and acidified with hydrochloric acid (10%, 5 mL). A yellow precipitate of the dinitrobenzoate was removed by filtration and washed with aqueous sodium bicarbonate (10%, 5 mL). Recrystallization from cold carbon tetrachloride gave the 3,5-dinitrobenzoate as an amorphous golden yellow powder (0.29 g, 0.89 mmol, 82%): mp 127–128 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.27–3.33 (dd, 2 H), 3.67–3.74 (dd, 2 H), 5.96–6.04 (m, 1 H), 9.13–9.25 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 23.3, 70.6, 122.7, 129.4, 133.5, 148.7; IR (KBr) 1740 (vs), 1640 (s), 1550 (vs), 1350 (vs), 1180 (s), 740 (s), 730 (s) cm^{-1}; MS (70 eV), *m/e* (relative intensity) 334 (1), 332 (7, M), 330 (2), 329 (1), 328 (1), 196 (7), 195 (100), 149 (42), 122 (13), 121 (49), 120 (78), 119 (30), 118 (42), 117 (21), 116 (13), 103 (13), 96 (3), 94 (22), 93 (22), 92 (11), 91 (17), 75 (80), 74 (26). Anal. Calcd for $C_{10}H_8O_6N_2Se$: C, 36.27; H, 2.44. Found: C, 35.54; H 2.64. The elemental analysis is not satisfactory due to the instability of the compound.

3-Acetoxyselenetane. 3-Hydroxyselenetane (0.30 g, 2.20 mmol) was mixed with acetic anhydride (2 mL, 2.36 mmol) and sodium acetate (0.28 g, 2.80 m mol) and refluxed gently under a nitrogen atmosphere for 1.5 h. A fine, red precipitate could be seen at the bottom of the flask. The reaction mixture was poured into distilled water (5 mL) and extracted with ether (3 × 20 mL). The ether extracts were dried ($MgSO_4$) and concentrated to give a red-yellow oil. Preparative TLC (silica gel, 3:7 ether–petroleum ether) gave 3-acetoxyselenetane as yellow oil (0.105 g, 0.58 mmol, 27%): ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 3.1–3.5 (dd, 2 H), 3.39–3.46 (dd, 2 H), 5.55–5.68 (M, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.6, 68.7, 169.4; MS (70 eV), *m/e* (relative intensity) 182 (1), 180 (4, M), 178 (2), 177 (1), 176 (1), 121 (8), 120 (11), 118 (6), 117 (4), 116 (2), 94 (8), 93 (11), 92 (4), 91 (7), 90 (3), 43 (100), 42 (5), 41 (8), 39 (19). Attempted distillation caused decomposition with precipitation of red selenium.

Treatment of 3-Hydroxyselenetane with the Dess–Martin Periodinane. 3-Hydroxyselenetane (0.05 g, 0.37 mmol) was dissolved in chloroform-d_1 (0.5 mL) in an NMR tube (5 mm), and the solution was cooled to −60 °C and mixed with the periodinane[19] (0.20 g, 0.47 mmol) dissolved in chloroform-d_1 (2 mL). The ^{1}H NMR spectrum showed the complete disappearance of the complex absorption of the hydroxyselenetane and the appearance of a new singlet absorption at δ 4.22 corresponding to the 3-ketoselenetane.[26] Similar observations were made on treatment of 3-thietanol with the periodinane. The selenetanone could not be isolated, decomposition occuring on removal of solvent.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 3-Hydroxyselenetane, 73903-64-7; 3-hydroxyselenetane 3,5-dinitrobenzoate, 112422-92-1; 3-phenyl-3-hydroxyselenetane, 112422-88-5; 3-(*p*-methoxyphenyl)-3-hydroxyselenetane, 112422-89-6; 3-ethyl-3-hydroxyselenetane, 112422-90-9; (chloromethyl)oxirane, 106-89-8; 2-(chloromethyl)-2-phenyloxirane, 1005-91-0; 2-(chloromethyl)-2-(*p*-methoxyphenyl)oxirane, 109202-00-8; 2-(chloromethyl)-2-ethyloxirane, 75484-32-1; 1,3-dibromo-2-propanol, 96-21-9; 2-propanol, 67-63-0; 2-phenyl-2-propen-1-ol, 6006-81-1; 2-phenyl-2-propen-1-ol 3,5-dinitrobenzoate, 112422-91-0; 2-phenyl-2-propen-1-ol benzoate, 86148-32-5; 2-(*p*-methoxyphenyl)-2-propen-1-ol, 89619-03-4; 3,5-dinitrobenzoyl chloride, 99-33-2; benzoyl chloride, 98-88-4; 3-acetoxyselenetane, 112422-93-2.

(26) The singlet ^{1}H NMR absorption of the known sulfur analogue, 3-thietanone, appears at δ 4.21.

Improved Syntheses of Substituted Carbazoles and Benzocarbazoles via Lithiation of the (Dialkylamino)methyl (Aminal) Derivatives

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The lithiation of *N*-[(dialkylamino)methyl]carbazoles occurs readily and exclusively at the protonated carbon adjacent to the nitrogen atom. Reaction with a variety of electrophiles produces good to excellent yields of monosubstituted derivatives. Removal of the lithio-directing and nitrogen-protecting function is readily achieved by mild acid-catalyzed hydrolysis during workup of the reaction. Thus, carbazole undergoes lithiation at the 1-position, dibenzo[*c,g*]carbazole at the analogous 6-position, and benzo[*c*]carbazole at both the 6- and 8-positions, with the former predominating. 1,2,3,4-Tetrahydrocarbazole undergoes lithiation at the 8-position, but with 2,3-dimethylindole reaction occurs at the 2-methyl group. Benzo[*a*]carbazole fails to form an aminal derivative, but on direct lithiation in ether it can be substituted exclusively at the 1-position of the fused benzene ring.

Introduction

Although a number of routes are available for the preparation of substituted carbazoles, usually involving either electrophilic addition or ring closure methods,[3] there are few reports of their synthesis via lithiation. Gilman obtained a very poor product yield for the lithiation and subsequent carbonation of carbazole itself,[4] and although higher yields were obtained with *N*-alkylcarbazoles,[5,6] they were still not synthetically useful. Therefore it was generally assumed that the carbazole system did not lithiate very easily. However, more recently it has been shown that very good yields of 1-deuteriocarbazole (**3**) can be obtained from the lithiation of carbazole (**1**)[7] and that in fact the lithiation of carbazole occurs as readily as that of the related tricyclic systems phenothiazine[8] and 5*H*-dibenz[*b,f*]azepine.[9] These observed differences in reactivity were

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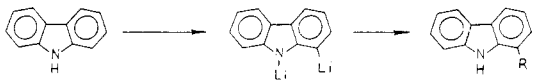
interpreted as being due to steric, and possibly also electronic, effects in the earlier carbonation work.[7]

Because of this intriguing difference in product yield when CO_2 and D_2O were used as the electrophiles, we chose to reinvestigate the lithiation of carbazole to see just what steric and electronic factors might be involved, both in the initial lithiation and in the subsequent electrophilic addition steps. We now report that when the NH group of carbazole is unprotected, as in the original work, low reaction yields are normally observed. However, when the amino function is converted to an aminal (Mannich Base) derivative, the lithiation of carbazole occurs readily at the 1-position, and good yields of electrophilic addition products can be achieved, regardless of the size of the electrophile.

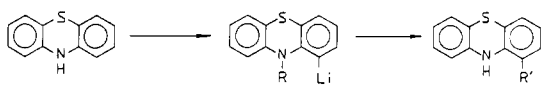
Results and Discussion

Initial experiments on the lithiation of carbazole (1) were conducted by using the same conditions as those in ref 7, namely, 2.5 equiv of *n*-butyllithium in diethyl ether at room temperature for 28 h. Reaction of the resulting dilithio anion 2 with carbon dioxide gave the 1-carboxylic acid 4 in 2% yield, confirming the earlier reports of a 1% yield,[4] while use of the more reactive hexachloroethane gave, after chromatography, a 16% yield of 1-chlorocarbazole (5). When combined with the reported 92% yield for the reaction with D_2O,[7] these results confirm that the reactivity of the dianion 2 is highly dependent on the nature of the electrophile and that, apart from the deuteriation reaction, the direct lithiation route is not synthetically useful.



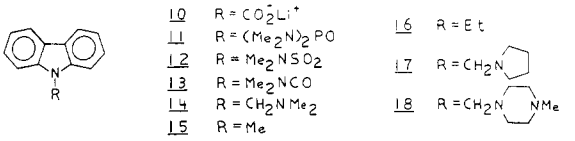
1 2 3 R = D; 4 R = CO_2H; 5 R = Cl

We have recently described the use of carbon dioxide as a protecting group for the amino function during the lithiation of N–H heterocycles,[10] and, in particular, in the case of phenothiazine (6) we found that significantly improved yields of 1-substituted derivatives 9 can be achieved via the lithio carbamate 8 when compared to those obtained from dianion 7.[11] We also investigated the CO_2



6 7 R = Li; 8 R = $CO_2^-Li^+$ 9

protection system with carbazole, but none of the desired product 4 was observed on sequential treatment of the lithio carbamate 10 with *tert*-butyllithium and carbon dioxide. Therefore, a number of other amino protecting groups were investigated to see if better results might be achieved. The N-substituents chosen for investigation were those that were expected to provide some activation by acting as lithiation directing agents, namely, the bis(dimethylamino)phosphoryl and the dimethylsulfonamoyl, both of which are known lithio-coordinating species when bound to nitrogen,[12,13] and the dimethylcarbamoyl and (dimethylamino)methyl groups because of their known efficacy in carbocyclic systems.[14] The first three derivatives 11, 12, and 13 were formed by treatment of carbazole with sodium hydride and the appropriate acyl chloride in THF at 0 °C, while compound 14 was prepared from carbazole via a Mannich reaction involving formaldehyde and aqueous dimethylamine in ethanol.[15]



10 R = $CO_2^-Li^+$; 11 R = $(Me_2N)_2PO$; 12 R = Me_2NSO_2; 13 R = Me_2NCO; 14 R = CH_2NMe_2; 15 R = Me; 16 R = Et; 17 R = CH_2N; 18 R = CH_2N NMe

In each case the appropriate N-substituted carbazole was treated with *tert*-butyllithium in THF at −78 °C and, after stirring for several hours at −10 °C, carbon dioxide gas was added as the electrophile at −78 °C. With the phosphorus- and sulfur-containing derivatives 11 and 12, no reaction was observed, whilst for the urea 13 a mixture of products was obtained, none of which were base-soluble. Only in the case of the (dimethylamino)methyl compound 14 was the hoped for reaction observed, and this was confirmed when mild acid-catalyzed hydrolysis of the protecting group gave the 1-carboxylic acid 4, albeit in low yield (12%).

The fact that lithiation occurred successfully only with the (dimethylamino)methyl group is probably a reflection of both its greater flexibility and its smaller steric bulk, since steric hindrance is known to be a factor in the lithiation of *N*-alkylcarbazoles. Thus *N*-methylcarbazole (15) gives rise to some 1,8-dicarboxylic acid,[5] even when treated with only 1 equiv of *n*-butyllithium followed by carbon dioxide, whereas *N*-ethylcarbazole (16) gives only the 1-monoacid when treated with an excess of the same reagents.[6] Since the (dimethylamino)methyl compound 14 is more closely related to *N*-ethylcarbazole than to carbazole itself, we would expect that steric effects should be similar. Thus it was possible that further reduction in the steric bulk of 14 might result in improved reaction yields, and it was for the investigation of this point that the pyrrolidinomethyl compound 17 was next prepared.

Lithiation of 17 in hexane, diethyl ether, and THF in the presence of tetramethylethylenediamine (TMEDA) followed by treatment with carbon dioxide showed that the best results were achieved in hexane at room temperature, although the product acid 4 was still not obtained in good yield. Therefore in order to increase the lithio directing ability of the nitrogen-protecting group, the *N'*-methylpiperazinyl derivative 18 was prepared. Since 18 already possessed the basic structural features of TMEDA, the lithiation reaction was performed in the absence of this species, in both THF and hexane. The experiment in hexane gave a yellow-orange precipitate of a lithio derivative, and after addition of carbon dioxide and subsequent hydrolysis, carbazole-1-carboxylic acid (4) was obtained as the sole product. No trace of unreacted carbazole was observed by TLC. In contrast the reaction in THF gave only a small amount of the acid product, with carbazole being recovered as the major component after the very facile hydrolysis step.

Since it was possible that the addition of TMEDA might have the same effect on the reaction as solvation by THF, the earlier lithiation in hexane of the pyrrolidinomethyl

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Table I. Synthesis of 1-Substituted Carbazoles from 9-(1-Pyrrolidinomethyl)carbazole (17)

electrophile	time, h	product	R	yield, %
CO_2	0.25	**4**	CO_2H	86
Cl_3CCCl_3	1	**5**	Cl	100
CH_3I	24	**20**	CH_3	70
$CH_3(CH_2)_3I$	24	**21**	$CH_3(CH_2)_3$	68
$[(CH_3)_3SiO]_2$[a]	1	**22**	OH	40
$(CH_3)_2CHCH_2O$-NO_2	1	**23**	NO_2	38
C_6H_5CHO	1	**24**	C_6H_5CO	63
$C_6H_5CO_2CH_2CH_3$	1	**24**	C_6H_5CO	36
		25	(Cbz)(C_6H_5)COH[b]	10
p-$CH_3C_6H_4CHO$	1	**26**	p-$CH_3C_6H_4CO$	70
$(C_6H_5)_2CO$	1	**27**	$(C_6H_5)_2COH$	75

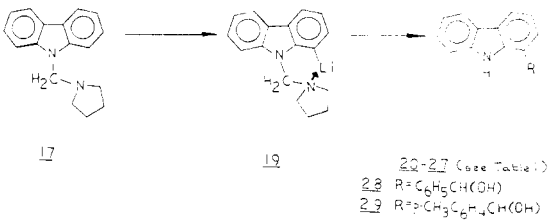
[a] See: Taddei, M.; Ricci, A. *Synthesis* **1986**, 633. [b] Cbz = 1-carbazoloyl.

compound **17** was repeated, this time without the added complexing agent. As with the piperazine **18** a bright yellow-orange precipitate was obtained, although at a slower rate, and subsequent carboxylation and hydrolysis gave the desired carboxylic acid **4** as the sole product in 85% yield.

To determine the relative activating effect of the amino substituent, the reaction of *N*-ethylcarbazole (**16**) was also investigated under the same conditions, but no product was obtained. This result confirms the necessity of having a nitrogen atom in the substituent group, while the earlier results show that a single nitrogen is sufficient.

A direct comparison of the [(dialkylamino)methyl]carbazoles **14**, **17**, and **18** showed that, although the piperazine **18** underwent both the lithiation and subsequent hydrolysis at a faster rate than **14** or **17**, the actual yield of product obtained was less. In addition, while the two monoamino derivatives **14** and **17** could readily be synthesized via Mannich reactions and purified by extraction with very dilute hydrochloric acid at room temperature, the piperazine **18** rapidly hydrolyzed back to carbazole under the latter conditions. It could be obtained pure by chromatography on neutral alumina, but the extra manipulation involved, as well as the lower product yields from the lithiation, made use of the monoamino derivatives more attractive. The pyrrolidinomethyl compound **17** could actually be obtained in better yield, and gave better product yields, than the (dimethylamino)methyl compound **14** so it was chosen for the subsequent study.

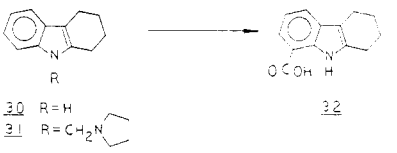
The synthesis of a variety of 1-substituted carbazoles was readily achieved from **17**, and the results are shown in Table I. Hydrolysis of the pyrrolidinomethyl protecting group was readily achieved during the workup by gently warming the reaction mixture for a few minutes in the presence of dilute aqueous hydrochloric acid. In certain cases, such as with the butyl derivative **21**, it was found that greatly improved yields could be obtained if THF was added to the reaction mixture prior to addition of the electrophile, and this modification was used for all subsequent work. The purpose of the added THF was to enble the lithio complex **19** to dissolve and therefore become more available for reaction. The fact that the presence of THF actually improves the reactivity of the lithio derivative tends to indicate that the lower product yields obtained from the earlier lithiation of **17** in THF were due to solvent effects on the initial metalation and not to inhibition of electrophile addition.



A most interesting result was obtained when aromatic aldehydes such as benzaldehyde and tolualdehyde were used as the electrophiles. Instead of the expected α-hydroxybenzyl derivatives **28** and **29**, the analogous aryl ketones **24** and **26** were obtained. Monitoring by TLC showed that the α-hydroxybenzyl products were, in fact, initially formed but that they underwent rapid aerial oxidation on replacement of the argon atmosphere of the lithiation reaction by air. The aryl ketones produced by this route were actually obtained more cleanly and in superior yield than when ethyl benzoate was used as the electrophile, since in this latter case further reaction occurred, giving rise to the triarylcarbinol **25**. Thus the aldehyde addition and subsequent aerial oxidation represents a very good route to 1-aroylcarbazoles. Attempted reaction with aliphatic aldehydes such as butanal resulted in complex product mixtures being obtained, showing that this particular method cannot be extended to the synthesis of aliphatic acylcarbazoles.

Even when allowance is made for the 80% yield in the initial conversion of carbazole to **17**, a comparison of our lithiation method with other synthetic routes to 1-substituted carbazoles shows that the high yields obtained in most cases make our system the method of choice for many of these compounds.

We next prepared the *N*-pyrrolidinomethyl derivative of 1,2,3,4-tetrahydrocarbazole (**30**) since, like carbazole, this



compound had previously failed to undergo lithiation using the carbon dioxide N-protection system.[10] Compound **31** has available two possible sites of reaction adjacent to the ring nitrogen, but lithiation was found to occur cleanly in the aromatic ring and no evidence for allylic deprotonation was seen. Thus, treatment of the reaction mixture with

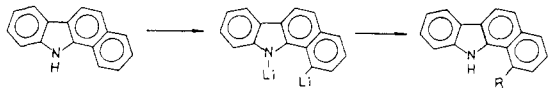
Table II. ^{1}H NMR Chemical Shifts for 1-Substituted Carbazoles

compd	H-2 (d)	H-3 (t)	H-4 (d)	H-5 (d)	H-6 (t)	H-7 (t)	H-8 (d)	H-9 (s)	R
1[7]	7.40	7.15	8.02	8.02	7.15	7.40	7.40	10.75	
4	8.38	7.29	8.15	8.03	7.24	7.43	7.77	11.33	0.30 (1 H)
5	7.64	7.22	8.13	8.08	7.17	7.47	7.47	11.62	
20	7.10	7.10	7.94	8.08	7.10	7.38	7.58	11.20	2.60s (3H)
21	7.10	7.10	7.92	8.06	7.10	7.37	7.52	11.15	0.93 t (3 H), 1.40 m (2 H)
22	6.84	6.96	7.48	8.01	7.10	7.33	7.54	11.04	9.76 s (1 H)
23	8.28	7.30	8.55	8.20	7.26	7.49	7.75	12.18	
24	7.60	7.25	8.44	8.20	7.25	7.46	7.60	11.80	7.60 m (2 H), 7.80 m (3 H)
25	6.52	6.96	8.10	8.07	7.12	7.30	7.58	10.34	7.37 m (5 H)
26	7.40	7.25	8.44	8.20	7.25	7.40	7.40	11.78	2.40 s (3 H), 7.70 m (4 H)
27	6.60	7.01	8.04	8.07	7.10	7.34	7.61	10.30	7.29 br s (10 H)

CO_2 gave the known[16] 8-substituted aryl acid **32** in 71% yield after hydrolysis of the pyrrolidinomethyl function. We also investigated the lithiation of the 2,3-dimethylindole derivative **33**; in this case the carbon dioxide method does work,[10] but metalation occurs on the C-2 methyl group. The same site of lithiation was found in the present case when, after treatment of **33** with *tert*-butyllithium followed by D_2O, both ^1H NMR and ^{13}C NMR spectra showed that deuteriation had occurred solely on the C-2 methyl carbon. The fact that different reaction pathways are followed by 2,3-dimethylindole and 1,2,3,4-tetrahydrocarbazole implies a difference in conformation about the aliphatic carbon adjacent to the nitrogen, with the protons in the latter case being positioned in a way that is unfavorable for lithio-anion formation.

33 **34**

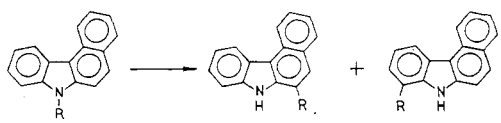
The lithiation of some benzo- and dibenzocarbazoles was also investigated, starting with benzo[*a*]carbazole (**35**).



35 **36** **37** R=CO_2H; **38** R=Cl

Attempted formation of the *N*-pyrrolidinomethyl derivative of **35** was unsuccessful, presumably due to steric factors, so the lithiation was performed directly on the unsubstituted compound with 2.5 equiv of *n*-butyllithium in diethyl ether at room temperature. Treatment of the reaction mixture with carbon dioxide gas gave the known 1-substituted acid **37**[17] as the sole product in 70% yield, thereby showing that reaction had occurred exclusively at the 1-position of the benzo-fused ring. Similarly reaction of the lithio dianion **36** with hexachloroethane gave the previously unknown 1-chloro derivative **38** in quantitative yield. The fact that the lithiation occurred exclusively on the benzo-fused ring was not unexpected, since the same result is observed on treatment of benzo[*a*]phenothiazines with *n*-butyllithium.[18]

Benzo[*c*]carbazole (**39**) failed to undergo direct dilithiation, mainly due to the poor ether solubility of the monoanion, but lithiation was readily achieved after conversion to the pyrrolidinomethyl derivative **40**. However,



39 R=H; **40** R=CH_2N (6-sub) (8-sub)

unlike benzo[*c*]phenothiazine, where lithiation occurred exclusively at the 6-position in the more substituted (naphtho) ring,[19] a mixture of 6- and 8-substituted products was obtained in the present case. ^{13}C NMR analysis of the mixtures indicated that the 6-substituted product predominated, but because of the difficulties associated with the separation of the isomeric products, the benzo[*c*] system was not investigated further.

Finally, the symmetrical dibenzo[*c*,*g*]carbazole system was investigated, since in this case isomer formation could not occur. The extra benzo rings meant that all of the compounds produced were much less soluble than their carbazole analogues, but by the appropriate modification of the experimental conditions the desired products could be obtained. Thus, reaction of dibenzo[*c*,*g*]carbazole (**41**) with pyrrolidine and formaldehyde gave the N-protected derivative **42** which was lithiated as for compound **17**. Treatment of the reaction mixture with carbon dioxide and hexachloroethane then gave the new 6-substituted derivatives **43** and **44** in 57% and 65% yields, respectively.

41 R=H; **42** R=CH_2N **43** R=CO_2H; **44** R=Cl

Conclusion

For a protecting group to be of utility in organic synthesis it is necessary that it be both introduced and removed readily, as well as being uneffected by the actual conditions of the chemical reaction involved. The protection of carbazoles with an *N*-(dialkylamino)methyl group meets all of these requirements in the present case. Thus the protecting group is readily introduced via a Mannich reaction, it is stable under the conditions of the lithiation reaction, and it is readily removed by acidic hydrolysis during the workup of the reaction. In addition, coordination of the aliphatic nitrogen atom to the butyllithium results in a dramatic improvement in the lithiation efficiency. The lithio-directing effect of the dialkylamino group in carbocyclic chemistry is well-known,[14] and its current extension to heterocyclic systems such as carbazole represents a valuable addition to its usefulness.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. IR spectra were recorded on a Perkin-Elmer 283B spectrophotometer. ^1H NMr spectra (60 MHz) were obtained on a Varian EM 360 spectrometer and ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded on a Varian XL200 (FT mode) spectrometer. Elemental analyses were performed under the supervision of Dr. R. W. King of this department.

Carbazole (Kodak) was purified by recrystallization from ethanol. Benzo- and dibenzocarbazoles were available from other work.[20] Hexane was washed successively with concentrated H_2SO_4 and water, dried over $MgSO_4$, and distilled from CaH_2. Tetrahydrofuran (THF) and diethyl ether were dried by distillation from sodium–benzophenone ketyl. All lithiations were carried out in a dry argon atmosphere. Column chromatography was carried out by using MCB silica gel (230–400 mesh).

Lithiation of Carbazole (1). General Procedure. According to the method of ref 7, 4.0 mL (10 mmol) of 2.5 M *n*-butyllithium in hexanes (Aldrich) was added dropwise to a solution of 0.67 g (4 mmol) of carbazole (**1**) in 30 mL of dry ether at room temperature. After stirring the reaction mixture for 28 h, the electrophile was added and after a further 15 min it was treated with water.

Carbazole-1-carboxylic Acid (4). Passage of a slow stream of carbon dioxide gas through the above reaction mixture for 15 min, followed by extraction with dilute ammonia solution, gave,

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after filtration and acidification with concentrated hydrochloric acid, a low (2%) yield of **4**: mp (chloroform) 271–273 °C (lit.[16] mp 271–273 °C).

1-Chlorocarbazole (5). To the carbazole lithiation reaction was added 4.73 g of hexachloroethane (20 mmol) in 10 mL of ether, and after being stirred for 15 min the mixture was quenched with water and diluted with further ether. After being washed with water and 10% Na_2CO_3 solution, the solution was dried with $MgSO_4$ and the ether was removed. The residue was chromatographed on silica gel (eluting with benzene–hexane, 2:1) to give 0.13 g (16%) of **5**: mp (ethanol) 124–125 °C (lit.[21] mp 123–125 °C).

9-[Bis(dimethylamino)phosphoramidoyl]carbazole (11). A solution of 1.0 g (6 mmol) of carbazole in 15 mL of THF was cooled to 0 °C and 0.29 g (7.3 mmol) of 60% NaH was added with stirring. After hydrogen evolution had ceased (ca. 1–2 min), 1.2 mL (7.3 mmol) of bis(dimethylamino)phosphorochloridate (Aldrich, tech., 90%) was added dropwise, and the mixture was stirred for a further 2 h. After neutralization with water the solvent was removed under vacuum and the product was extracted with diethyl ether. After drying ($MgSO_4$) the ether was removed to give a colorless oil which was dissolved in hexane. Cooling to 0 °C gave, as white needles, 0.79 g (44%) of **11**: mp 101–103 °C (lit.[22] mp 103–104 °C); ^1H NMR ($CDCl_3$) δ 2.63 (d, J = 10 Hz, 12 H, CH_3) 7.10 (m, 4 H), and 7.76 (m, 4 H).

9-(Dimethylsulfamoyl)carbazole (12). A solution of 5.0 g (30 mmol) of carbazole in 50 mL of THF was cooled to 0 °C and treated with 1.44 g (36 mmol) of 60% NaH as above. Dimethylsulfamoyl chloride (3.9 mL, 36 mmol) was added dropwise over 5 min and, after a further 3 h, the solution was poured into water to give a white precipitate which was collected and dried. Recrystallization from ethanol gave 6.89 g (84%) of **12**: mp 111–112 °C; ^1H NMR ($CDCl_3$) δ 2.75 (s, 6 H, CH_3), 7.40 (m, 4 H), and 8.05 (m, 4 H); ^{13}C NMR δ 38.5 (CH_3), 114.6 (C-1,8), 119.8 (C-4,5), 123.1 (C-3,6), 125.1 (C-4a,4b), 127.0 (C-2,7), and 138.9 (C-8a,9a). Anal. Calcd for $C_{14}H_{14}N_2O_2S$: C, 61.29; H, 5.14; N, 10.21. Found: C, 61.68; H, 5.52; N, 9.93.

9-(Dimethylcarbamoyl)carbazole (13). A solution of 5.0 g (30 mmol) of carbazole in 50 mL of THF was treated with 1.44 g (36 mmol) of 60% NaH as above, and this was followed by dropwise addition of 3.3 mL (36 mmol) of dimethylcarbamyl chloride (Aldrich, 99%). After being stirred for a further 1 h, the mixture was neutralized with water, the solvent was removed, and the oily residue was extracted with diethyl ether. The ether was washed with water, dried ($MgSO_4$), and removed, to give an oil which was dissolved in hexane. After standing at room temperature overnight (cooling resulted in oiling) 2.47 g (35%) of **13** was obtained as white needles: mp 54.5–55.5 °C (lit.[23] mp 64.5–65.5 °C); ^1H NMR ($CDCl_3$) δ 2.98 (s, 6 H, CH_3), 7.25 (m, 6 H), and 7.85 (m, 2 H).

9-[(Dimethylamino)methyl]carbazole (14). A mixture of 10.02 g (60 mmol) of carbazole, 5.5 mL (68 mmol) of 37% aqueous formaldehyde, and 9.3 mL of 33% aqueous dimethylamine in 120 mL of ethanol was heated under gentle reflux for 12 h and cooled. The solvent was then removed under vacuum to give a white solid which was dissolved in 100 mL of ethyl acetate. The solution was extracted twice with 0.1 M hydrochloric acid, and after being washed with fresh ethyl acetate, the aqueous layer was bascified with concentrated ammonia to give a crystalline precipitate of 5.74 g (51%) of **14**: mp (ethanol) 68–70 °C (lit.[15] mp 68 °C); ^1H NMR ($CDCl_3$) δ 2.77 (s, 6 H, CH_3), 5.21 (s, 2 H, CH_2), 7.91, 7.95, and 8.56 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 42.9 (CH_3), 65.9 (CH_2), 109.4 (C-1,8), 119.2 (C-3,6), 120.4 (C-4,5), 123.0 (C-4a,4b), 125.6 (C-2,7), and 141.0 (C-8a,9a).

9-(1-Pyrrolidinomethyl)carbazole (17). A mixture of 10.02 g (60 mmol) of carbazole, 5.5 mL (68 mmol) of 37% aqueous formaldehyde, and 4.8 g (68 mmol) of pyrrolidine in 120 mL of ethanol was heated under gentle reflux for 12 h. Cooling and dilution with water gave an oil which was extracted with ethyl acetate and washed twice with water. After being extracted twice with 0.01 M HCl, the ethyl acetate was discarded and the aqueous layer was washed with further solvent. Bascification with concentrated ammonia gave an oil which rapidly solidified to give 11.97 g (80%) of **17**: mp (hexane) 74–75 °C; ^1H NMR ($CDCl_3$) δ 1.71 (m, 4 H, CH_2), 2.70 (m, 4 H, CH_2N), 5.13 (s, 2 H, CH_2), 7.22, 7.47 and 8.06 (m, 8 H, Ar); ^{13}C NMR ($CDCl_3$) δ 23.5 (CH_2), 51.6 (CH_2N), 61.4 (NCH_2N), 109.4 (C-1,8), 119.2 (C-3,6), 120.1 (C-4,5), 122.9 (C-4a,4b), 125.7 (C-2,7) and (C-8a,9a). Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.24; N, 11.19. Found: C, 81.87; H, 7.47; N, 11.23.

9-[(4-Methylpiperazinyl)methyl]carbazole (18). A mixture of 3.86 g (23 mmol) of carbazole, 5.00 g (50 mmol) of 1-methylpiperazine, and 4.0 mL (50 mmol) of 37% aqueous formaldehyde in 40 mL of ethanol was heated under gentle reflux for 12 h, and the solvent was removed under vacuum. The residue was dissolved in ethyl acetate, washed twice with water, and dried (Na_2SO_4). Removal of the solvent and chromatography on neutral alumina, eluting with hexane and dichloromethane, gave 2.85 g (44%) of **18**: mp (hexane) 116–118 °C; ^1H NMR ($CDCl_3$) δ 2.23 (s, 3 H, CH_3), 2.39 (m, 4 H, CH_2), 2.63 (m, 4 H, CH_2), 4.89 (s, 2 H, CH_2), 7.23, 7.49, and 8.50 (m, 8 H, Ar); ^{13}C NMR ($CDCl_3$) δ 46.0 (CH_3), 50.9 and 54.8 (CH_2N), 65.3 (NCH_2N), 109.7 (C-1,8), 119.4 (C-3,6), 120.1 (C-4,5), 123.1 (C-4a,4b), 125.7 (C-2,7), and 141.1 (C-8a,9a). Anal. Calcd for $C_{18}H_{21}N_3$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.43; H, 7.81; N, 14.89.

Lithiation of 9-(1-Pyrrolidinomethyl)carbazole (17). General Procedure. A solution of 0.50 g (2 mmol) of **17** in 60 mL of dry hexane was cooled to −78 °C under an argon atmosphere, and a solution of 1.7 M *tert*-butyllithium (1.8 mL, 1.5 equiv) in pentane was added dropwise to the resulting white suspension. The mixture was allowed to warm to room temperature, to give a clear colorless solution which was stirred for a further 16 h as a bright yellow-orange precipitate of **19** was formed. The reaction mixture was then cooled to −78 °C and 20 mL of dry THF was added to dissolve the solid. The electrophile (1.5 equiv) was then added either as a gas stream (CO_2) or dropwise as a neat liquid or as a solution in hexane. The mixture was allowed to warm to room temperature and after a further 1–24 h the solvent was removed under vacuum. The residue was then treated with 60 mL of 1 N hydrochloric acid and the resulting mixture was then heated on a steam bath for 30 min to ensure complete hydrolysis of the pyrrolidinomethyl group. The product was then extracted into ethyl acetate (3 × 50 mL) and dried ($MgSO_4$) and the solvent was removed under vacuum. With the exception of compound **4**, which was extracted with dilute aqueous ammonia, the compounds were purified by chromatography on silica gel. The optimum solvent sytem for each compound is given below.

1-Methylcarbazole (20): eluted with benzene–hexane, 2:1, mp (ethanol) 118–120 °C (lit.[24] mp 120.5–121 °C).

1-Butylcarbazole (21): eluted with hexane–ethyl acetate, 10:1; mp (ethanol) 56–57 °C. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.51; H, 8.04; N, 6.05.

1-Hydroxycarbazole (22): eluted with chloroform–ethyl acetate, 1:1; mp (ethanol) 165–167 °C (lit.[25] mp 160 °C).

1-Nitrocarbazole (23): eluted with benzene–hexane, 2:1, mp (methanol) 188–189 °C (lit.[26] mp 189–190 °C).

1-Benzoylcarbazole (24): eluted with benzene–hexane, 2:1, mp (methanol) 150–151 °C; IR ($CHBr_3$) δ 1,630 cm^{-1} (C=O); ^{13}C NMR (DMSO-d_6) δ 194.2 (C=O). Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.38; H, 4.72; N, 4.97.

Di(1-carbazolyl)phenylmethanol (25): eluted with benzene–hexane, 2:1, mp (methanol) 159–160 °C. Anal. Calcd for $C_{31}H_{22}N_2O{\cdot}CH_3OH$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.75; H, 5.45; N, 5.70.

1-*p*-Toluoylcarbazole (26): eluted with benzene–hexane, 2:1, mp (methanol) 153–154 °C; IR ($CHBr_3$) ν 1,630 cm^{-1} (C=O); ^{13}C NMR (DMSO-d_6) δ 193.8 (C=O). Anal. Calcd for $C_{20}H_{15}NO$: C, 84.19; H, 5.30; N, 4.91. Found: C, 84.29; H, 5.25; N, 4.65.

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(1-Carbazolyl)diphenylmethanol (27): eluted with benzene–hexane, 2:1; mp (methanol) 153–154 °C. Anal. Calcd for $C_{25}H_{19}NO$: C, 85.93; H, 5.48; N, 4.01. Found: C, 85.53; H, 5.47; N, 3.76.

9-(1-Pyrrolidinomethyl)-1,2,3,4-tetrahydrocarbazole (31). A mixture of 5.14 g (30 mmol) of 1,2,3,4-tetrahydrocarbazole (**30**), 2.75 mL of 37% formaldehyde solution, and 2.85 mL (34 mmol) of pyrrolidine in 60 mL of ethanol was heated under gentle reflux for 12 h. The solvent was removed under vacuum and the residue was extracted with ethyl acetate and washed with water. The solution was extracted twice with 0.1 N hydrochloric acid, and the organic layer was discarded. After being washed with fresh ethyl acetate, the aqueous layer was bascified with concentrated ammonia solution and extracted with hexane. After being dried (Na_2SO_4) the solution was concentrated and cooled to give 5.7 g (75%) of **31**: mp 55–56 °C (lit.[27] mp 56.5–57 °C); ^{1}H NMR (DMSO-d_6) δ 1.61 (brs, 4 H, CH_2), 1.83 (m, 4 H, CH_2) 2.49 (brs, 4 H, CH_2N), 2.66 (m, 4 H, CH_2), 4.76 (s, 2 H, NCH_2N), and 6.98 and 7.39 (2 m, 4 H, Ar H); ^{13}C NMR (DMSO-d_6) δ 20.6, 21.7, 22.0, 22.7 (CH_2), 23.0 (pyrrolidine CH_2), 50.9 (CH_2N), 60.6 (NCH_2N), 108.5 (q), 109.5, 117.0, 118.3, 120.1, 126.9 (q), 135.6 (q), and 136.8 (q).

1,2,3,4-Tetrahydrocarbazole-8-carboxylic Acid (32). Lithiation of 0.50 g (2 mmol) of **31** with *tert*-butyllithium as for **17** followed by the addition of carbon dioxide gas gave, after purification by basic extraction, 0.30 g (71%) of **32**: mp 202–203 °C (lit.[16] mp 201–203); ^{1}H NMR (DMSO-d_6) δ 1.80 (m, 4 H, CH_2), 2.63 and 2.78 (2 m, 4 H, CH_2), 7.03 (t), 7.59 (d), and 7.68 (d) (3 H, Ar H), 10.61 (s, 1 H, NH), and 12.92 (s, 1 H, CO_2H); ^{13}C NMR (DMSO-d_6) δ 20.3, 22.7 and 22.8 (×2) (CH_2), 108.4 (q), 112.5 (q), 117.4, 122.2, 122.6, 128.8 (q), 134.7 (q), and 136.2 (q) and 168.1 (q, CO_2H).

2,3-Dimethyl-1-(1-pyrrolidinomethyl)indole (33). A mixture of 4.35 g (30 mmol) of 2,3-dimethylindole, 2.75 mL of 37% formaldehyde solution, and 2.85 mL (34 mmol) of pyrrolidine was heated under reflux and worked up as for **31** to give an oil which was distilled to give 4.0 g (60%) of **33**: bp 132–134 °C/15 mmHg; mp 32–34 °C; ^{1}H NMR (DMSO-d_6) δ 1.58 (m, 4 H, CH_2), 2.10 and 2.25 (2 s, 6 H, CH_3), 2.45 (m, 4 H, CH_2N), 4.75 (s, 2 H, NCH_2N), and 6.95 and 7.35 (2 m, 4 H, Ar H); ^{13}C NMR (DMSO-d_6) δ 8.4 and 9.8 (CH_3), 22.8 (CH_2), 50.8 (CH_2N), 60.9 (NCH_2N), 105.8 (C-3), 109.2 (C-7), 117.2 (C-4), 118.4 (C-5), 120.1 (C-6), 128.0 (C-3a), 132.8 (C-1), and 136.5 (C-7a).

2-(Deuteriomethyl)-3-methylindole (34). Lithiation of **33** with *tert*-butyllithium according to the general procedure for **17** gave, after treatment with D_2O and acidic hydrolysis of the pyrrolidinomethyl group, a 90% yield of a 1:9 mixture of 2,3-dimethylindole and **34**: ^{1}H NMR (DMSO-d_6) δ 2.17 (s, 3 H, CH_3), 2.32 (s, 2 H, CH_2D), 6.95 (m, 2 H), 7.26 (dd, 1 H), 7.34 (d, 1 H), and 10.62 (brs, 1 H, NH); ^{13}C NMR (DMSO-d_6 δ 8.2 (CH_3), 10.8 (t, CH_2D), 104.9 (C-3), 110.1 (C-7), 117.2 (C-4), 117.8 (C-5), 119.8 (C-6), 128.9 (C-3a), 131.1 (C-2), and 135.1 (C-6a).

Lithiation of Benzo[*a*]carbazole (35). General Procedure. To a solution of 0.54 g (2.5 mmol) of **35** in 20 mL of dry ether at room temperature was added dropwise a solution of 2.5 mL of 2.5 M *n*-butyllithium (6.25 mmol) in hexane. After being stirred for a further 28 h, the mixture was then treated with the appropriate electrophile as follows.

Benzo[*a*]carbazole-1-carboxylic Acid (37). A slow stream of carbon dioxide gas was passed through the reaction mixture for 15 min and 20 mL of 0.1 M hydrochloric acid was then added. After dilution with further ether the organic layer was separated and extracted with a 1 M ammonia solution. The aqueous layer was washed with ether and acidified with 2 M hydrochloric acid to give a fine precipitate which was extracted into ethyl acetate. After being dried ($MgSO_4$), the solvent was removed to give 0.46 g (70%) of **37**: mp (chloroform) 230–232 °C (lit.[17] mp 230–231.2 °C); ^{1}H NMR (DMSO-d_6) δ 7.30 (t, 1 H), 7.47 (t, 1 H), 7.63 (t, 1 H), 7.82 (t, 2 H), 8.34 (m, 4 H), and 11.66 (s, 1 H, NH).

1-Chlorobenzo[*a*]carbazole (38). A solution of 1.48 g (6.25 mmol) of hexachloroethane in 10 mL of ether was added to the lithiation reaction, and after 30 min the mixture was quenched with water and diluted with further ether. The solution was washed with water and 10% Na_2CO_3 solution and dried with $MgSO_4$. The solvent and byproduct tetrachloroethylene were removed under vacuum to give, as a single product by TLC, 0.62 g (100%) of **38**: mp (ethanol) 114–115 °C; ^{1}H NMR (DMSO-d_6) δ 7.31 (t, 1 H), 7.53 (m, 2 H), 7.74 (m, 2 H), 8.03 (m, 2 H), 8.22 (d, 1 H), 8.33 (d, 1 H), and 11.75 (s, 1 H, NH). Anal. Calcd for $C_{16}H_{10}NCl$: C, 76.35; H, 4.00; N, 5.56. Found: C, 75.97; H, 3.63; N, 5.28.

7-(1-Pyrrolidinomethyl)benzo[*c*]carbazole (40). Reaction of benzo[*c*]carbazole with aqueous formaldehyde and pyrrolidine as previously described for the synthesis of **17** from carbazole gave a 61% yield of **40**: mp (aqueous ethanol) 93–94 °C; ^{1}H NMR (DMSO-d_6) δ 1.53 (brs, 4 H, CH_2), 2.55 (brs, 4 H, CH_2N), 5.29 (s, 2 H, NCH_2N), 7.40 (m, 3 H), 7.75 (m, 2 H), 7.92 (s, 2 H), 8.01 (d, 1 H), 8.59 (d, 1 H), and 8.79 (d, 1 H). Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.99; H, 7.03; N, 9.15.

7-(1-Pyrrolidinomethyl)dibenzo[*c*,*g*]carbazole (42). A mixture of 4.0 g (15 mmol) of dibenzo[*c*,*g*]carbazole (**41**), 1.37 mL of 37% formaldehyde solution, and 1.42 mL of pyrrolidine in 30 mL of ethanol and 15 mL of benzene was heated under gentle reflux for 24 h and the solvents were then removed under vacuum. The residue was extracted into benzene and washed with water. Treatment of the organic layer with 0.1 N hydrochloric acid resulted in the formation of an insoluble hydrochloride salt which was collected by filtration and stirred with a mixture of ethyl acetate and dilute ammonia for 1 h. The resulting ethyl acetate solution was dried (Na_2SO_4) and the solvent removed to give 0.32 g, (60%) of **42**: mp (ethanol) 130–131 °C; ^{1}H NMR (DMSO-d_6) δ 1.54 (brs, 4 H, CH_2), 2.58 (brs, 4 H, CH_2N), 5.46 (s, 2 H, NCH_2N), 7.49 (t, 2 H), 7.68 (t, 2 H), 8.01 (m, 6 H), and 9.05 (d, 2 H). Anal. Calcd for $C_{25}H_{22}N_2$: C, 85.68, H, 6.33; N, 7.99. Found: C, 84.76; H, 6.63; N, 7.44.

Dibenzo[*c*,*g*]carbazole-6-carboxylic Acid (43). Lithiation of 0.53 g (1.5 mmol) of **42** was performed in hexane as for **17** and, because of the lower solubility of the lithio complex, the mixture was then diluted with an equal volume of THF at −78 °C. Addition of carbon dioxide gas followed by workup in chloroform gave, after purification by ammonia extraction, 0.226 g (57%) of **43**: mp (chloroform) 286–288 °C; ^{1}H NMR (DMSO-d_6) δ 11.14 (s, 1 H, NH), and 7.10–9.40 (m, 11 H).

6-Chlorodibenzo[*c*,*g*]carbazole (44). Reaction as above followed by addition of 0.46 g (1.5 mmol) of hexachloroethane in THF gave, after workup in ethyl acetate and chromatography on silica gel (benzene–hexane, 1:1), 0.30 g (65%) of **44**: mp (ethanol) 193–195 °C; ^{1}H NMR (DMSO-d_6) δ 7.52 (t, 2 H), 7.71 (t, 2 H), 8.00 (m, 5 H), 9.10 (t, 2 H), and 12.6 (s, 1 H, NH). Anal. Calcd for $C_{20}H_{12}NCl$: C, 79.60; H, 4.01; N, 4.64. Found: C, 79.34; H, 3.91; N, 4.35.

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