(t, J = ~2 Hz, 1 H, H-3), 7.37 (s, 1 H, H-2), 7.24 (t), 7.31 (t), 7.42 (m), 7.50 (m), 7.85 (d), and 7.98 (d) (aromatic H); ^{13}C NMR δ 22.8, 29.1, 32.4 (2C), 48.5, 52.3, (3C), 54.9, 56.3, 113.7, 116.1, 119.4, 120.5, 123.1 (2C), 124.8, 126.7, 129.7, 129.3, 130.8, 133.8, 135.1, 138.1, 168.2 (2C); MS, m/e (relative intensity) 523 ($M^{+\cdot}$, 3), 496 (25), 382 (10), 365 (35), 284 (15), 253 (75), 226 (100), 95 (70), 94 (30); exact mass m/e 523.1776 (calcd for $C_{27}H_{29}N_3O_6S$ m/e 523.1776).

Preparation of Indole 38 by Deprotection of 37. As described for the deprotection of **27**, the *N*-phenylsulfonyl amino nitrile **37** (1.2 g, 2.29 mmol) was reacted in THF with a fivefold excess of potassium *tert*-butoxide (argon atmosphere). After 30 min a saturated solution of ammonium chloride was added, and the mixture was extracted three times with methylene chloride. The combined organic fractions were dried over sodium sulfate and concentrated to give a viscous red brown oil. The crude product mixture was separated by medium-pressure chromatography on silica gel (20 g), eluting with ethyl acetate. Essentially pure **38** (640 mg, 78%) was obtained as a viscous yellow oil: IR 3480 (NH), 2220 (w, CN), 1750–1720 cm^{-1} ($COOCH_3$); UV (MeOH) λ_{max} 275, 283, 290 nm; ^{1}H NMR δ 1.43 (qd, J = 4, 12.5 Hz, 1 H, H-20ax), 1.73 (td, overlapped, J = 4, 12.5 Hz, 1 H, H-14ax), 1.77 (dq overlapped, 1 H, H-20eq), 2.00 (dq, J = 2, 12.5 Hz, 1 H, H-14eq), 2.45 (m + td, J = 3, 12.5 Hz, 2 H, H-15ax,21ax), 2.82, 2.93 (2 m, 4 H, H-5,6), 2.98 (dt overlapped, J = ~2 Hz, 1 H, H-21eq), 3.25 (d, J = 8 Hz, 1 H, H-16), 3.75 (s, 6 H, OCH_3), 4.04 (t, J = ~2 Hz, 1 H, H-3), 7.04, (d, J = ~1 Hz, 1 H, H-2), 7.12 (t), 7.20 (t), 7.35 (d), and 7.59 (d) (aromatic H), 8.02 (br s, 1 H, NH); ^{13}C NMR δ 23.1, 29.0, 32.2, 32.5 (2C), 48.6, 52.3, 52.5 (3C), 56.3, 111.2, 113.0, 116.1, 118.5, 119.1, 121.8, 127.2, 136.1, 168.2 (2C); MS, m/e (relative intensity) 383 ($M^{+\cdot}$, 5), 356 (20), 226 (100), 147 (20), 95 (15), 94 (15); exact mass m/e 383.1875 (calcd for $C_{21}H_{25}N_3O_4$ m/e 383.1844).

Cyclization of 38. Preparation of Indoles 39 and 40. Silver tetrafluoroborate (0.175 g, 0.9 mmol) in dry THF (2 mL) was added via syringe to a solution of deprotected amino nitrile **38** (0.320 g, 0.818 mmol) in THF (10 mL). The reaction mixture was stirred under a steady stream of argon for 6 h by which time the THF had completely evaporated. A saturated solution of HCl in methanol (15 mL) was then added, and stirring under an argon atmosphere at 60–80 °C was continued overnight. The reaction mixture was then poured into ice–water, neutralized with sodium bicarbonate, and extracted three times with methylene chloride. The methylene chloride fractions were dried over sodium sulfate and concentrated to give a deep orange oil. The crude product mixture was separated by column chromatography on silica gel (7 g). Compound **39** was eluted with ethyl acetate/methanol/triethylamine (98:1.5:0.5) and compound **40** with a mixture of the same solvents (95:4:1).

Pure **39** (0.024 g, 8%) was obtained as a pale yellow oil: IR 3470 (NH), 2850–2750 (Bohlmann bands), 1750–1725 cm^{-1} ($CO-OCH_3$); UV (MeOH) λ_{max} 290, 285, 275 nm; ^{1}H NMR δ 1.39 (q, J = 12 Hz, 1 H, H-14ax), 1.60 (qd, J = 4.0, 12 Hz, 1 H, H-20ax), 1.75 (dt, J = 12 Hz, 1 H, H-20eq), 2.22 (br d, J = 12 Hz, 1 H, H-14eq), 2.37 (m, 1 H, H-15ax), 2.46 (td, J = 2.5, 12 Hz, 1 H, H-21ax), 2.61 (td, J = 4, 12 Hz, 1 H, H-5), 2.72 (br d, J = 12 Hz, 1 H, H-5), 2.93 (m, 1 H, H-6), 3.05 (m, 2 H, H-6,21eq), 3.27 (d, J = 9 Hz, 1 H, H-16), 3.30 (br d, J = ~9 Hz, 1 H, H-3), 3.73 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 7.08 (t), 7.13 (t), 7.30 (d), and 7.42 (d) (aromatic H), 7.81 (s, 1 H, NH); ^{13}C NMR (Table I) δ 21.8, 29.9, 34.0, 36.2, 52.7 (2C), 53.1, 55.1, 57.2, 59.5, 108.4, 110.9, 118.2, 119.5, 121.5, 127.4, 134.3, 136.1, 168.9 (2C); MS, m/e (relative intensity) 356 (100, $M^{+\cdot}$), 355 (98), 225 (90), 223 (40), 197 (20), 184 (10), 169 (10), 156 (10); exact mass m/e 356.1749 (calcd for $C_{20}H_{24}N_2O_4$ m/e 356.1735).

Pure **40** (0.073 g, 25%) was also obtained as a pale yellow oil: IR 3470 (NH), 1750–1725 ($COOCH_3$); UV (MeOH) λ_{max} 290, 285, 275 nm; ^{1}H NMR δ 1.51 (m, 1 H, H-20ax), 1.69 (m, 1 H, H-20eq), 1.78 (td, J = 4.5, 12 Hz, 1 H, H-14ax), 2.16 (m, 1 H, H-15), 2.25 (br d, J = 12 Hz, 1 H, H-14eq), 2.65 (m, 2 H, H-21eq, H-5 or H-6), 2.78 (m, 1 H, H-21ax), 3.00, 3.10, 3.21 (3 m, 3 H, H-5,H-6), 3.40 (d, J = 10 Hz, 1 H, H-16), 3.70 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 4.20 (hump, 1 H, H-3), 7.11 (t), 7.15 (t), 7.38 (d), and 7.48 (d) (aromatic H), 8.12 (s, 1 H, NH); ^{13}C NMR (Table I) δ 18.2, 29.1, 31.7, 31.8, 46.5, 51.5, 52.6 (2C), 54.1, 55.3, 107.8, 111.2, 117.9, 119.3, 121.4, 127.5, 133.1, 136.0, 168.8, 169.1; MS, m/e (relative intensity) 356 (100%, $M^{+\cdot}$), 355 (95), 341 (10), 325 (15), 297 (10), 241 (8), 225 (85), 223 (20), 197 (20), 184 (15), 179 (15), 156 (12); exact mass m/e 356.1731 (calcd for $C_{20}H_{24}N_2O_4$ m/e 356.1735).

Acknowledgment. We express our thanks to Mrs. M.-T. Adeline for her technical assistance and to Mr. P. Potier for his continued encouragement.

Registry No. 13, 82980-06-1; (±)-**14**, 82980-07-2; **15**, 82980-08-3; (±)-**16**, 82980-09-4; (±)-**17**, 82980-10-7; **18**, 82980-11-8; **19**, 82980-12-9; (±)-**21**, 82980-13-0; **22**, 24716-27-6; **23**, 82980-20-9; **24**, 82980-21-0; (±)-**26**, 82980-22-1; (±)-**27**, 82980-14-1; (±)-**28**, 82980-15-2; (±)-**29**, 82980-16-3; (±)-**30**, 83024-19-5; (±)-**31**, 83024-20-8; (±)-**32**, 82980-17-4; (±)-**33**, 82995-03-7; (±)-**34**, 82980-18-5; (±)-**35**, 82980-19-6; **37**, 82980-23-2; **38**, 82995-04-8; (±)-**39**, 82980-24-3; (±)-**40**, 82980-25-4; *N*-[β-(3-indolyl)ethyl]-3-ethylpyridinium bromide, 24716-24-3; sodium dimethyl malonate, 18424-76-5; *N*-[β-(3-indolyl)ethyl]-pyridinium bromide, 50676-26-1.

Electrochemical Reduction of Di-Schiff Bases. Synthesis of Piperazines, Indoloindoles, Diazepines, and Diazocines

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The electrochemical reduction of a series of di-Schiff bases has led to examples where products representing reduction, cyclization, and transannular cyclization are found. Useful synthetic pathways for piperazines, indoloindoles, diazepines, and diazocines are described.

Introduction

Most reports pertaining to the electrochemical reduction of Schiff bases have dealt with polarography in aqueous systems, and only infrequently with product analysis and/or nonaqueous systems. Almost no electrosynthetic studies on di-Schiff bases exist. Some azines have been examined in methanol–water mixtures by Bezuglyi et al.[1] The product obtained from two successive two-electron reduction steps was a substituted hydrazine. Lund[2] supported this work by isolating benzaldehyde benzylhydrazone on reduction of dibenzalazine in alkaline solution. Two groups, Bezuglyi et al.[3] and Scott and Jura,[4]

(1) V. D. Bezuglyi and S. P. Shimanskaya, *Zh. Obshch. Khim.*, **35**, 15 (1965).

(2) H. Lund, *Acta. Chem. Scand.*, **13**, 249 (1959).

(3) N. F. Levchenko, L. Sh. Afanasiadi, and V. D. Bezuglyi, *Zh. Obshch. Khim.*, **37**, 624 (1967).

(4) J. M. W. Scott and W. H. Jura, *Can. J. Chem.*, **45**, 2375 (1967).

0022-3263/82/1947-4452$01.25/0

Table I. Electrochemical Data[a]

compd	polarography: 1st wave $-E_{1/2}$	1st wave n	2nd wave $-E_{1/2}$	2nd wave n	n prep scale cpe	solvent
N-(diphenylmethylene)aniline (5)					1.87	DMF[b]
	2.40		2.60	1.95[c]		glyme[d]
N,N'-dibenzylideneethylenediamine (7)	2.90	3.88			3.50	DMF
	2.85		3.20		3.68	glyme
N,N'-bis(diphenylmethylene)ethylenediamine (10)	2.80		3.30	3.53[c]	3.62	DMF
	3.05	1.75			3.25	glyme
2,2'-bis[(phenylimino)methyl]biphenyl (12)	2.40	0.94	3.18		1.67	DMF
	2.43	1.82			2.30	glyme
2,2'-bis(benzylideneamino)biphenyl (14)	2.60	1.94			2.34	DMF
	2.55	1.67			2.32	glyme
2,2'-bis[(phenylimino)benzyl]biphenyl (15)					4.12	DMF
	2.58	2.07			3.98	glyme
2,2'-bis[(diphenylmethylene)amino]biphenyl (17)					4.32	DMF
	2.60	3.00			4.13	glyme
9,20-diazotetrabenzo[*a,c,g,i*]cyclododecene (19)	2.53	1.15	3.18		1.56	DMF
	2.60	2.08			2.52	glyme
6,12-diphenyldibenzo[*b,f*][1,5]diazocine (22)	2.45	1.95				DMF
	2.45	2.14			2.39	glyme
2,8-dichloro-6,12-diphenyldibenzo[*b,f*][1,5]diazocine (24)	2.25					DMF
	2.30	1.09			2.26	glyme

[a] $Ag^+|Ag$ (10^{-3} M) reference and TBAP (tetra-*n*-butylammonium perchlorate) was used as the supporting electrolyte in all cases. [b] DMF, dimethylformamide. [c] Total number of electrons for both waves. [d] Glyme-dimethoxyethane.

have examined the polarographic reduction of monoazomethine compounds in dimethylformamide (DMF). In both cases it was reported that two well-defined one-electron polarographic waves were exhibited. Scott and Jura suggested a mechanism that is a specific example of a general mechanism proposed by Laitinen and Wawzonek.[5] The main thrust of Scott and Jura's study, however, was toward attempts to correlate polarographic half-wave potentials with Hückel molecular orbital energies, and a detailed examination of the mechanism and products was not made. Bezuglyi's group studied the correlation of the half-wave potentials with structural or polar substituent changes. Ono and Uehara[6] have studied *N*-benzylideneaniline in *nonaqueous media* by polarographic reduction and macroscopic scale electrolysis with product analysis. Their published results differ from Benzuglyi et al.[3] and Scott and Jura.[4] In the nonaqueous media they observed one well-defined wave that represented a two-electron reduction of *N*-benzylideneaniline to give *N*-benzylaniline. A more detailed mechanistic study on the reduction of Schiff bases was published by Fry and Reed in 1969.[7] They also observed a single two-electron wave for the Schiff bases studied in DMF. From this and other experimental data, they suggested that the well-known "ece" mechanism was involved.

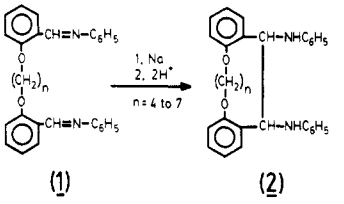
In the area of di-Schiff bases Lund[8] has reported stilbene products from the reduction of benzil dianil.

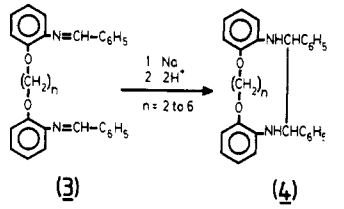
However, a large volume of literature concerning the chemical reduction of Schiff bases has been published, involving both product and mechanistic studies. Eisch et al.[9] and Smith et al.[10] have rationalized the reduction products from *N*-benzylideneaniline in terms of solvent and reducing agent used. Smith and Ho[11] have reported on the reductive dimerization of Schiff bases by alkali metals in an excellent mechanistic study.

Smith[12] has also published a paper on the reactions of the chemically reduced Schiff bases. He reduced *N*-benzylideneaniline with sodium metal in ethereal solvents and reacted the dimeric dianion with methyl benzoate or benzaldehyde. Both reactions afforded the same product, *N*-benzoyl-*N,N'*,1,2-tetraphenylethylenediamine.

Smith and Veach[13] have also prepared the disodium adduct of *N*-(diphenylmethylene)aniline and reacted it with a variety of reagents. With alkyl halides, ethylene oxide, and diethyl sulfate, alkylation occurs at the carbon atom. Substituted pyrrolidine and piperidine derivatives were produced by alkylation at both the carbanion and nitrogen anion, using tri- and tetramethylene dibromide as the alkylating agent. Esters react to form the *N*-acyl derivatives, whereas benzaldehyde abstracts the alkali metal from the disodium adduct.

Jaunin et al.[14,15] produced macrocyclic compounds by the chemical reduction of di-Schiff bases. The compounds reduced and the products obtained are shown below.



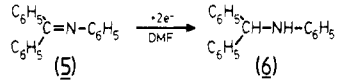


This work describes the electrochemical cyclization of a series of di-Schiff base compounds to produce a variety of bicyclic structures.

(5) H. L. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).
(6) S. Ono and M. Uehara, *J. Electrochem. Soc. Jpn.* **27**, 93 (1959).
(7) A. J. Fry and R. G. Reed, *J. Am. Chem. Soc.*, **91**, 6448 (1969).
(8) J. G. Monet and H. Lund, *Bull. Soc. Chim. Fr.*, 2547 (1975).
(9) J. J. Eisch, D. D. Kaska, and C. J. Peterson, *J. Org. Chem.*, **31**, 453 (1966).
(10) J. G. Smith and C. D. Veach, *Can. J. Chem.*, **44**, 2497 (1966).
(11) J. G. Smith and I. Ho, *J. Org. Chem.*, **37**, 653 (1972).
(12) J. G. Smith, *Can. J. Chem.*, **44**, 59 (1966).
(13) J. G. Smith and C. D. Veach, *Can. J. Chem.*, *44*, 2245 (1966).
(14) R. Jaunin and R. Holl, *Helv. Chem. Acta*, **41**, 1783 (1958).
(15) R. Jaunin and J. P. Magnenat, *Helv. Chem. Acta*, **42**, 328 (1959).

Results and Discussion

Each of the Schiff bases studied was subjected to an initial polarographic investigation in order to determine the half-wave potential and to a small-scale electrolysis to determine the number of electrons consumed (Table I). These data were used to initiate preparative-scale electrolyses. The polarogram of compound **5** showed two

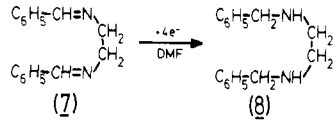


(5) (6)

polarographic waves ($E_{1/2}$ = −2.40 and −2.60 V) (vs. 10^{-3} M $Ag^+|Ag$ reference) with a total of two electrons consumed upon reduction at the plateau of the second wave.

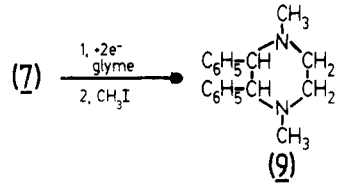
Large-scale electrolysis of *N*-(diphenylmethylene)aniline (**5**) in DMF afforded *N*,1,1-triphenylmethylamine (**6**), which was isolated as its hydrochloride salt in an 82% yield. This is consistent with the initial formation of a radical anion followed by an addition of a second electron and protonation to form the indicated product. This is supported by literature reports of the isolation of a stable radical anion from **5** in THF, using sodium metal as the reducing agent.[16] Dimerization of compound **5** upon reduction is not observed, presumably because of steric hindrance in the radical anion.[17]

The polarogram on *N*,*N*′-dibenzylideneethylenediamine (**7**) in DMF showed only one wave at $E_{1/2}$ = −2.90 V. Controlled-potential electrolysis indicated that 3.88 electron equiv/mol was consumed. Preparative-scale electrolysis of **7** in DMF, followed by quenching with ethanol yielded 69% of the expected diamine **8**.



(7) (8)

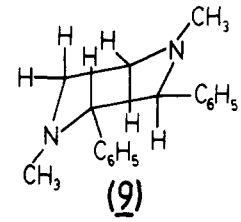
The polarogram of **7** in *glyme* showed two close reduction waves at $E_{1/2}$ = −2.85 and −3.20 V. The characteristic shape and closeness of the waves was similar to that observed for compound **5**. No coulometric data was obtained for this compound/solvent pair on a small scale; however, preparative reduction at $E_{3/4}$ of the first wave did not affect the second wave, suggesting the formation of a two-electron product. A preparative-scale electrolysis carried out at the plateau of the second wave indicated the consumption of 3.68 electron equiv/mol. Reaction of the reduced solution with 4 equiv of methyl iodide immediately destroyed the red-yellow anion produced. Upon being worked up, the product, 1,4-dimethyl-2,3-diphenyl-1,4-piperazine (**9**), was produced in 42% yield (isolated as its dihydrochloride salt).



(9)

The high electron count (3.68 found, 2.0 required) might be explained by the formation of the tetraanion as well as the dianion. This competing reaction would produce an electron count greater than three. However, since no other product was found an alternative explanation is preferred. In applying the high cathodic potential (−3.30 V) necessary, one risks the possibility of reaction with the supporting electrolyte; this might include (1) reduction of supporting electrolyte, (2) anion attack on the supporting electrolyte, (3) formation of tetra-*n*-butylammonium amalgam, which reduces the compound or decomposes, and (4) combined pathways. Indeed tri-*n*-butylamine was found upon workup of the reduced solution.

The most likely configuration for **9** is the trans diequatorial form. In this configuration the phenyl groups

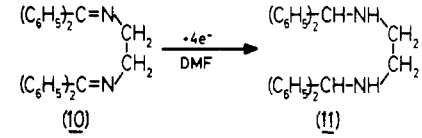


(9)

are in the most stable position (the diaxial conformation has four gauche butane type interactions—two with the axial hydrogens and two with the NCH_3 substituents). The hydrogens on the 2- and 3-carbon atoms would be equivalent and would be expected to show a singlet in the NMR and this was observed.

The polarogram of *N*,*N*′-bis(diphenylmethylene)-ethylenediamine (**10**) in DMF showed two waves at $E_{1/2}$ = −2.80 and −3.30 V. Reduction at the plateau of the first wave led to the consumption of 3.88 electron equiv/mol. Preparative-scale electrolysis of this compound at −3.10 to −3.20 V in DMF afforded a 39% yield of *N*,*N*′-bis(diphenylmethyl)ethylenediamine (**11**) and a 54% yield of benzophenone. The benzophenone was most likely produced by a decomposition reaction that occurs at the high potential applied. No cyclization was observed in agreement with the results obtained with compound **5**.

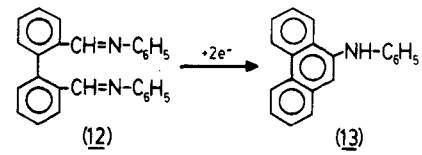
Electrolysis of compound **10** using glyme as the solvent instead of DMF gave compound **11** in poor yield.



(10) (11)

The polarogram of 2,2′-bis[(phenylimino)methyl]biphenyl (**12**) in glyme showed one wave at $E_{1/2}$ = −2.43 V. Coulometric analysis indicated that 2 electron equiv/mol was consumed. In DMF, the polarogram exhibited two waves, $E_{1/2}$ = −2.40 and −3.18 V. The number of electrons used in reducing at the plateau of the first was found to be 1.0 equiv/mol (duplicate experiments). However, upon preparative-scale electrolysis, the number of electrons consumed was closer to two in both solvents (Table I).

Preparative-scale electrolysis of **12** in glyme or DMF afforded 9-anilinophenanthrene (**13**), with a yield of 60%. The elimination of an anilino fragment is an interesting process.

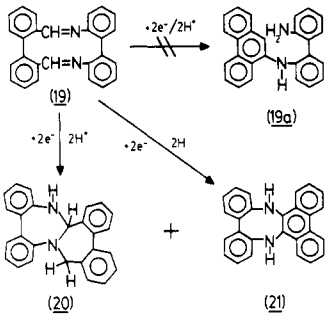


(12) (13)

Several other unidentified products were present in trace amounts as evidenced by TLC. In order to determine whether the aromatization step occurred during the electrolysis or upon workup, the UV spectra of the starting material, the reduced solution, the quenched solution, and 9-anilinophenanthrene were obtained. These demonstrate the presence of the phenanthrene group (ca. 249 nm vs. literature 251 nm) after reduction and before quenching.

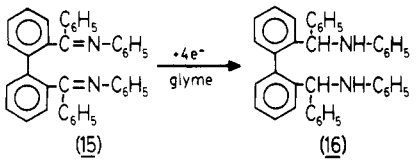
(16) A. G. Evans and J. C. Evans, *J. Chem. Soc. B*, 271 (1966).
(17) A. G. Evans and B. D. Phillips, *Chem. Ind.*, 1718 (1964).

Scheme I. Reduction Products from 9,20-Diazotetrabenzo[*a,c,g,i*]cyclododecene (19)



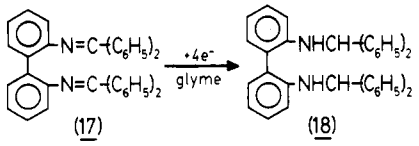
The reduction of the isomeric 2,2′-bis(benzylideneamino)biphenyl (**14**) in either glyme or DMF afforded a tan material in good yield, which could not be characterized.

In order to determine whether or not cyclization could occur where elimination and aromatization are blocked, 2,2′-bis[(phenylimino)benzyl]biphenyl (**15**) was prepared. In this compound there are no α hydrogens present; therefore, aromatization could not occur, and the 9,10-dihydro form of the substituted phenanthrene might be expected. A polarogram of **15** in glyme showed one wave at $E_{1/2}$ = −2.58 V. Coulometric analysis indicated consumption of 2.07 electron equiv/mol. This would be the value expected for the formation of the 9,10-dihydro derivative. However, on preparative electrolysis of **15**, coulometric analysis indicated 4.0 electron equiv/mol was consumed in either glyme or DMF. Upon workup of the resulting solution, a mixture of *dl*- and *meso*-2,2′-bis(anilinobenzyl)biphenyl (**16**) was isolated in 70% yield. This



four-electron reduction is not unlikely, since the reduction of *N*-(diphenylmethylene)aniline (**5**) proceeded by a two-electron reduction and **15** is structurally similar.

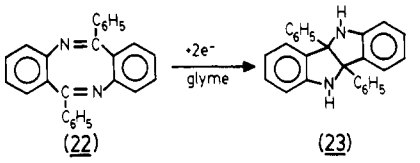
A polarogram of 2,2′-bis[(diphenylmethylene)amino]-biphenyl (**17**) in glyme showed one wave at $E_{1/2}$ = −2.60 V; coulometric analysis indicated 3 electron equiv/mol (sic). Preparative-scale electrolysis of **17** in glyme afforded 2,2′-bis(diphenylmethylamino)biphenyl (**18**) in an 85% yield. The same product was obtained in DMF but in a

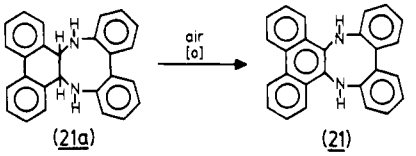


lower yield. The number of electrons consumed was 4.0 in both solvents (Table I). The NMR spectrum showed two partially resolved doublets, one at δ 4.44 (NH) and the other at δ 5.53 (CH). The NH doublet disappears and the CH doublet collapses to a singlet upon shaking the sample with D_2O.

The elimination–aromatization results obtained on compound **12** prompted us to examine 9,20-diazotetrabenzo[*a,c,g,i*]cyclododecene (**19**). This compound is so constructed that if a process related to that followed by compound **12** was pursued (elimination–aromatization), no fragments would be lost and **19a** would result (Scheme I). The polarogram of **19** showed the same type of results as did **12**, that is, in glyme only one wave requiring 2.0 electrons and in DMF two waves with the first wave requiring only one electron (Table I). Cyclic voltammetry also showed one irreversible wave in glyme, the same as **12**. Preparative-scale electrolysis afforded two products, 9a,18-dihydro-9*H*-dibenz[3,4:5,6]azepino[1,2-*a*]dibenzo-[*d,f*][1,3]diazepine (**20**) in 60% yield and 9,18-dihydrodibenzo[*e,g*]phenanthro[9,10-*b*][1,4]diazocine (**21**) in 20% yield. None of the expected product **19a** was observed. Compound **21** most likely arises from an air oxidation raction of the initially formed transannular ring closure product **21a**.

Scheme II. Diazocine Ring Closure to Indoloindole





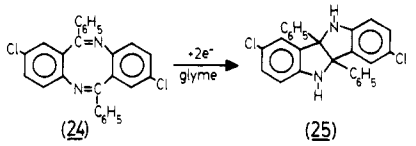
Additional evidence for the structure of **20** was obtained by preparing the monoacetyl derivative, using excess acetic anhydride in BF_3/ether. The expected product was obtained in 90% yield.

Additional evidence for the structure of **21** was obtained by preparing it independently. Reduction of dibenzo[*e,g*]phenanthro[9,10-*b*][1,4]diazocine with lithium aluminum hydride afforded an 83% yield of **21**. Further proof as to the identity of **21** was obtained by preparing the *N,N*′-dimethyl derivative by the reaction of **21** with NaH/glyme followed by addition of methyl iodide. The expected product was obtained in 74% yield.

Other compounds in which transannular ring closure could occur were therefore prepared. The polarogram of 6,12-diphenyldibenzo[*b,f*][1,5]diazocine (**22**) in glyme or DMF showed only one wave at $E_{1/2}$ = −2.45 V. Coulometric analysis indicated that 2 electron equiv/mol was used in either solvent (Table I). In extremely pure glyme (obtained by bulb-to-bulb distillation from sodium–potassium alloy on a vacuum line), a well-formed oxidation wave appeared at $E_{1/2}$ = −1.50 V after reduction at E_p = −2.80 V. Upon oxidation at E_p = −0.90 V, starting material was not recovered, indicating that the reduction is chemically irreversible. Cyclic voltammetry also indicated the reduction to be electrochemically irreversible. These data point to the transannular ring closure product. Preparative-scale electrolysis yielded 94% of 4b,5,9b,10-tetrahydro-4b,9b-diphenylindolo[3,2-*b*]indole (**23**; Scheme II). The phenyl groups are cis because of the steric requirements for the ring junctions. Sternback has reported the chemically induced transannular ring closure of substituted diazocines using zinc and acetic acid, or catalytic reduction involving platinum oxide and hydrogen.[18,19] The electrochemical yields are higher than those with these chemical methods.

A dichloro derivative of compound **22**, 2,8-dichloro-6,12-diphenyldibenzo[*b,f*][1,5]diazocine (**24**) also reduced to give 3,8-dichloro-4b,5,9b,10-tetrahydro-4b,9b-diphenylindolo[3,2-*b*]indole (**25**) in 69% yield.

(18) W. Metlesics and L. H. Sternbach, *J. Am. Chem. Soc.*, 88, 1077 (1966).
(19) W. Metlesics, R. Tavares, and L. H. Sternbach, *J. Org. Chem.* 31, 3356 (1966).



(24) (25)

Conclusion

Electrochemical reduction of di-Schiff bases result in the formation of cyclic and open-chain amines.

Open-chain diamines are favored when di-Schiff bases derived from ethylenediamine and a carbonyl compound are reduced in DMF. They are also obtained when steric factors are present.

Cyclization of di-Schiff bases derived from ethylenediamine and a carbonyl compound occur predominately in glyme, e.g., the proper choice of solvent is essential in the electrolysis of *N,N'*-dibenzylideneethylenediamine. This is attributed to the difference in polarity of the solvents used (DMF and glyme). With the less polar solvent (glyme) more ion pairing can occur, thereby holding the compound in a conformation favorable to cyclization. With DMF as the solvent, solvent separation is favored, promoting formation of the open-chain diamine.[20] Compounds containing the biphenyl substituent favored cyclization in either glyme or DMF, only if there was one hydrogen atom on the azomethine carbon. The absence of solvent effects in these compounds can be attributed to the increased rigidity in the molecule by incorporation of the biphenyl group. In cases in which two phenyl groups were on the azomethine carbon only diamines were formed.

Transannular ring closure has been shown to occur and in excellent yields. The minimum ring size normally formed by transannular ring closure appears to be five. This is shown by the formation of only the 5,5 fused ring system from the [1,5]diazocines. There was no evidence of the 4,6 ring system. In the case of the diazododecene ring system both the 6,8 and 7,7 ring systems were isolated. There appears to be no solvent effect in the transannular ring closure reactions; however, not enough work was performed on this reaction in order to make further correlations between the solvent used and structure of the products obtained.

It would be of interest to explore the limitations of ring size in the transannular reactions and to try other intramolecular reactions. Such reactions may occur by the intramolecular reaction of the anion, formed upon reduction of the C=N bond, with other functional groups (esters, amides, nitriles, halo compounds, etc.).

Experimental Section

Equipment. Polarographic, cyclic voltammetry, and small-scale controlled-potential electrolysis experiments were made in a standard H-cell, the anodic and cathodic compartment being separated by fine glass frit.[21]

Polarograms were made with a Metrohm Polarecord E261 in conjunction with a Sargent IR Compensator (Model A). Solution concentrations were 0.001 M unless specified otherwise.

The triangular voltammetry data were obtained employing a unit based on standard operational amplifier circuitry.[22] The hanging drop electrode consisted of a standard capillary tube attached to a micrometer-type syringe head.

Small-scale controlled-potential electrolysis was effected with use of circuits based on standard operational amplifier design[22] and a stirred mercury pool.

For larger runs (1–2 g) two Kepco CK 60-0.5 power supplies, properly boot-strapped and master-slaved, were used in conjunction with a voltage reference source.[22]

The preparative-scale electrolytic cell was composed of three main components. The cathodic compartment, 60 mm diameter and 60 mm high, was fitted with three standard taper joints (10/18 female) symmetrically situated around the cell peripheral. In the three standard taper joints were placed respectively a reference electrode, the electrical contact bridge, and a gas dispersion tube for degassing. At the top was placed a large standard taper through-joint (45/20 female), which held the anodic compartment. The anodic compartment consisted of two separate parts. The lower part was a cylindrical tube, 30 mm diameter and 77 mm high. A 30-mm fine glass frit was sealed at the bottom. A lower standard taper joint (45/20 male) was so situated that the glass fritted cylinder could be replaced. Into the upper standard taper joint (45/20 female) was placed a standard taper joint (45/20 male) with a 10-mm-diameter glass tube sealed through the top. At the bottom of the tube was sealed a platinum wire to which was attached a platinum disk 25 mm in diameter and 1 mm thick. The platinum disk was situated 7 mm from the glass frit. Magnetically coupled stirring bars were used in both the anodic and cathodic compartments.

All electrochemical work was performed in a Vacuum Atmospheres Dry Lab–Dry Train HE931 drybox (Los Angeles, CA), using an argon atmosphere in which the water vapor and oxygen content was controlled at about 1–2 ppm.

The reference electrode was a 1×10^{-3} M $Ag^+|Ag$ electrode.[22]

Chemicals. 1,2-Dimethoxyethane (Ansul 121) was predried over molecular sieve and then distilled from calcium hydride followed by distillation from lithium aluminum hydride. When extremely dry glyme was desired, the glyme was further purified by a double bulb-to-bulb distillation on the vacuum line from sodium–potassium alloy. On the final distillation the glyme was distilled directly into a small round-bottom flask and sealed under vacuum.

Dimethylformamide (DMF) was obtained as certified grade. It was predried over molecular sieve or activated alumina and then doubly distilled from activated alumina. The solvent was then degassed on the vacuum line and stored in sealed flasks as mentioned previously.

Tetra-*n*-butylammonium perchlorate (TBAP) was obtained as polarographic grade from the G. F. Smith Chemical Co. and was dried in an Abderhalden drying pistol at the boiling point of mixed xylenes and 0.1 mm, using P_2O_5 as the desicant for 24 h.

Tetra-*n*-butylammonium nitrate (TBAN) was prepared by the stoichiometric reaction between tetra-*n*-butylammonium bromide and silver nitrate in ethanol–acetonitrile. The silver bromide was filtered from the solution and the solvent removed under vacuum. The viscous oil that remained crystallized upon heating to 70 °C under a vacuum (ca. 0.1–1.0 mm). The TBAN was then recrystallized from benzene three times, treating with activated charcoal each time. The TBAN was dried in an Abderhalden drying pistol at the boiling point of water and 0.1 mm, using P_2O_5 as the desicant for 24 h, mp 120–121 °C.

The mercury employed (Eastern Smelting and Refining Co.) was triply distilled and was used as obtained.

The cathodic limit in the systems is −3.3 V vs. 1×10^{-3} M $Ag^+|Ag$ electrode.

Preparation of Schiff Bases. The following compounds were prepared according to literature procedures: *N*-(diphenylmethylene)aniline (**5**),[13,23] *N,N'*-dibenzylideneethylenediamine (**7**),[24,25] *N,N'*-bis(diphenylmethylene)ethylenediamine (**10**),[26] 2,2'-bis(phenyliminomethyl)biphenyl (**12**),[27] 9,20-diazotetrabenzo[*a,c,g,i*]cyclododecene (**19**;[28] recrystallized from methylene chloride–absolute ethanol), 6,12-diphenyldibenzo[*b,f*][1,5]diazocine (**22**),[29] 2,8-dichloro-6,12-diphenyldibenzo[*b,f*][1,5]diazocine (**24**),[29]

(20) A reviewer suggests that the acidity of DMF, in comparison to glyme, may be the causative agent.

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(24) A. E. Frost and H. H. Freedman, *J. Org. Chem.*, **24**, 1905 (1959).

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(27) J. A. Hawthorne, E. L. Mihelic, M. S. Morgan, and M. H. Wilt, *J. Org. Chem.*, **28**, 2831 (1963).

(28) E. D. Bergmann, I. Agranat, and M. A. Kraus, *J. Org. Chem.*, **32**, 600 (1967).

and 2,2′-bis(benzylideneamino)biphenyl (**14**).[30]

2,2′-Bis(phenyliminobenzyl)biphenyl (15). A solution of 3.62 g (0.01 mol) of 2,2′-dibenzoylbiphenyl, 3.72 g (0.04 mol) of aniline, and ca. 0.02 g of aluminum chloride as a catalyst in 75 mL of chlorobenzene was heated under reflux for 3 h. The solution was cooled to room temperature and extracted with 20% sodium hydroxide solution. Methylene chloride (100 mL) was added and the mixture extracted with water until neutral. The organic layer was dried over anhydrous magnesium sulfate and filtered and the filtrate evaporated to dryness under a vacuum. The yellow solid that remained was dissolved in methylene chloride (25 mL). Absolute ethanol (15 mL) was added and the methylene chloride removed on the steam bath until crystals started to precipitate from the solution. At this time the solution was cooled to room temperature and then to −20 °C in a refrigerator. Bright-yellow crystals were obtained, 2.7 g (52.7%). An analytical sample was obtained by two additional recrystallizations from methylene chloride–absolute ethanol: mp 189–189.5 °C; IR ($CHCl_3$) 1602 (C=N) cm^{-1}.

Anal. Calcd for $C_{38}H_{28}N_2$: C, 89.03; H, 5.50; N, 5.46. Found: C, 88.97; H, 5.35; N, 5.57.

2,2′-Bis[(diphenylmethylene)amino]biphenyl (17). This compound was prepared by the method of Sternbach et al.;[29] 4.80 g (0.026 mol) of 2,2′-diaminobiphenyl, 7.28 g (0.04 mol) of benzophenone, and 0.268 g (0.006 mol) of aluminum chloride were mixed in 75 mL of chlorobenzene. The solution was heated under reflux for about 24 h. The solution was worked up as described in the reference cited and recrystallized from methanol–methylene chloride; 3.5 g (17%); bright-yellow crystals, mp 246–249 °C; IR ($CHCl_3$) 1625 (N=C), 1600 and 1585 (skeletal C=C) cm^{-1}.

Anal. Calcd for $C_{38}H_{28}N_2$: C, 89.03; H, 5.50; N, 5.46. Found: C, 89.40; H, 5.13; N, 5.77.

Compounds from Macroscale Electrolysis and General Macroscale Electrolysis Procedure. A solution of the electroactive species (1 or 2 g) in 25 mL of the desired solvent (DMF or glyme) containing 2.55 g (0.3 M) of TBAP as supporting electrolyte was introduced into the cathode compartment. Mercury (15 mL) was added as the cathode. The anode compartment was charged with 2.04 g (0.6 M) of TBAP in 10 mL of the appropriate solvent. The solution was then reduced at the E_p (plateau potential) until the current dropped to a constant residual. The cathode solution was separated from the mercury, quenched with ethanol, and evaporated to dryness under reduced pressure (ca. 20 mm). The residue that remains was thoroughly extracted with ether, thereby removing the TBAP. The extract was evaporated to dryness on a steam bath or under reduced pressure. The product was then recrystallized from the appropriate solvent or solvents.

***N*,1,1-Triphenylmethylamine (6).** A solution of 1.0 g (0.003 88 mol) of **5** in DMF was reduced at −2.80 V until the current dropped to a constant residual. The total number of coulombs passed was 703 or 1.87 electrons equiv^{-1} mol^{-1}. The ether extracts were combined and concentrated to a volume of about 100 mL. Dry hydrogen chloride gas was bubbled into the cold ethereal solution. A white precipitate formed almost immediately. The product was filtered, washed with ether, and dried under vacuum. The yield of compound **6·HCl** was 0.94 g (82%): mp 191–192 °C [lit.[31] mp 188–190 °C]. Anal. Calcd for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; N, 4.74. Found: C, 77.09; H, 5.94; N, 4.55. The free amine **6** was obtained by treating the hydrochloride salt with an excess of a 20% NaOH solution. The amine was extracted with ether and the ethereal extract dried over anhydrous $MgSO_4$. The ether was removed by vacuum distillation. The white solid that remained was recrystallized from ethanol: mp 57.5–59 °C [lit.[31] mp 56–57 °C]; IR ($CHCl_3$) 3420 (NH), 1590 (C=C) cm^{-1}.

***N*,*N*′-Dibenzylethylenediamine (8).** A solution of 1.0 g (0.004 24 mol) of **7** in DMF was reduced at −3.30 V as described in the general procedure. The total number of coulombs passed was 1440. The product obtained contained some supporting electrolyte and tri-*n*-butylamine. The tri-*n*-butylamine was removed by vacuum distillation at 1.0 mm, using a water bath at 50 °C. Elimination of the supporting electrolyte was achieved by redissolving the oily solid in ether and filtering it from the solution. The ether layer was treated with activated charcoal and filtered and the filtrate evaporated to dryness. The light-yellow oil that remained was distilled under vacuum twice, giving 0.7 g (68.6%) of the diamine **8**: bp 165–175 °C (1.0–2.0 mm) [lit.[32] bp 160 °C (0.75 mm)]; IR (neat) 3300 cm^{-1} (NH), also indicated the presence of some DMF by the carbonyl present. Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.66. Found: C, 80.43; H, 8.58; N, 10.98. The oil was dissolved in absolute ether (25 mL) and anhydrous hydrogen chloride was bubbles into the solution. A white precipitate formed, which was filtered and washed with several portions of anhydrous ether. The resulting white solid was dried under reduced pressure. The diamine dihydrochloride salt melted at 296–298 °C [lit.[33] mp 298 °C].

Anal. Calcd for $C_{16}H_{22}Cl_2N_2$: C, 61.35; H, 7.08; N, 8.94. Found: C, 61.42; H, 6.93; N, 8.70.

1,4-Dimethyl-2,3-diphenyl-1,4-piperazine (9). A solution of 1.0 g (0.004 24 mol) of **7** in glyme (distilled by bulb-to-bulb method on vac line) was reduced as in the previous experiment. The total number of coulombs passed was 1510. The resulting deep reddish-yellow solution was quenched with 2.41 g or 1.06 mL (0.016 96 mol, 2.28 g/mL) of methyl iodide. The red color disappeared immediately, leaving a yellow solution. The initial workup was the same as the general procedure. The ether extract was concentrated and dry hydrogen chloride gas bubbled into the solution. The white solid that precipitated was filtered and washed with ether. The product was dried under vacuum and 0.6 g (41.5%) of the dihydrochloride salt was obtained. Anal. Calcd for $C_{18}H_{24}Cl_2N_2$: C, 63.34; H, 7.68; N, 8.21. Found: C, 63.87; H, 7.66; N, 8.11. The free base was obtained by reacting the dihydrochloride salt with an excess of a 20% sodium hydroxide solution and extracting thoroughly with ether. The ether was removed on a steam bath. The oil that remained was crystallized from petroleum ether (bp 30–60 °C). After two additional recrystallizations, compound **9** was obtained as beautiful, colorless plates: mp 84–85.5 °C; IR (neat) 3070 (Ar H), 2980 and 2850 (aliphatic C-H), 1600 (skeletal C=C), 755 and 700 (Ar H out-of-plane bend, mono aromatic substitution) cm^{-1}; NMR ($CDCl_3$) δ 2.02 (s, 6), 2.83 (m, 4, AA′BB′ pattern), 2.96 (s, 2, overlaps with multiplet), 7.15 (s, 10); mass spectrum (70 eV) *m/e* 266, 251, 236.

Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.33; N, 10.51. Found: C, 81.51; H, 8.75; N, 10.49.

***N*,*N*′-Bis(diphenylmethyl)ethylenediamine (11).** A solution of 1.0 g (0.002 58 mol) of **10** in DMF was reduced at −3.10 to −3.20 V as previously described. The total number of coulombs passed was 900. The product was extracted with petroleum ether (bp 30–60 °C). The petroleum ether solution was concentrated to about 50 mL and 0.4 g (39.4%) of compound **11** crystallized, melting at 103.5–105 °C. An analytical sample was obtained by two additional recrystallizations from petroleum ether: mp 105–106 °C [lit.[34] mp 105.5 °C]; IR (Nujol) 3325 (NH), 1600 (skeletal C=C) cm^{-1}; NMR ($CDCl_3$) δ 1.82 (s, 2, NH), 2.71 (s, 4, CH_2), 4.78 (s, 2, CH), 7.32 (m, 20, Ar H), after D_2O was added the signal at δ 1.82 disappeared and a water signal at δ 4.67 appeared; mass spectrum (70 eV), *m/e* 392, 225, 182, 167. Anal. Calcd for $C_{28}H_{28}N_2$: C, 85.67; H, 7.19; N, 7.14. Found: C, 85.66; H, 6.95; N, 7.05. The mother liquor that remained from above was evaporated to dryness, leaving an oil. An infrared spectrum of the oil showed a carbonyl similar to that of benzophenone (C=O, 1675 cm^{-1}). Crystals were obtained from the oil by crystallization from petroleum ether after seeding with a crystal of benzophenone. The yield of benzophenone was 0.5 g (54.2%): mp 52 °C; IR (neat) 1675 (C=O) cm^{-1}, the infrared spectrum was identical with the IR spectrum of an authentic sample.

Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.46; H, 5.55.

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9-Anilinophenanthracene (13). A solution of 2.0 g (0.005 56 mol) of **12** in DMF/TBAN was reduced at −2.70 V as previously described. The total number of coulombs passed was 897. The electrolyzed solution was quenched with ethanol and separated from the mercury. The solvent was removed by vacuum distillation. The dry solid including the TBAN was dissolved in a minimum amount of carbon tetrachloride and chromatographed on an alumina column using carbon tetrachloride, cyclohexane, and benzene as elutants, respectively. The middle fractions were chromatographed by use of thin-layer procedures on activated alumina with 50/50 benzene/cyclohexane for 1 h as the developing solvent. Fraction 2–8 showed the identical compound (R_f value 0.47) while fraction 9 also showed this compound as well as other trace impurities. The combined appropriate fractions were recrystallized from ligroine (bp 66–75 °C), givine 0.9 g (60%) of compound **13**. Two additional recrystallizations from ligroine yielded light-cream crystals: mp 133.5–135 °C [lit.[35] mp 133–134.5 °C]; UV max (glyme) 339 nm (ε 8.330), 248 (29 100); IR ($CHCl_3$) 3425 (NH), 1600 (skeletal C=C) cm^{-1}; NMR ($CDCl_3$) δ 5.68 (s, 1 NH), 6.44–8.78 (m, 14, Ar H), upon shaking with D_2O, the peak at δ 5.68 disappears; mass spectrum (70 eV), *m/e* 269.

Anal. Calcd for $C_{20}H_{15}N$: C, 89.19; H, 5.61; N, 5.20. Found: C, 89.28; H, 5.69; N, 5.16.

Reduction of 2,2′-Bis(benzylideneamino)biphenyl (14). A solution of 2.0 g (0.005 55 mol) of **14** in DMF was reduced at −2.95 V. The total number of coulombs passed was 1250. The ether was evaporated to dryness on a steam bath. The oily solid that remained was dissolved in methylene chloride and methanol added to precipitate the product. A main fraction was obtained that weighed 1.27 g. Its infrared spectrum ($CHCl_3$) had an NH absorption at 3450 cm^{-1} as well as a weak C=O absorption at 1670 cm^{-1}. Upon repeating the above procedure, three additional fractions *and* a residue were obtained. The carbonyl absorption increased in strength with each fraction obtained, while the NH absorption decreased. Attempted recrystallization of the first fraction failed to give any well-formed crystals. Only amorphous solids were obtained. Recrystallization from cyclohexane–petroleum ether raised the melting point from 166–180 to 185–200 °C with some solid still at 225 °C. Liquid chromatography of a sample believed to be reasonably pure showed that several different compounds were still present. Use of column chromatography, taking close fractions, failed to isolate any pure material also. Sublimation at 170–180 °C (1 mm) melted and decomposed the product. No further procedures were attempted.

2,2′-Bis(anilinobenzyl)biphenyl (16). A solution of 2.0 g (0.003 92 mol) of **15** in glyme was reduced at −2.95 V as previously described. Most of the material was not soluble, but the reduction proceeded smoothly. The total number of coulombs passed was 1610. The ether was removed by distillation on a steam bath and the solid obtained was dissolved in 200 mL of hot ligroine (bp 90–120 °C), treated with activated charcoal, and filtered and the filtrate concentrated to about 100 mL. Upon cooling, 1.23 g of product was collected. Further concentration of the mother liquor produced an additional 0.17 g or a total yield of 69.5% of a cream-colored, fluffy material. The melting point of this material was 180–200 °C (mixture of isomers, *dl* and meso). Attempts to separate the isomers failed, but several recrystallizations from methanol–methylene chloride increased the melting point to 217–223 °C; IR ($CHCl_3$) 3415 (NH), 3050 (Ar H), 3000 (aliphatic CH), 1600 (skeletal C=C) cm^{-1}; NMR ($CDCl_3$) δ 4.07 (s, 2, NH, br), 5.50 (s, 2, CH, br), 6.05–7.70 (m, 28, Ar H), upon shaking with D_2O, the peak at δ 4.07 disappears and a water peak appears at δ 4.69; mass spectrum (70 eV), *m/e* 514, 423, 346, 331, 254, 241.

Anal. Calcd for $C_{38}H_{32}N_2$: C, 88.34; H, 6.24; N, 5.42. Found: C, 88.02; H, 6.41; N, 5.28.

2,2′-Bis[(diphenylmethyl)amino]biphenyl (18). A solution of 2.0 g (0.003 92 mol) of **17** in glyme was reduced at −3.10 V as previously described. The total number of coulombs passed was 1570. The electrolyzed solution was quenched with ethanol and separated from the mercury, and the solvent was removed by vacuum distillation. The dry solid was dissolved in methylene chloride–methanol. The methylene chloride was slowly removed by means of a steam bath, yielding two crops of compound **18**, 1.72 g (85%). Three additional recrystallizations from methylene chloride–methanol gave colorless crystals of compound **18**: mp 169.5–171 °C; IR ($CHCl_3$) 3450 (NH), 1600, and 1575 (skeletal C=C) cm^{-1}; NMR ($CDCl_3$) δ 4.44 (poorly resolved doublet, 2, NH, br, J = 3 Hz), 5.53 (poorly resolved doublet, 2, CH, J = 3 Hz), 6.40–7.70 (main absorption δ 7.23, m, Ar H), upon shaking with D_2O, the peak at δ 4.46 disappears and the doublet at δ 5.53 collapsed to a singlet at δ 5.53; mass spectrum (70 eV), *m/e* 516, 349, 173, 167.

Anal. Calcd for $C_{38}H_{32}N_2$: C, 88.34; H, 6.24; N, 5.42. Found: C, 88.53; H, 6.34; N, 5.34.

9a,18-Dihydro-9*H*-dibenz[3,4:5,6]azepino[1,2-*a*]dibenzo[*d*,*f*][1,3]diazepine (20). A solution of 2.0 g (0.005 56 mol) of **19** in DMF was reduced at −2.80 V as described previously. The total number of coulombs passed was 840. The ether was removed and absolute ethanol added. A cream-colored solid weighing 1.21 g (60%) was obtained by filtration, mp 215–220 °C. Recrystallization from absolute ethanol gave light-cream crystals of **20**: mp 230–232.5 °C; IR ($CHCl_3$) 3340 (NH), 3060 and 3000 (Ar H), 2920 and 2840 ($\nu_{as}(CH_2)$ and $\nu_s(CH_2)$, respectively), and 1580 (skeletal C=C) cm^{-1}; NMR ($CDCl_3$) δ 3.54 (s, 1, NH br), a double doublet centered at 3.70 and 3.92 (dd, 2, H_aCH_b, J = 3 Hz), 5.60 (s, 1, CH), 6.60–7.80 (m, 16, Ar H), the broad absorption at δ 3.54 (NH) disappears upon shaking with D_2O and a water peak appears at δ 4.71; mass spectrum (70 eV), *m/e* 360, 344, 330, 193, 180, 167, 165.

Anal. Calcd for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.57; H, 5.47; H, 7.57.

9,18-Dihydrodibenzo[*e*,*g*]phenanthro[9,10-*b*][1,4]diazocine (21). The mother liquor from the previous reaction was concentrated and cooled, 0.40 g (19.8%) of a light-tan solid crystallized from the ethanol solution. Compound **21** was recrystallized from benzene–petroleum ether: mp 272–273 °C; IR (KBr) 3400, 3330, and 3260 (NH), 3070 (Ar H), 1600 (skeletal C=C) cm^{-1}; NMR (Me_2SO-d_6) δ 5.20 (s, 2, NH, br), 6.20–9.20 (m, 16, Ar H); mass spectrum (70 eV), *m/e* 358, 343, 328, 176 and 152.

Anal. Calcd for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.41; H, 5.15; N, 7.65.

4b,5,9b,10-Tetrahydro-4b,9b-diphenylindolo[3,2-*b*]indole (23). A solution of 1.0 g (0.0028 mol) of **22** in glyme was reduced at −2.60 to −2.70 V as previously described. The total number of coulombs passed was 645. The reduced solution was quenched with absolute ethanol inside of the drybox, poured into a round-bottom flask and the solvent removed under vacuum. The solid was extracted with ether to remove the TBAP and mercury. The ether was distilled off under a nitrogen blanket on a steam bath. Traces of tri-*n*-butylamine were still present; therefore, the compound was redissolved in ether and extracted with water. The solvent was again removed and a high vacuum applied to dry the product. Crude **23** was obtained in 94% (0.96 g) yield; mp 184–204 °C. Recrystallization from chloroform–ethanol yielded 0.73 g (71%) of pure material: mp 201.5–202.5 °C; IR (KBr) 3359 and 3339 (NH), 3025 (Ar H), 1592 (skeletal C=C) cm^{-1}; NMR ($CDCl_3$) δ 4.54 (s, 2, NH, br, exchanges with D_2O), 6.60–7.38 (m, 18, Ar H); UV (glyme) 303 nm (ε 5800), 237 (20 600); mass spectrum (70 eV), *m/e* 360, 283, 269, 256, 180.

Anal. Calcd for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.89; H, 5.45; N, 7.59.

3,8-Dichloro-4b,5,9b,10-tetrahydro-4b,9b-diphenylindolo[3,2-*b*]indole (25). A solution of 1.0 g (0.002 34 mol) of **24** in glyme was reduced at −2.40 to −2.50 V as described earlier. The total number of coulombs passed was 511. The solution was worked up as described in the previous experiment. Recrystallization from ethanol–methylene chloride yielded two fractions. The first fraction, 0.4 g (39.6%), mp 200–210 °C, had an infrared spectrum identical with an authentic sample prepared by the method of Sternbach et al.[18,19] The second fraction, 0.3 g (29.7%), also had an identical infrared spectrum. Several recrystallization were required to raise the melting point to that reported in literature. The melting point obtained on the pure material was 223–226.5 °C [lit.[19,36] mp 225–228 and 228–230 °C]; mixture melting point 221–230 °C; IR ($CHCl_3$) 3450 (NH), 2940 (Ar H), 1600 (skeletal C=C) cm^{-1}; TLC (1.25 h/benzene) R_f 0.90 (R_f 0.91, 0.89 on au-

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thentic sample same conditions).

Preparation of Compounds Used in the Characterization of the Electrochemical Products. 2,2'-Bis[(diphenylmethyl)amino]biphenyl (18). A solution of 1.0 g of (0.001 96 mol) of **17** and 0.152 g (0.004 mol) of lithium aluminum hydride ($LiAlH_4$) in 125 mL of anhydrous ether was heated under reflux for 24 h. Ice was added slowly to destroy the excess $LiAlH_4$ and the solution then poured into a cold 20% sodium hydroxide solution. The two layers were separated and the aqueous layer extracted two additional times with 50 mL of ether. The combined ether extracts were dried over anhydrous $MgSO_4$ and filtered, and the ether was removed on a steam bath. The oil was dissolved in methylene chloride and diluted with methanol. The methylene chloride was slowly distilled from the solution. Cooling yielded two crops of compound **18**, 0.9 g (89%). The total yield of diamine **18** was 0.9 g (89%). Three recrystallizations from methanol–methylene chloride yielded a compound melting at 168.5–171.5 °C; the mixture melting point was identical with that of the compound obtained from the electrochemical reduction of the di-Schiff base **17**; the infrared spectra were also identical.

9-Acetyl-9a,18-dihydro-9*H*-dibenz[3,4:5,6]azepino[1,2-*a*]-dibenzo[*d*,*f*][1,3]diazepine (20a). To a stirred solution of 15 mL of acetic anhydride containing 0.2 mL of boron trifluoride etherate was added 0.4 g of **20**. The solution was stirred for 30 min, poured into water, and stirred to decompose the acetic anhydride. The precipitate that formed was filtered, washed with water, and air-dried. The material isolated, 0.4 g (89.5%), was used as obtained: mp 248–252 °C; NMR ($CDCl_3$) δ 1.60 (s, 3, $COCH_3$), 4.05 (s, 2, CH_2, br), 6.48 (s, 1, CH), 7.08–8.27 (m, 16, Ar H); mass spectrum (70 eV), *m/e* 402, 387, 359, 344.

9,18-Dihydrodibenzo[*e*,*g*]phenanthro[9,10-*b*][1,4]diazocine (21). A solution of 9.0 g (0.0253 mol) of dibenzo[*e*,*g*]-phenanthro[9,10–*b*][1,4]diazocine[37] and 2.0 g (0.0506 mol) of lithium aluminum hydride in 200 mL of anhydrous glyme was heated under reflux for 3 h. Ice was added to destroy the excess $LiAlH_4$. The solution was poured into a cold 20% sodium hydroxide solution. The two layers were separated, and the aqueous layer was extracted two additional times with 100-mL portions of ether. The combined extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness; 7.5 g (82.8%) of a light-tan solid was obtained. Several recrystallizations from benzene–petroleum ether yielded a fluffy, light-tan material identified as **21**, mp 272.5–273.5 °C. The infrared spectrum ($CHCl_3$) and mixture melting point proved this compound to be identical with one of the products isolated by the electrochemical reduction of **19**.

9,18-Dihydro-9,18-dimethyldibenzo[*e*,*g*]phenanthro[9,10-*b*][1,4]diazocine (21b). To a solution of 1.0 g (0.0028 mol) of **21** in 50 mL of glyme prepared under nitrogen was added 1.0 g of 60% suspension of sodium hydride in mineral oil. The mixture was stirred and heated under reflux for 30 min. After addition of 10 mL of methyl iodide, stirring and heating under reflux was continued for 2 h and the mixture was poured into ice–water. Extraction with methylene chloride and replacement of this solvent by ethanol gave 0.8 g (74%) of light-cream crystals. Recrystallization from a mixture of methylene chloride–ethanol gave off-white prisms melting at 180.5–183.5 °C: NMR ($CDCl_3$) δ 2.52 (s, 6, NCH_3), 6.68–8.92 (m, 16, Ar H).

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.47; H, 5.75; N, 7.18.

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Registry No. 5, 574-45-8; **6**, 1865-12-9; **6**·HCl, 2101-21-5; **7**, 104-71-2; **8**, 140-28-3; **8**·2HCl, 3412-76-8; **9**, 81577-03-9; **9**·2HCl, 83027-12-7; **10**, 64042-50-8; **11**, 83027-13-8; **12**, 7443-50-7; **13**, 3920-79-4; **14**, 83027-14-9; **15**, 83027-15-0; *dl*-**16**, 83027-16-1; *meso*-**16**, 83027-24-1; **17**, 83027-17-2; **18**, 83027-18-3; **19**, 7428-21-9; **20**, 83027-19-4; **20a**, 83027-22-9; **21**, 83027-20-7; **21b**, 83027-23-0; **22**, 7139-42-6; **23**, 83027-21-8; **24**, 3646-61-5; **25**, 10127-72-7; 2,2'-dibenzoylbiphenyl, 24018-00-6; aniline, 62-53-3; 2,2'-diaminobiphenyl, 1454-80-4; benzophenone, 119-61-9; dibenzo[*e*,*g*]phenanthro[9,10-*b*][1,4]diazocine, 214-45-9.

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Stereospecific Synthesis of the Phosphono Analogues of α- and β-D-Glucose 1-Phosphate

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The present paper describes the convenient stereospecific synthesis of the analogues of α- and β-D-glucose 1-phosphate. The β analogue, (1-deoxy-β-D-glucopyranosyl)methanephosphonic acid, was synthesized by treatment of 2,6-anhydro-1-bromo-1-deoxy-3,4,5,7-tetra-*O*-acetyl-D-*glycero*-D-*gluco*-heptitol with triethyl phosphite, followed by deethylation of the obtained diethyl (1-deoxy-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)methanephosphonate and deacetylation with ion-exchange resin. The α analogue, (1-deoxy-α-D-glucopyranosyl)methanephosphonic acid, was synthesized by starting from 2,3,4,6-tetra-*O*-benzyl-D-glucose through the following sequence: Wittig reaction with methylenetriphenylphosphorane, mercuriocyclization, bromodemercuriation, Arbuzov reaction, and removal of the protecting groups.

In recent years great interest has developed in the synthesis of phosphonic acids which might be considered isosteric analogues of naturally occurring phosphates.[1] These compounds, in which a substitution of methylene for oxygen occurs at the phosphonic ester group, may be able to inhibit or regulate metabolic processes. This is due to their geometrical similarity with the naturally occurring analogues and to the incapability of the carbon–phosphorous bond to be hydrolyzed.

In the carbohydrate field a number of phosphonate analogues have been synthesized,[1-7] although in many cases

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