Studies on Intramolecular NH-Bridging in Aromatic Compounds.
Part 3 [1-3]

Takaaki Horaguchi

Department of Chemistry, Faculty of Science, Niigata University
Ikarashi, Niigata 950-21, Japan

L. H. Klemm* and Eric S. Norris [4]

Department of Chemistry, University of Oregon
Eugene, Oregon 97403-1253
Received December 2, 1994

A study was made of the use of calcium oxide as a catalyst at a temperature of 400-700° for the dehydrocyclization of four primary arylamines: 2-aminobiphenyl, 1-aminotriphenylene (5c), 2-phenoxyaniline, and N-(2-aminophenyl)pyrrole. Maximal yields of cyclized products isolated were 53% (carbazole), 52% (4H-naphtho[1,4-def]carbazole), 18% (phenoxazine), and 0%, respectively. Comparison is made with reported cyclizations of the corresponding nitro and azido starting materials. In one case, treatment of 1-nitrotriphenylene with triethyl phosphite produced mainly diethyl N-(1-triphenylenyl)phosphoramidate (51%). Mono- and hemihydrochlorides of 5c are described. A mechanism for the catalyzed dehydrocyclization is proposed.
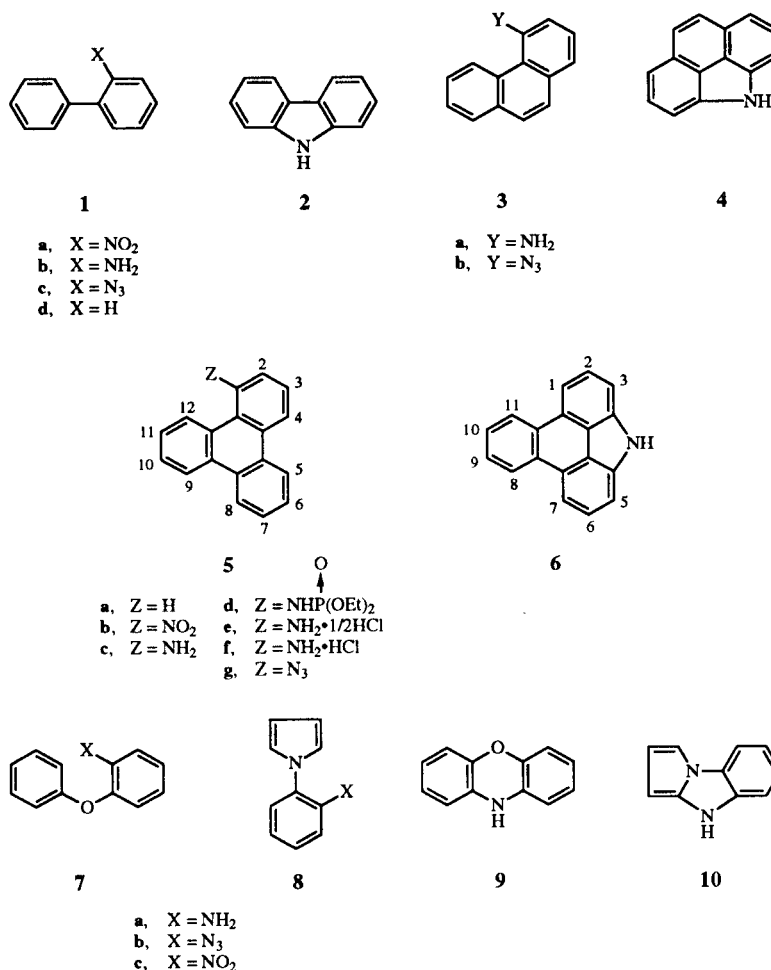
A survey of the chemical literature shows that three general procedures have been reported for cyclizing a 2-substituted biphenyl **1** into carbazole (**2**). We designate these procedures as "intramolecular NH-bridging." The starting material consists of 2-nitrobiphenyl (**1a**), 2-aminobiphenyl (**1b**), or 2-azidobiphenyl (**1c**). The bridging process involves the loss of two atoms of oxygen (deoxygenation), two atoms of hydrogen (dehydrogenation), or two atoms of nitrogen (denitrogenation), respectively, per molecule of starting material. Deoxygenation was effected by Waterman and Vivian by heating **1a** with an oxygen acceptor such as some metals, carbon, or ferrous oxalate [5]. More recently Cadogan and coworkers used triethyl phosphite to abstract the oxygen and give carbazole in 83% yield [6]. Morgan and Walls heated **1b** preferably with oxidizing agents (*e.g.* vanadium pentoxide, molybdenum trioxide, or manganese dioxide) to give carbazole (42-60%) plus biphenyl (4-6%) at 555-600°. Surprisingly, using calcium oxide, magnesium oxide, or pumice also gave these products, but with carbazole in lower yield (32%) [7]. Weinmayr heated **1b** with a nitro compound, such as 1,3-dinitrobenzene, at 250-360° for several hours in order to obtain carbazole [8]. Smith and Brown decomposed **1c** either thermally or photochemically to yield carbazole in *ca.* 77% yield [9].

Two of the preceding intramolecular NH-bridging methods have been employed in the synthesis of 4H-benzo[def]carbazole (**4**) from a 4-substituted phenanthrene **3**. Thus Kruber and Grigoleit obtained **4** in 20% yield by passing vapors of amino compound **3a** in a nitrogen carrier gas over calcium oxide at 400° [10]. Horaguchi *et al.* increased this yield to 53% by raising the

reaction temperature to 560° [1]. Kreher and Köhler converted azide **3b** into **4** (66% yield) by thermolysis at 240° in diphenyl ether solution. However, when they used xylene as a solvent **3b** reverted to **3a** in 71% yield [11].

In an earlier paper Klemm *et al.* [2] used the Cadogan reaction [12] to transform 1-nitrotriphenylene (**5b**) into 4H-naphtho[1,4-def]carbazole (**6**) in 30% yield [13]. We have had difficulty in reproducing this result, however. Thus, in the present study an attempt to scale up the reaction under otherwise closely similar conditions gave only a 6% yield of **6**, plus a 51% yield of the uncyclized phosphoramidate **5d** [14]. At this point it was decided to attempt to synthesize **6** from 1-aminotriphenylene (**5c**) by means of calcium oxide, and to initiate a study of the scope and mechanism of the calcium-oxide-induced cyclization process (*vide infra*).

1-Nitrotriphenylene (**5b**) obtained from nitration of triphenylene [15], was reduced by means of palladium-charcoal and hydrazine hydrate to amine **5c** (78% yield), characterized by spectral data including sharp infrared bands (measured in a potassium bromide wafer) at 3425 and 3349 cm^{-1} for the primary amino group [16]. Treatment of a benzene solution of **5c** with anhydrous hydrogen chloride gave the monohydrochloride **5f**, obtained as needles from ethanol, mp 255-258° dec (appropriate C, H and N analyses), with broad infrared bands at 2990 and 2550 cm^{-1} for the protonated primary amino group [16]. Meanwhile, refluxing phosphoramidate **5d** in ethanolic hydrochloric acid readily precipitated needles, mp 248-252° dec, believed to be **5f** also (89% yield), but which changed to a white crystalline hemihydrochloride **5e** (appropriate C, H and N analyses) on vacuum sub-

1

a, X = NO$_2$
b, X = NH$_2$
c, X = N$_3$
d, X = H

2

3

a, Y = NH$_2$
b, Y = N$_3$

4

5

a, Z = H   d, Z = NHP(OEt)$_2$
b, Z = NO$_2$ e, Z = NH$_2$·1/2HCl
c, Z = NH$_2$ f, Z = NH$_2$·HCl
                 g, Z = N$_3$

6

7

a, X = NH$_2$
b, X = N$_3$
c, X = NO$_2$

8

9

10

limation, mp 247° dec, infrared bands at 3434 and 3348 cm^{-1} (sharp) plus 2814 and 2555 cm^{-1} (broad). The mass spectra of all three compounds **5c**, **5e**, and **5f** were closely similar, with the most abundant peak at m/z 243 for the amine parent ion in each case. Surprisingly, the ^{1}H nmr spectra of the two hydrochloride salts (measured in hexa-deuteriodimethyl sulfoxide) were considerably different. In the aromatic region the spectrum of the hemihy-drochloride showed a pattern of signals almost identical to that of the free amine (albeit measured in deuteriochloro-form), with the alpha proton signals spread out in the region 8.1-9.2 ppm and the beta ones falling in the region 7.0-7.8 ppm. Corresponding sets of signals for the mono-hydrochloride were squeezed more tightly in the regions 8.5-9.2 and 7.5-7.8 ppm, respectively. While the free amine showed a typical broad amino signal at 4.39 ppm, the two salts showed only a general broadened hump over the range of 3.5-7 (maximum at 5.3) for **5f** and 2.5-7 (maximum at 3.8) for **5e**. In summary, it appears that vac-uum sublimation of the monohydrochloride causes loss of half of the hydrogen chloride present to give a molecular compound **5e≡5c·5f**, but **5e** and **5f**, show markedly differ-

ent ^{1}H nmr spectral patterns in the aromatic region.

For the cyclization of 1-aminotriphenylene (**5c**) a ben-zene solution of the amine was added dropwise to the top of a column of calcium oxide granules packed in a stain-less steel tube and maintained at a constant temperature in the range of 400-700°. The tube was flushed continuously with nitrogen carrier gas. Product mixtures were collected from the cooled effluent and from Soxhlet extraction of the spent packing and were separated by column chro-matography. At a reaction temperature of 560° there resulted a 52% yield of naphthocarbazole **6** (41% overall yield from 1-nitrotriphenylene) and 20% recovery of **5c**. Even at a temperature of 600°, yields were 40% and 13%, respectively. At least in our hands, this dehydrocyclizative synthesis of **6** is preferable to the Cadogan reaction [17].

Table I summarizes various experiments which were conducted with other starting materials in an effort to syn-thesize carbazole (**2**), phenoxazine (**9**), and pyrrolo-[1,2-a]benzimidazole (**10**) or to elucidate the function of the calcium oxide in the cyclization reaction. Experiments 1 and 2 confirm that 2-aminobiphenyl (**1b**) is convertible into carbazole (53% yield at 600°) by use of calcium

Table I

Studies on the Synthesis of Carbazole and Related Compounds by Heterogeneously Catalyzed Dehydrocyclization at Elevated Temperature

Experiment No.	Starting Material [a]	Tube Packing	Reaction Temperature °C	Products Isolated		From Recovery, %	Biphenyl % [b]
				From Cyclization			
				Compound	Yield, %		
1	1b	CaO	560	carbazole	42	36	
2	1b	CaO	600	carbazole	53	9	
3	1b	soda lime [c]	400	carbazole	3	81	
4	1b	soda lime [c]	560	carbazole	2	15	
5	1b	glass beads [d]	560	carbazole	2	91	0.1
6	1d [e]	CaO	560	carbazole	0	99	
7	7a	CaO	500	phenoxazine	3	56	
8	7a	CaO	560	phenoxazine	18	17	
9	8a	CaO	560	[f]	—	60	
10	8a	CaO	700	[f]	—	0	1

[a] Added in benzene solution. Nitrogen was used as a carrier gas. [b] Byproduct from benzene solvent. [c] A mixture of sodium hydroxide and calcium oxide. Water present was lost during conditioning of the packing. [d] Pyrex, 5 mm in diameter. [e] Ammonia gas was used instead of nitrogen. [f] Only a small amount of liquid which gave a long smear on a tlc plate was obtained. No separation of crystalline 10 (lit mp 98-100° [20]) resulted.

oxide. Experiment 5, conducted with non-catalytic glass beads, indicates that a small amount of dehydrocyclization (2%) occurs thermally at 560°. In experiments 3 and 4, soda lime gave only thermal cyclization. From these five experiments it appears that calcium oxide is, indeed, a heterogeneous catalyst (rather than an inert tube packing). Experiment 6 is a single unsuccessful attempt to see if calcium oxide can cause reaction between biphenyl and ammonia to yield carbazole under the conditions of experiment 1. While we have confirmed that calcium oxide can catalyze the conversion of 1b into 2, one should note that better yields of 2 have been reported from the 2-nitro- and 2-azidobiphenyl precursors (vide supra).

Another useful synthetic result is shown in experiment 8, where 2-phenoxyaniline (7a) cyclized to crystalline phenoxazine (9) in 18% yield. In contrast the azide 7b produced no identifiable 9 [18] and the Cadogan reaction on the nitro ether 7c yielded only a tarry mixture [6,19]. Contrasting results were obtained for the N-(2-substituted-phenyl)pyrroles, where the amino compound 8a gave only an unidentified liquid mixture (experiments 9 and 10), but the nitro compound 8c formed 10 (26% yield) and some 2-nitroaniline (4%) [20]. Apparently, azide 8b is unknown.

Cyclizations involving the Cadogan reaction and azide decomposition are reported to proceed via a nitrene intermediate or its equivalent [6,12,21]. The differences in yields of products between those cyclizations and the calcium oxide catalyzed one augurs against the formation of a nitrene intermediate in dehydrocyclization. Since Morgan and Walls [7] indicated that magnesium and calcium oxides give comparable results in the cyclization of 2-aminobiphenyl, it seems reasonable to examine data on these two catalysts to look for similar physicochemical properties which may lead to a rational mechanistic

hypothesis for their actions. These properties, as reported in the literature, are summarized below.

Our calcium oxide (prepared commercially by thermal decarboxylation of marble, probably at a temperature of ca. 900° [22,23]) is only 95-97% pure [24]. Thus, it should contain metal ions other than calcium as well as trapped electrons or holes [25-28]. Both magnesium and calcium oxides have the sodium chloride lattice structure [29] and are solid bases [30]. In fact, calcium oxide prepared as noted above is termed a "solid superbase" and certain preparations of magnesium oxide may also fall in this category [30]. Three independent types of catalytic sites are recognized on both of these oxides, viz. ones that cause (a) isomerization of alkenes, (b) H-D exchange and/or amination of conjugated dienes, and (c) hydrogenation of double bonds. These sites become available, in the succession shown, as the temperature of activation of the catalyst is increased. It is unlikely that site (c) is available in our calcium oxide. Sites (a) and (b) are fundamentally basic sites (i.e., oxide ions) which differ in strengths due to the natures of their nearby neighbors on the catalyst surface. In isomerization and amination these sites abstract protons from alkenes (to leave π-allyl anions) and from primary or secondary alkylamines (to leave amide ions), respectively, as their mechanistic functions [31]. We suggest that such a basic site (probably of type b) initiates dehydrocyclization by abstraction of a proton from the amino group of the starting material to form an ArNH anion adsorbed to the catalyst surface.

Numerous studies have been made on the nature of electronic defects in magnesium oxide and, to a lesser extent, in calcium oxide. Even though magnesium oxide is a classical insulator it exhibits considerable electrical conductivity (in the temperature range of 400-800°) which is ascribed to the presence of highly mobile oxygen

Scheme I

Possible mechanism for the Calcium Oxide [a] Catalyzed Dehydrocyclization of 2-Aminobiphenyl (1b) to Give Carbazole (2) [b]
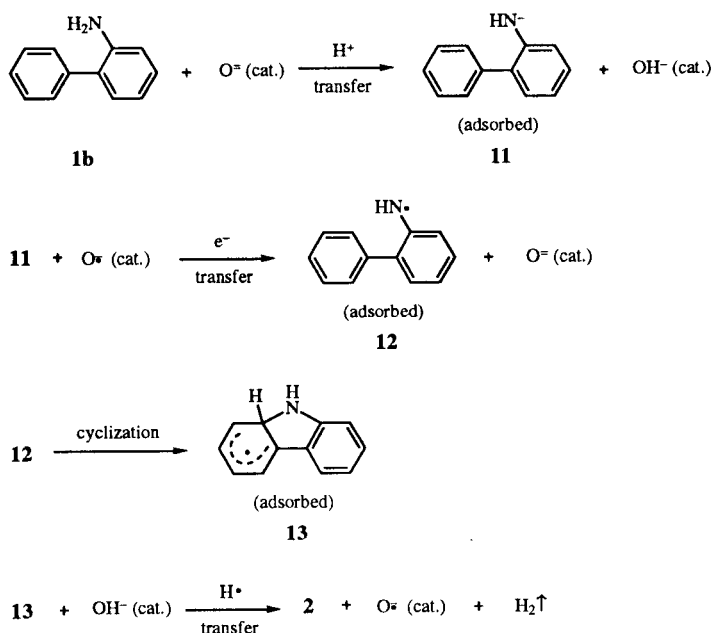
[a] Magnesium Oxide should act in the same manner. [b] The cyclizations 5c→6 and 7a→9 are presumed to occur analogously.

holes, *i.e.*, oxygen anion radicals [32]. It is also claimed that these holes exist in calcium oxide [33]. Moreover, they are implicated in the catalytic properties of both compounds. We invoke the action of such a hole (or of an extraneous reducible cation) as a temporary electron attractor to oxidize the aforementioned ArNH anion to an ArNH free radical, which then undergoes cyclization. The various steps in our hypothetical dehydrocyclizative reaction mechanism are presented in Scheme I for 2-amino-biphenyl → carbazole as an example.

EXPERIMENTAL [34]

1-Aminotriphenylene (5c).

1-Nitrotriphenylene (**5b**) was obtained by nitration of tri-phenylene (**5a**) [15] and chromatographic separation of isomers by means of alumina/toluene-petroleum ether (35-60°) (ratio 7:3 by volume) [2]. A solution of one g (3.66 mmoles) of **5b** and 8.3 ml (171 mmoles) of hydrazine hydrate in 200 ml of ethanol was refluxed with 330 mg of 5% palladium charcoal for 30 minutes. Filtration and evaporation of the filtrate gave crystals which were chromatographed with alumina/benzene. A fraction of R_f 0.54 was collected as **5c**, yield 698 mg (78%), mp 91-93°, raised to 93-94° on recrystallization from ethanol as colorless prisms [35]; ir: 3425 and 3349 (sharp, NH_2), 815, 756 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.21 (dd, J = 3, 7 Hz, 1 H, H-12), 8.30-8.75 (m, 3 H, H-5, H-8, H-9), 8.11 (d, J = 8 Hz, 1 H, H-4), 7.5-7.8 (m, 4 H, H-6, H-7, H-10, H-11), 7.43 (t, J = 8 Hz, 1 H, H-3),

6.99 (d, J = 8 Hz, 1 H, H-2), 4.39 (broad s, 2 H, NH_2) [36]; ms: m/z 244 (20), 243 (M$^+$, 100), 242 (35), 241 (25), 215 (M$^+$ -H_2CN, 8).

Also isolated from the preceding chromatograph was 34 mg (4%) of triphenylene, R_f 0.77, identified by direct comparison with an authentic sample (mp, mmp, and tlc).

1-Aminotriphenylene Monohydrochloride (5f).

Into a solution of 204 mg (0.84 mmole) of **5c** in benzene was passed dry hydrogen chloride gas. The colorless crystals which precipitated were collected by filtration, washed with benzene, and dried to give 215 mg (92%) of monohydrochloride **5f**, mp 250-254° dec. Recrystallization from ethanol gave needles, mp 255-258° dec; ir: 2990 and 2550 (broad, NH_3^+), 750, 720 cm^{-1}; ^1H nmr (DMSO-d$_6$): δ 8.5-9.2 (m, 5 α-H atoms), 7.5-7.8 (m, 6 β-H atoms), 3.5-7 (very broad, NH_3^+); ms: m/z 244 (17), 243 (5c$^+$, 100), 242 (36), 241 (26), 215 (5c$^+$ -H_2CN, 10).

Anal. Calcd. for $C_{18}H_{13}N•HCl$: C, 77.28; H, 5.04; N, 5.01. Found: C, 77.60; H, 5.09; N, 5.06.

Diethyl *N*-(1-Triphenylenyl)phosphoramidate (5d).

Into an oven-dried reflux apparatus fitted with a cannula and rubber septum for introduction of gas, plus a drying tube and attached Bunsen valve for emission of gas, were placed 2.1 g (7.7 mmoles) of **5b** and 72 ml (0.42 mole) of triethyl phosphite. The mixture was stirred and maintained at 110° for 23 hours in a fume hood, while a slow stream of nitrogen gas was passed through the apparatus. Volatile components of the reaction mixture were removed under reduced pressure, with the assistance of 100 ml of xylene as a chaser. The residue was chromatographed (alumina/chloroform) to yield 115 mg of recovered **5a**, R_f (alumina/chloroform) 0.85; 110 mg (6%) of 4*H*-naph-tho[1,4-*def*]carbazole (**6**), mp 238-240°, R_f 0.60 [2]; and 1.50 g

(51%) of phosphoramidate **5d**, mp 150.5-151.5°, R_f 0.40. Recrystallization of **5d** from toluene gave faintly tan needles, mp 154.5-155.5°; ir: 3132 (NH), 1466, 1434 (PNH), 1245 (P→O), 1040 (POEt), 966, 745 (NP) [37,38]; ^{1}H nmr (deuteriochloroform): δ 1.37 (t, J_{Et} = 7.2 Hz, 6 H, 2 Me), 4.1-4.4 (2 overlapping m, 4 H, 2 methylene groups), 6.06 (d, J_{PNH} = 7.8 Hz, 1 H, NH), 7.5-7.7 (m, 6 β-H), 8.28 (d, J = 7.8 Hz, 1 H, H-4), 8.5 (m, 2 H, H-5 and H-8), 8.62 and 8.96 (2 partially split d, J ≅ 2, 8 Hz, 1 H each, H-9 and H-12); ^{31}P nmr (deuteriochloroform): δ 1.00 (2 overlapping t, J_{POCH} = 7.8 Hz) [39,40]; ms: m/z 381 (29), 379 (M[+], 100), 324 (M[+] -C_3H_5N, 30), 242 (53), 241 (6[+], 83), 240 (61), 213 (6[+] -H_2CN, 21) [2].

Anal. Calcd. for $C_{22}H_{22}NO_3P$: C, 69.65; H, 5.85; N, 3.69. Found: C, 69.62; H, 5.82; N, 3.58.

1-Aminotriphenylene Hemihydrochloride (**5e**).

A mixture of 123 mg of phosphoramidate **5d**, 10 ml of concentrated hydrochloric acid, and 15 ml of ethanol was refluxed for 1.5 hours. The precipitate which formed on cooling the solution was collected by filtration, washed once with cold water, and dried in air, yield 81.1 mg (89%) of light tan needles, mp 248-252° dec [41]. Recrystallization from absolute ethanol plus double sublimation at 120° (0.02 mm) gave a white solid, mp 247° dec, positive Beilstein test, soluble in water; ir: 3434 and 3348 (sharp, NH_2), 2814 and 2555 (broad, NH_3^+), 815, 756 cm^{-1} [16,42]; ^{1}H nmr (DMSO-d_6): δ 9.19 (d, 1 H), 8.3-8.8 (m, 3 H), 8.22 (d, 1 H), 7.5-7.8 (m, 4 H), 7.45 (t, 1 H), 7.25 (d, 1 H), 2.5-7 (very broad, NH_3^+ and NH_2); ms: m/z 244 (22), 243 (5c[+], 100), 242 (70), 241 (43), 240 (13), 213 (10).

Anal. Calcd. for $C_{18}H_{13}N$•0.5HCl: C, 82.66; H, 5.20; N, 5.36. Found: C, 82.42; H, 5.12; N, 5.36.

Catalyzed Synthesis of 4*H*-Naphtho[1,4-*def*]carbazole (**6**).

Granules of calcium oxide (3-10 mm in size) were obtained by grinding and sieving irregular large pieces (Fluka, *ex* marble, 95-97% pure). A stainless steel tube (60 cm long, 24 mm i.d.), bearing a machined 24/40 standard taper plus an internal fine screen at the lower end, was packed to a height of 33 cm with the granules (137 g). The tube was positioned in a vertical, electric furnace with heating coils 30 cm in length. The upper end of the tube was fitted to a pressure-equalizing dropping funnel bearing a solution of 0.5 g (2.06 mmoles) of 1-aminotriphenylene (**5c**) in 20 ml of benzene. The top of the funnel was connected, *via* a flowmeter, to a source of nitrogen gas. The lower part of the tube was connected to an ice-cooled receiver plus attached tubing leading directly into the inlet of a hood. Nitrogen (303 ml/minute at ambient conditions) was passed through the apparatus as long as the furnace was heating. When the reaction temperature (controlled to ±10°) had stabilized the benzene solution was added dropwise over 40 minutes. This was followed by a benzene wash (20 ml added over 30 minutes) plus an extra 30-minute period with nitrogen only. The furnace was then shut off. Products were collected from evaporation of the effluent and of a benzene extract of the spent tube packing.

In an experiment at 560° there was a total yield of 403 mg of crystals, identified as a mixture of starting material **5c** (R_f 0.23 for tlc on silica gel/benzene-petroleum ether (35-60°), 1:1) and **6** (R_f 0.36) [2,43]. Column chromatography with the same system gave 257 mg (52%) of **6**, mp 245-250°, raised to 250-252° (colorless needles) on recrystallization from benzene, lit mp 248.5-251.5° [2], plus 101 mg (20%) of recovered **5c**.

Other Experiments with Calcium Oxide and Nitrogen Carrier Gas.

Experiments 1, 2, and 7-10 (Table I) were conducted in a manner similar to the preceding one. Starting materials were 2-aminobiphenyl (**1b**) (Lancaster Synthesis, Inc.) [44], 2-phenoxyaniline (**7a**) (Aldrich), and *N*-(2-aminophenyl)pyrrole (**8a**) (Aldrich). Authentic samples of carbazole (**2**) (Aldrich), phenoxazine (**9**) (Aldrich) and biphenyl (**1d**) were used to identify products by comparative tlc and mp. In experiment 1, 0.5 g of **1b** gave 419 mg of mixed product, separated by column chromatography (silica gel/benzene) into 210 mg (42%) of carbazole (R_f 0.73), mp 241-244° (raised to 245-247° on recrystallization from benzene) and 178 mg (36%) of **1b** (R_f 0.46), mp 44-46°. Tlc with alumina/benzene gave R_f values of 0.38 and 0.45, respectively [45]. In experiment 8, 1.5 g of **7a** gave 766 mg of mixed products, first separated into 266 mg (18%) of **9** (R_f 0.64, mp 153-156°), 256 mg (17%) of **7a** (R_f 0.31), plus unidentified components by chromatography with silica gel/benzene-petroleum ether (35-60°), 7:3 by volume. Then **9** was purified further (mp 157-159°) by chromatography with alumina/methylene chloride-petroleum ether, 2:3 by volume, and by recrystallization from benzene-petroleum ether.

Experiments 3-6.

In experiments 3 and 4 the reaction tube was packed with soda-lime (117 g, Mallinckrodt 4-8 mesh). The preheating process was continued until collection of water in the receiver ceased. In experiment 5 the tube was packed with 220 g of pyrex glass beads, 5 mm in diameter. Experiment 6 was conducted as for experiment 1 except that biphenyl (**1d**) was used as the starting material and gaseous ammonia (flow rate 303 ml/min) replaced nitrogen as a carrier gas.

Acknowledgment.

REFERENCES AND NOTES

[1] Paper 1: T. Horaguchi, R. Yamazaki and T. Abe, *Bull. Chem. Soc. Japan,* **53**, 494 (1980).

[2] Paper 2: L. H. Klemm, E. Hall and S. K. Sur, *J. Heterocyclic Chem.,* **25**, 1427 (1988).

[3] Experiments reported here were conducted at the University of Oregon.

[4] Undergraduate research student, 1992.

[5] H. C. Waterman and D. L. Vivian, U. S. Patent 2,292,808 (1943); *Chem. Abstr.,* **37**, 892 (1943).

[6] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie and R. J. G. Searle, *J. Chem. Soc.,* 4831 (1965).

[7] G. T. Morgan and L. P. Walls, *J. Soc. Chem. Ind.,* **57**, 358 (1938).

[8] V. Weinmayr, U. S. Patent 2,351,171 (1944); *Chem. Abstr.,* **38**, 5228 (1944).

[9] P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.,* **73**, 2435, 2438 (1951).

[10] O. Kruber and G. Grigoleit, *Chem. Ber.,* **87**, 1895 (1954).

[11] R. Kreher and W. Köhler, *Angew. Chem., Int. Ed. Engl.,* **14**, 264 (1975).

[12]   J. I. G. Cadogan, *Quart. Rev.*, **22**, 222 (1968).

[13]   See reference 2, footnote 31.

[14]   Other similar attempts gave variable results.

[15]   C. C. Barker, R. G. Emmerson and J. D. Periam, *J. Chem. Soc.*, 4482 (1955).

[16]   E. Pretsch, T. Clerc, J. Seibl and W. Simon, Spectral Data for Structure Determination of Organic Compounds, Springer Verlag, New York, NY, 1983, p I100.

[17]   We have not investigated the possibility of using the unknown azide **5g**.

[18]   P. A. S. Smith, B. B. Brown, R. K. Putney and R. F. Reinisch, *J. Am. Chem. Soc.*, **75**, 6335 (1953).

[19]   J. I. G. Cadogan, D. S. B. Grace, P. K. K. Lim and B. S. Tait, *J. Chem. Soc., Perkin Trans. 1*, 2376 (1975).

[20]   J. M. Lindley, I. M. McRobbie, O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc., Perkin Trans 1*, 2194 (1977).

[21]   P. A. S. Smith, Derivatives of Hydrazine and Other Hydronitrogens Having N-N Bonds, Benjamin/Cummings Publishing Co., Reading, MA, 1983, Chapter 6.

[22]   D. N. Todor, Thermal Analysis of Minerals, Abacus Press, Turnbridge Wells, Kent, England, 1976, pp 158-162.

[23]   W. Smykatz-Kloss, Differential Thermal Analysis, Springer Verlag, New York, NY, 1974, pp 43-44.

[24]   Fluka Chemica-Biochemika Catalog, Fluka Chemie AG, CH-9470 Buchs, Switzerland, p 273.

[25]   A. S. Marfunin, Spectroscopy, Luminescence and Radiation Centers in Minerals, Springer Verlag, New York, NY, 1979, pp 242-247.

[26]   F. Freund, F. Battlo and M. M. Freund, in Spectroscopic Characterization of Minerals and Their Surfaces, L. M. Coyne, S. W. S. McKeever and D. F. Blake, eds, Am. Chem. Soc., Washington, D.C., 1990, Chapter 16.

[27]   F. Agullo-Lopez, C. R. A. Catlow and P. D. Townsend, Point Defects in Materials, Academic Press, New York, NY, 1988, pp 149-153.

[28]   B. Henderson and J. E. Wertz, Defects in the Alkaline Earth Oxides, Halsted Press, New York, NY, 1977, pp 6-8, 142-144.

[29]   A. F. Wells, Structural Inorganic Chemistry, 4th Ed, Clarendon Press, Oxford, England, 1975, pp 444-445.

[30]   K. Tanabe, M. Misono, Y. Ono and H. Hattori, New Solid Acids and Bases—Their Catalytic Properties, Elsevier, New York, NY, 1989, pp 1-3, 29-41, 215-220, 329-333.

[31]   K. Tanabe, Solid Acids and Bases, Academic Press, New York, NY, 1970, pp 50-53.

[32]   M. M. Freund, F. Freund and F. Battlo, *Phys. Rev. Letters,* **63**, 2096 (1989).

[33]   M. Che and A. J. Tench, in Advances in Catalysis, D. D. Eley, H. Pines and P. B. Weisz, eds, Vol **31**, Academic Press, New York, NY, 1982, pp 95-96.

[34]   Infrared spectra were obtained on potassium bromide wafers by means of a Nicolet Magna IR 500 spectrometer; ^1H and ^{31}P nmr spectra, by Stephen Brand, Dr. Gerald W. O'Bannon and Dr. Michael Haley by means of a General Electric QE-300 instrument; and electron-impact mass spectra, by Dr. Richard Wielesek at 70 eV with a VG 12-250 instrument. Elemental analyses were conducted by Desert Analytics Labs., Tucson, Arizona.

[35]   Barker *et al.* [15] report mp 96-101°, raised to 103-104° on recrystallization from ethanol, while P. M. G. Bavin and M. J. S. Dewar [*J. Chem. Soc.*, 164 (1956)] report yellow needles from toluene, mp 104-105°. Repeated crystallizations of our sample did not change the melting point.

[36]   Our nmr spectrum is consistent with that reported by R. H. Martin, N. Defay and F. Geerts-Evrard [*Tetrahedron*, **20**, 1091 (1964)] for use of a 60 MHz instrument. These authors cite Bavin and Dewar [35] as the source of their sample.

[37]   R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta,* **22**, 1449 (1966); R. A. Nyquist, *Spectrochim. Acta,* **19**, 713 (1963); L. J. Bellamy, The Infrared Spectra of Complex Molecules, 3rd Ed, John Wiley & Sons, New York, NY, 1975, pp 348, 354-355, 361.

[38]   Compare with spectral data for diethoxyphosphoryl amide [B. Holmstedt and L. Larsson, *Acta Chem. Scand.*, **5**, 1179 (1951).]

[39]   G. Martin and G. Mavel, *C. R. Hebd. Seances Acad. Sci.,* **253**, 2523 (1961).

[40]   J. B. Hendrickson, M. L. Maddox, J. J. Sims and H. D. Kaesz, *Tetrahedron,* **20**, 449 (1964). Compare the chemical shift value of 0.9 ppm for triethyl phosphate; N. Muller, P. C. Lauterbur and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

[41]   The percentage yield is based on the assumption of the formation of the monohydrochloride at this stage.

[42]   L. J. Bellamy, The Infrared Spectra of Complex Molecules, 3rd Ed, John Wiley & Sons, New York, NY, 1975, p 279.

[43]   Product mixtures plus authentic samples were compared directly by tlc.

[44]   The commercial sample was heated with benzene, diluted with petroleum ether (35-60°), and filtered to remove an insoluble component. Evaporation of the filtrate gave brown crystals of **1b**, mp 45-47°, used directly in this reaction.

[45]   Note the change in the order of the Rf values on silica gel (R_f smaller for the more basic compound) and on alumina (R_f smaller for **2**, which adsorbs by ionization); L. R. Snyder, Principles of Adsorption Chromatography, Marcel Dekker, Inc., New York, NY, 1968, pp 285, 313, 381-383.