, 138.7; C-5a, 155.6; C-1', 117.4; C-2', 117.6; C-3', 146.2; C-4', 104.5; C-10a', 113.0; C-10b', 125.8; C-4a', 136.4; C-5a', 134.7; N'-CH_3, 29.4. Anal. Calcd for $C_{28}H_{32}N_2$: C, 84.84; H, 8.08; N, 7.07; found: C,84.04; H, 8.25; N, 6.69.

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REFERENCES AND NOTES

1. This paper is respectfully dedicated to Dr. Ulrich Weiss of the National Institutes of Health in honor of his 75th birthday.
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