

REACTIONS OF BORANES WITH AROMATIC AZIDES

III *. A SIMPLE ROUTE TO 1,2-DIHYDRO-*N*-PHENYL, THIENO[*b*]- AND THIENO[*c*]-[1,2]AZABORINES **

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Summary

Some halogeno(organyl)boranes have been formed to promote fragmentation of organic azides, through decomposition of the Lewis acid–base adducts, to give products whose structures depend on the nature of the reagents. The reactions between α,β -unsaturated *ortho*-thienylazides and phenylboron dichloride gave 1,2-dihydro-1-phenyl-2-chloro, thieno[*b*]-, or thieno[*c*]-[1,2]azaborines in very good yield, via 1,6-cyclisation of the intermediate *N,N*-phenyldichloroborylamine resulting from a 1,2-shift of the phenyl group. New 1-phenyl-2-oxybis-(dithieno)-, and -(thieno)-[1,2]-azaborines were prepared by hydrolysis of the labile [1,2]azaborinechloro derivatives; cyclisation to give these systems involves an intramolecular electrophilic substitution which occurs regiospecificity at the α -position in the thiophene ring. Similar reactions with 2-azidobiphenyl using wider example of chloroboranes, i.e. diphenylboron chloride, phenylboron dichloride, or boron trichloride, led to [1,1'-biphenyl]-2-amine-*N*-phenyl or carbazole in different ratios (9.8/0.2; 8.0/2.0; 0/10). The results can be interpreted in terms of the degree of concertedness of the three steps of the rearrangement.

Halogeno(organyl)boranes (R_nBX_{3-n}) are primarily of interest for their reducing and hydroborating properties [2], in addition to their possible use in incorporating boron into ring systems. Much effort has been expended on formation and study of cyclic six member systems in which nitrogen, and, or alkenes are directly bonded to boron [3]. The parent 1,2-dihydro[1,2]azaborine was found to be prone to polymerization, whereas 1,2-di- or mono-substituted [1,2]azaborines are quite stable as are the fused polycyclic compounds isoconjugate with naphthalene (i.e. 1,2-dihydrobenzo[*e*][1,2]azaborine) or phenanthrene (i.e. 9,10-dihydrodibenzo[*c,e*][1,2]aza-

* For part I and II see ref. 1.

** In honour of A. Mangini on the occasion of his eightieth birthday.

borine) and other polyheterocyclic systems usually made by an intramolecular Friedel–Crafts type cycloaddition of an aryne to an amino borane [4].

In addition to their pharmacological properties [5] the interest in such systems is related to their pseudoaromaticity based on the analogy of a BN unit and an aryne CC unit arising from the possibility of π -interaction between the atoms [6,7]. Recently we have studied the spectroscopic properties of some di-thieno[*c,e*][1,2]azaborines*, prepared by reaction of *ortho*-aminobithienyls and phenylboron dichloride [8], but no direct synthetic method for 1,2-dihydro-*N*-substituted [1,2]azaborine is available. Recent reports of the syntheses of *ortho*-azido bithienyls [9] prompted us to undertake a study of the reactions of some of these azides with phenylboron dichloride as a possible source of these compounds. Lewis acid, such as aluminium trichloride, catalyse the decomposition of the azido group to form a complex which usually decomposes at room temperature, with rapid loss of dinitrogen and formation of a reactive nitrogen intermediate [10]. The related reaction with alkyl- or phenyl-dichloroboranes involves cleavage of a BC bond and formation of *N,N*-substituted dichloroborylamines (produced by rearrangement of the alkyl or aryl group), which gave, after hydrolysis, secondary amines in nearly quantitative yield [11]. Thus if the boron atom of these intermediates permits a 1,6-cyclisation through an electrophilic substitution these reactions may be also regarded as a possible source of fused heterocycles containing boron and nitrogen [12]. Despite the fact that these fragmentations of the azido group catalysed by Lewis acid could provide many interesting new synthetic possibilities, only a few relevant random observations have been recorded [13]. We now report a study of fragmentation of suitable α,β -unsaturated *ortho*-aryl azides by some halogeno(organyl)boranes as route for heteroaromatic boron compounds, and an examination of the scope and limitations of the formation of cyclic N–B bond-containing products by reaction of boron with another site of the same molecule.

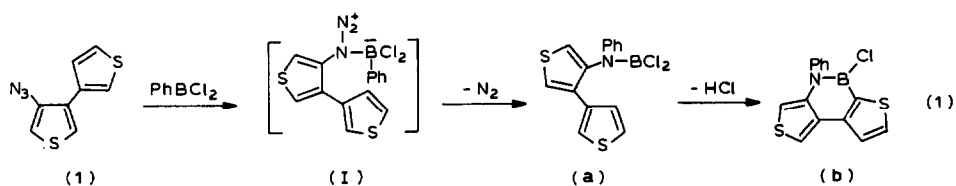
Results and discussion

The results of the reactions of phenylboron dichloride and *ortho*-substituted aryl azides (1–M5) are summarized in Scheme 1.

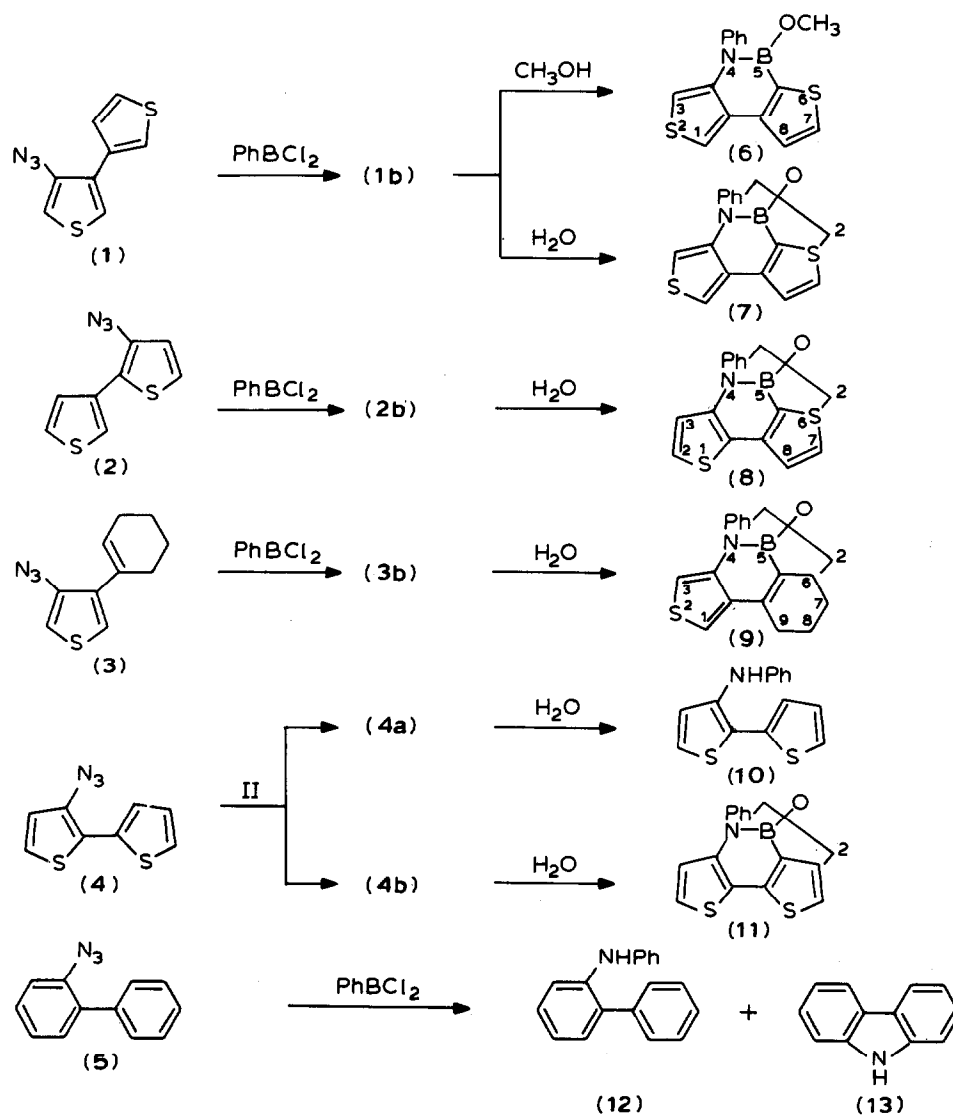
When 4-azido-3,3-bithienyl (1), 3-azido-2,3'-bithienyl (2), or 3-azido-4-cyclohex-1-enylthiophene (3) were treated with phenylboron dichloride at room temperature in dry benzene an exothermic reaction took place, with the immediate evolution of dinitrogen. The reactions were monitored by TLC, which revealed the disappearance of the starting azides and the formation of a single product, which was probably the corresponding 1-phenyl-2-chlorothieno[1,2]azaborine derivative.

Loss of dinitrogen from the unstable Lewis acid–base adduct (I) gives, through a 1,2-shift of the phenyl group from boron to nitrogen, the *N*-dichloroborylamine (1a). This would lead to an intramolecular 1,6-cyclisation of the boron at the most reactive α -position of the thiophene ring or vinylic carbon of cyclohexene to give the corresponding 4,5-dihydro-4-phenyl-5-chlorodithieno[2,3-*c*; 3,4-*e*][1,2]azaborine (1b), as depicted in eq. 1 for the azide 1.

* The nomenclature of these compounds has been a point of controversy [7]; IUPAC rules for naming organic compounds: "Nomenclature of Organic Chemistry", Section A, B, C, D, E, F, and M, Pergamon, Oxford, 1979 are utilized here.



The labile chloro derivative (**1b**) was not isolated, and the oily residue obtained after solvent removal from the reaction mixture of compound **1** was treated with boiling methanol to give the most stable ester, 4,5-dihydro-4-phenyl-5-methoxy,



SCHEME 1

dithieno[2,3-*c*;3,4-*e*][1,2]azaborine (**6**), in 84% yield. There was no evidence for the formation of the other possible cyclisation isomer, i.e. 4,5-dihydro-4-phenyl-5-methoxy, dithieno[3,4-*c*;3,4-*e*][1,2]azaborine.

A similar reaction of 3-azido-2,2'-bithienyl (**4**) with phenylboron dichloride did not give cyclic product containing boron but instead gave 3-phenylamino-2,2'-bithienyl (**10**) by hydrolysis of the intermediate *N*-dichloroborylamine (**4a**), which was unable to undergo ring closure at room temperature at the less reactive thiophenic β -position. However when this reaction was carried out in boiling benzene the desired 4,5-dihydro-4-phenyl-5-chlorodithieno[3,2-*c*;2,3-*e*][1,2]azaborine (**4b**) was produced. The chloro derivatives (**1b–4b**) proved to be very sensitive to moisture, being smoothly converted into bis[1,2]azaborine ethers **7–9**, and **11**, probably through the free acids. Thus direct hydrolysis of the product mixture from compound **1** gave 4,5-dihydro-4-phenyl-5,5'-oxybis(dithieno)[2,3-*c*;3,4-*e*][1,2]azaborine (**7**) in 42% yield, and hydrolysis of the product mixtures from compounds **2–4** gave 4,5-dihydro-4-phenyl-5,5'-oxybis(dithieno)[2,3-*c*;2,3-*e*][1,2]azaborine (**8**) (40%) (none of the other possible isomer was detected), 4,5,6,7,8,9-hexahydro-4-phenyl-5,5'-oxybis(benzo)[*c*]thieno[3,4-*e*][1,2]azaborine (**9**) (46%), and 4,5-dihydro-4-phenyl-5,5'-oxybis(dithieno)[3,2-*c*;2,3-*e*][1,2]azaborine (**11**) (39%). The structures of compounds **6–9** and **11** were established from their spectra and elemental analyses. In particular, the ^1H NMR spectra in all cases showed typical AB systems for disubstituted thiophene rings with coupling constant J_{23} 5.4 Hz for compounds **8**, and **11**, $J_{78/67}$ 5.2–5.1 Hz for **6**, **7**, **8**, and **11**, and J_{13} 3.4 Hz for **6**, **7**, and **9**. In view of the electron-donating properties of nitrogen atoms the high field doublets were assigned to the *peri*-hydrogens in the 3-positions. The ^1H NMR data are listed in Table 1. Except for the remarkable upfield shifts of *peri*-protons at C(3), the pattern agrees with that previously reported for related compounds [8].

It is difficult to correlate the chemical shift with the effects of the substituent in the molecule, but the shielding increments of 1.0 and 0.4 ppm exhibited respectively by α - and β -protons at C(3), which fall in the shielding region of the nearby hindered phenyl group, are probably ascribable to an aromatic ring current effect. No significant change in the ^{13}C NMR shifts of thiophenic carbons (which are readily assigned to α - and β -carbons by use of the $^1\text{J}(\text{CH})$ couplings) were found when a comparison was made with data in ref. 8. Since there is a good correlation between the *para*-substituent chemical shift in substituted benzenes and their charge densities [14], steric hindrance to conjugation of the phenyl group with nitrogen lone

TABLE 1
PROTON NMR DATA FOR COMPOUNDS **6–9** AND **11** IN CDCl_3 ^a

	δ_1	δ_2	δ_3	δ_6	δ_7	δ_8	$\delta(\text{Cy}/\text{OCH}_3)$	$\delta(\text{Ph})$	J_{13}	J_{23}	$J_{78/67}$
6	7.52		5.92		7.72	7.63	3.86	7.30	3.4		5.1
7	7.25		5.80		7.52	7.40		7.30	3.4		5.1
8		7.10	6.44		7.70	7.40		7.30		5.4	5.2
9	7.15		5.82				1.70 2.20 2.60	7.20	3.4		
11		7.02	6.40	6.98	7.22			7.15		5.4	5.2

^a For numbering, see formulae scheme.

TABLE 2

REACTIONS OF 2-AZIDOBIPHENYL (5) WITH ORGANYLCHLOROBORANES

$R_n\text{BCl}_{3-n}$	$[5](M)^a$	12	13		Solvent	Time (h)	Temperature
BCl_3	0.25	—	100	98	benzene	1/3	r.t.
$n\text{-BuBCl}_2$	0.25	—	100	98	benzene	1/2	r.t.
PhBCl_2	0.25	80	20	90	benzene	2	r.t.
Ph_2BCl	0.25	98	2	80	toluene	36	reflux

^a The concentration of the azide was determined using the $\gamma(\text{N}_3)$ bond in the IR spectrum.

almost exclusively [1,1'-biphenyl]-2-amine-*N*-phenyl (12), with only 2% of carbazole. The results of reactions of 2-azidobiphenyl (5) and some boranes ($R_n\text{BCl}_{3-n}$) are summarized in Table 2.

Conclusion

The reaction depicted in eq. 1 shows fairly good general applicability as a route to polyheterocyclic[1,2]azaborines. Almost quantitative yields of *N*-phenyl-thieno[*b*]-, or -thieno[*c*]-, [1,2]azaborine derivatives were obtained directly with phenylboron dichloride and *ortho*-azidobithienyls 1, 2, (which showed regioselectivity towards the α -position), 4, and 3-azido-4-cyclohex-1-enylthiophene (3), while the electrophilic ring closure of the intermediate 5a with a phenyl group as α,β -unsaturated substituent, required aluminium chloride as catalyst. Consideration of the whole range of reactions of 2-azidobiphenyl- and organochloro-boranes shows that the 1,2 boron-nitrogen shift of the boron-substituent (Cl, alkyl or aryl) is not always synchronous with loss of molecular nitrogen. The nitrogen sextet species thus formed may be of considerable synthetic utility. By careful choice of the nature of the starting azides and on the Lewis acidity of the boranes, it may be possible to direct the reaction towards the derived products.

Experimental

Materials. Azidobithienyls [9] 1, 2 and 4, 3-azido-4-cyclohex-1-enylthiophene [15] (3), 2-azidobiphenyl [16] (5), together with phenylboron dichloride [17] diphenylboron chloride [18] and *n*-butylboron dichloride [19] were prepared as previously described. Benzene was dried over sodium. Boron trichloride and carbazole were obtained from Aldrich Chem. Co.

Spectra. IR spectra were recorded on a Perkin-Elmer grating spectrometer Model 257; a Varian EM 360L spectrometer was used for ^1H NMR spectra, ^{13}C NMR were recorded on a Varian XL100; a JEOL DMS 100 instrument was used for mass spectra, a Perkin-Elmer model 552 spectrophotometer for UV spectra.

Reaction of azido derivatives 1–4 with phenylboron dichloride. General procedure

A solution of the appropriate azide (0.41 g, 2 mmol) in benzene (5 ml) was added dropwise with stirring to a solution of phenylboron dichloride in benzene (3 ml, 0.7 *M*) under nitrogen at room temperature. The reaction was carried on until TLC showed that no starting material remained (~ 2 h), then the mixture was carefully

treated with water then extracted with dichloromethane. The extract was washed with aqueous sodium carbonate and water, dried, and evaporated to dryness. The residue was chromatographed on "Florisil" using n-pentane containing a gradually increasing amount of diethyl ether as eluant.

Reaction of 4-azido-3,3'-bithienyl (1). Chromatography gave 4-phenyl-5,5'-oxybis(dithieno)[2,3-*c*;3,4-*e*][1,2]azaborine (**7**) as a resinous product (0.46 g, 42%) which crystallized from n-hexane containing 2% diethyl ether m.p. 226–228°C (Found: C, 61.40; H, 3.33; N, 5.9; S, 23.05; M^+ , 548. $C_{28}H_{18}B_2N_2OS_4$ calcd.: C, 61.33; H, 3.31; N, 5.11; S, 23.39%). $\nu_{\max}$ (CS_2) 1310 br, 1370 s, 1400 br cm^{-1} (BN and BO stretching); $\lambda_{\max}$ (cyclohexane) 212 (log ϵ 4.90), 238 (4.49), 295 (4.72), and 303 nm (4.74); δ (H) (60 MHz, $CDCl_3$) 7.52 and 7.40 (2H, q, J 5.1 Hz), 7.25 and 5.80 (2H, q, J 3.4 Hz), 7.30 br (5H, m); δ (C) (100 MHz, $CDCl_3$) 144.68, 141.64 (2C tert) 133.42 (1C(7)) 130.35, 129.14, 128.45 (3C_{phenyl}), 126.75 (1C_{para}), 123.70 (1C(8)), 116.08 (1C(1)), and 102.36 (1C(3)).

Reaction of 3-azido-2,3'-bithienyl (2). Chromatography gave 4-phenyl-5,5'-oxybis(dithieno)[2,3-*c*;2,3-*e*][1,2]azaborine (**8**) (0.44 g, 40%) after crystallization from ligroin, m.p. 207–208°C (Found: C, 61.35; H, 3.35; N, 5.05; S, 23.19; M^+ , 548. $C_{28}H_{18}B_2N_2OS_4$ calcd.: C, 61.33; H, 3.31; N, 5.11; S, 23.39%). $\nu_{\max}$ 1300 br, 1370 s, 1400 br cm^{-1} (BN and BO stretching); $\lambda_{\max}$ (Cyclohexane) 208 (log ϵ 4.87), 243 (4.83), 263 (4.66), 272 (4.66), 318 (4.67), and 330 nm (4.57); δ (H) (60 MHz, $CDCl_3$) 7.70 and 7.40 (2H, q, J 5.2 Hz), 7.10 and 6.44 (2H, q, J 5.4 Hz) 7.30 br (5H, m); δ (C) (100 MHz, $CDCl_3$) 145.81, 142.86 (2C_{tert}) 130.18, 128.96, 128.29 (3C_{phenyl}), 126.73 (C_{para}), 122.06, 122.73 (2C(8/3)), 134.23 (1C(7)) and 119.56 (1C(2)).

Reaction of 3-azido-4-cyclohex-1-enylthiophene (3). Chromatography gave 6,7,8,9-tetrahydro-4-phenyl-5,5'-oxybis(benzo)[*c*],thieno[3,4-*e*][1,2]azaborine (**9**) (0.50 g, 46%) m.p. 230–231°C from ligroin. (Found: C, 70.56; H, 5.50; N, 5.12; S, 11.56, M^+ 544. $C_{32}H_{30}B_2N_2OS_2$ calcd.: C, 70.60; H, 5.55; N, 5.15; S, 11.78%). $\nu_{\max}$ 1320 br, 1360 s, 1390 br cm^{-1} (BN and BO stretching); $\lambda_{\max}$ (cyclohexane) 211 (log ϵ 4.87), 282 (4.89), 292 (4.87), and 310 nm (4.45); δ (H) (60 MHz $CDCl_3$) 7.15 and 5.82 (2H, q, J 3.4 Hz), 7.25 br (5H, m), 2.60 br (2H, s) 2.20 br (2H, s), 1.70 br (4H, s); δ (C) (100 MHz, $CDCl_3$) 143.95, 143.91 142.43 (3C, tert) 132.68, 128.94, 128.21, (3C, phenyl), 126.38 (1C *para*), 115.72 (1C(1)), and 100.30 (1C(3)).

Reaction of 3-azido-2,2'-bithienyl (4) at room temperature. Chromatography gave [2,2'-bithienyl]-3-amine-*N*-phenyl (**10**) (0.46 g, 90%) m.p. 84–86°C (Found: C, 65.35; H, 4.33; N, 5.40 S, 24.86. $C_{14}H_{11}NS_2$ calcd.: C, 65.33; H, 4.31; N, 5.44; S, 24.91%), $\nu_{\max}$ 3410 cm^{-1} (NH), m/z 257 [M^+ 100%] 223 [M^+ – H₂S] (20), 212 [M^+ – HCS] (20), 112 (20), 77 (39), 45 (40).

Reaction of 3-azido-2,2'-bithienyl (4) in boiling benzene. The same procedure was used except that after the addition of phenylboron dichloride the mixture was refluxed for 30 min. Chromatography gave 4-phenyl-5,5'-oxybis(diethieno)[3,2-*c*;2,3-*e*][1,2]azaborine (**11**) (0.43 g, 39%), m.p. 227–228°C (Found: C, 61.38; H, 3.29; N, 5.08; S, 23.31; M^+ , 548. $C_{28}H_{18}B_2N_2OS_4$ calcd.: C, 61.33; H, 3.31; N, 5.11; S, 23.39%). $\nu_{\max}$ 1300 br, 1360 s, 1400 br cm^{-1} (BN and BO stretching), $\lambda_{\max}$ (cyclohexane) 208 (log ϵ 4.78), 245 (4.71), 265 (4.55), 274 (4.55), 318 (4.55) and 32 nm (4.45); δ (H) (60 MHz, $CDCl_3$) 7.22 and 6.98 (2H, q, J 5.2 Hz) 7.02 and 6.40 (2H, q, J 5.4 Hz), 7.15 br (5H, m); δ (C) (100 MHz $CDCl_3$) 148.47, 143.44, 142.62 (3C tert), 128.96, 128.82 (2C phenyl), 126.67 (1C *para*), 130.25 (1C(7)), 122.47, 121.56 (2C(3/6)), 119.56 (1C(2)).

Preparation of 4-phenyl-5-methoxy,dithieno[2,3-c;3,4-e][1,2]azaborine (6) from azide (1). This was prepared by the procedure described above except that before hydrolysis the solvent was removed and the oily residue was treated with boiling methanol. A solid was obtained on cooling (0.52 g, 84.0%), m.p. 125–126°C (Found: C, 60.58; H, 4.05; N, 4.65; S, 21.44. $C_{15}H_{12}BNOS_2$ calcd.: C, 61.62; H, 4.07; N, 4.71; S, 21.57%). $\nu_{\max}$ (CS_2) 1320 br, 1350 s, 1380 br (BN and BO stretching); $\lambda_{\max}$ (cyclohexane), 212 (lg ϵ 4.92), 238 (4.49), 243 (4.47), 295 (4.73), and 303 nm (4.76); δ (H) (60 MHz, $CDCl_3$), 7.72 and 7.63 (2H, q, J 5.1 Hz), 7.30 br (5H, m), 7.52 and 5.92 (2H, q, J 3.4 Hz), 3.86 (3H, s); m/z 297 [M^+ , 85%], 296 (55), 252 (20), 141 (27), 77 (50), 44 (100).

Reaction of 2-azidobiphenyl (5) with phenylboron dichloride. A solution of the azide 5 (0.39 g, 2 mmol) and phenylboron dichloride (0.32 g, 2 mmol) in benzene (8 ml) was stirred under nitrogen at room temperature until the IR spectrum at 2100–2140 cm^{-1} no longer showed the bond due to N_3 (6 h). The mixture was carefully hydrolyzed and extracted twice with dichloromethane. The extract was washed with aqueous sodium carbonate solution and water, dried, and evaporated to dryness. Chromatography on silica gel with n-pentane containing a gradually increasing amount of diethyl ether as eluant yielded (i) -[1,1'-biphenyl]-2-amine, *N*-phenyl (12) as an oil, b.p. 130–136°C (0.5 mmHg) (0.35 g, 72%), with spectral data identical with literature data [20]. m/z 245 [M^+ , 63%] 200(28), 185(30), 86(30), 84(20), 57(100), 56(100); (ii) carbazole (13) (0.06 g, 18%) m.p. 245–246°C (lit. 245–246°C) identified by IR spectrum (IR 3.1262 D).

Reaction of azide (5) and diphenylboron chloride. Azide (5) (2 mmol) and diphenylboron chloride (2 mmol) were allowed to react in refluxing toluene for 36 h (IR spectra showed no N_3 signal). After cooling the mixture was worked up as described above to give compounds 12 and 13 in 9.8/0.2 ratio. This ratio were confirmed in two similar experiments by GLC (Varian series 1400, ss. column 50 cm $\times$ 1/8" filled with O.V. 101 on Chrom. G. HP. 100/120, T 190°C, carrier nitrogen 10 psi).

Reaction of 2-azidobiphenyl (5) with boron trichloride. A solution of the azide (5) (2 mmol) in 5 ml of dry benzene was added dropwise with stirring under nitrogen to 3 ml of boron trichloride (0.7 M) in dry benzene at room temperature. The mixture, which showed rapid evolution of nitrogen, was stirred until TLC showed that no starting material remained (10 min). It was then hydrolyzed with a saturated sodium bicarbonate solution (15 ml) and extracted twice with diethyl ether. The combined organic layers were washed with water and dried. The solvent was evaporated and the solid residue was washed with n-hexane/diethyl ether (1/1; v/v) to leave carbazole as translucent solid (0.305 g, 91%) m.p. 245–246°C.

Reaction of azide (5) with n-butylboron dichloride. A procedure similar to that in the preceding experiment gave carbazole (13) as the only product (0.30 g, 90%) m.p. 245–246°C.

Acknowledgements

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