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PREPARATION AND REACTIVITY OF 2,2'-DILITHIO-1-PHENYLPYRROLE

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Summary

A simple preparation of 2,2'-dilithio-1-phenylpyrrole is described, and its use for the synthesis of new heterocyclic systems is demonstrated. The benzenoid lithium is shown to be more reactive towards electrophiles than the pyrrolic lithium.

Introduction

Numerous workers have used dilithiated species to prepare a wide variety of heterocyclic compounds [1—3]. One of the most extensively investigated systems is 1,4-dilithiotetraphenylbutadiene [2]. We were interested in the possibility of using dilithiated aryl pyrroles for the synthesis of new heterocycles. To date, very little is known about the lithium derivatives of pyrroles in general [4—6] and of aryl pyrroles in particular [5].

In their study of the metallation of 1-phenylpyrrole (I) with n-butyllithium, Shirley et al. [5] showed that the major product of metallation is 2-lithio-1-phenylpyrrole (II), even in the presence of excess reagent. However, to account for the formation of some cyclic ketone (III) (obtained after carboxylation of the reaction mixture), these authors suggested that some 2,2'-dilithio-1-phenylpyrrole (IV) was also formed, through dimetallation of the substrate (I). We now report the preparation and characterisation of the postulated dilithiophenylpyrrole (IV), and discuss some of its chemistry.

Preparation of 2,2'-dilithio-1-phenylpyrrole (IV)

2,2'-Dilithio-1-phenylpyrrole (IV) is prepared simply, rapidly, and in high yield, by the reaction (at 0°C) of an ethereal solution of 1-(2'-bromophenyl)-pyrrole (V) with two equivalents of n-butyllithium. Metal—halogen exchange almost certainly occurs first, followed by a directed metallation * of the pyrrole

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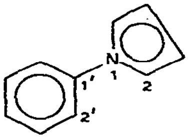
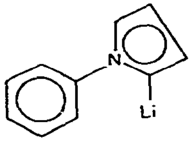
* The term "directed metallation" is here extended to include the metallation of one ring directed by the (possibly chelated) lithium cluster present on the adjacent ring. For a discussion of directed metallation, see ref. 7, chapter 12.



(I)



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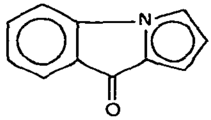

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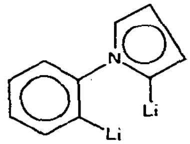

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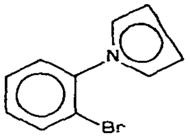

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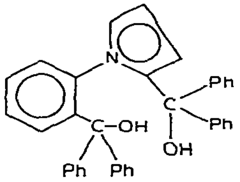

(VI)

ring. The solution of IV thus obtained may be used in situ or with inverse addition.

As an alternative to using the bromo compound (V), it was subsequently found that IV can also be prepared simply and rapidly by treating I with two equivalents of n-butyllithium, in the presence of *N*, *N*, *N'*, *N'*-tetramethylethylenediamine (TMED) *, the formation of IV was demonstrated by isolation of the bisbenzophenone adduct (VI) (see below). In this case, metallation probably occurs first at the pyrrole ring, followed by a directed metallation of the benzene ring. This result may be contrasted with that obtained in the absence of TMED, as described above [5]. This method has the advantages of easier accessibility of starting material and absence of the by-product, n-butyl bromide (which can undergo further reaction with the organolithium intermediates). For the exploratory work described herein, the bromo compound (V) was used to generate the reactive species.

Characterisation of 2,2'-dilithio-1-phenylpyrrole (IV)

The use of carbon dioxide to characterise organolithium compounds is widespread [1], but was found to be unsuited to this system, since extensive decomposition occurred on attempted isolation and purification of the reaction products. However, both deuterium oxide and (more conveniently) benzophenone were suitable for this purpose.

When the reagent was treated with an excess of deuterium oxide, a mixture of di-, mono-, and un-deuteriated 1-phenylpyrroles was obtained, as indicated by

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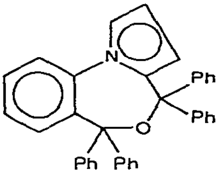
* A recent comprehensive account of the use of TMED with organolithium compounds is given in ref. 7.



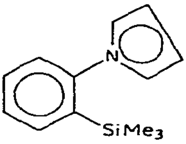
(VII)

mass spectral analysis. The 2-substitution of the pyrrole ring (in this and other products) was confirmed by the NMR spectrum.

When benzophenone was used, the expected 2,2'-bis adduct VI was obtained (67%), together with the cyclic ether (VII) (15%). The latter compound is presumably formed by loss of lithium monoxide from the intermediate adduct; however, cyclodehydration of VI during isolation or purification cannot be ruled out. The melting behaviour of VI suggests that cyclodehydration to VII does occur at elevated temperatures (see Experimental). The formation of VII provides additional confirmation of the 2,2'-dimetallation pattern. The isolation of both VI and VII established that IV is formed in high yield within minutes at 0°C. Gilman Tests I [8] and II [9] also showed that formation of IV was very fast. (The tests are summarised in ref. 1, pp. 72—73.)

Other electrophiles

Attempts to characterise the reactive species with other electrophiles were less satisfactory. For example, iodomethane failed to react under the conditions used (0°C, ca. 1 h), as did 1,2-dibromoethane, 1,3-di-iodopropane and bis(chloromethyl) ether. The reaction of IV with a large excess of trimethylchlorosilane gave only the monosilylated product (VIII) in 64% yield, together with I (24%); the latter, which is presumably formed by hydrolysis of unreacted IV, was isolated from most of the reactions described. Treatment of IV with mercuric chloride did not give a cyclic derivative, but the product of the 2/1 molecular reaction, IX (unreacted lithium atoms are removed by hydrolysis).



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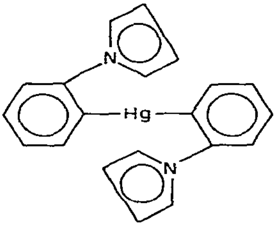

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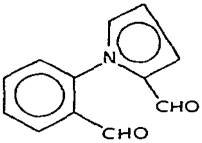
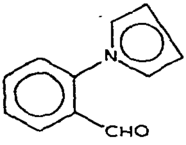


(X)

An attempt to prepare 2,2'-diformyl-1-phenylpyrrole (X) by treating IV with two equivalents of *N,N*-dimethylformamide gave mainly the monoformyl compound XI (79%) and a small quantity of a tarry material which may have been formed from the desired product. 1-(2'-Formylphenyl)pyrrole (XI), which has been made from the corresponding ester [10], can be prepared simply and in high yield by the reaction of the Grignard reagent of V with *N,N*-dimethylformamide.

Heterocyclic synthesis

Heterocyclic compounds incorporating the Group 4 and 5 elements have often been made by treating α,ω-dilithio species with appropriate *gem*-dihalides [1,11,12]. The application of this approach to 2,2′-dilithio-1-phenylpyrrole was straightforward, and the new tricyclic derivatives containing silicon (XII), germanium (XIII), phosphorus (XV) and arsenic (XVI) were readily prepared. The reaction with diphenyldichlorosilane was observed (from the Gilman test) to be stepwise, hence the reaction mixture was heated under reflux for several hours to ensure completion of cyclisation *. This stepwise reaction permitted the synthesis of the asymmetrically-bridged compound XVII (see below). The reaction with dimethyldichlorogermane also afforded the product of the 2/1 molecular reaction XIV, together with some di-n-butyldimethylgermane. Initial attempts to isolate carbon- and sulphur-bridged compounds (using such reagents as methylene iodide [2] and sulphur dichloride [2,3a]) were unsuccessful.



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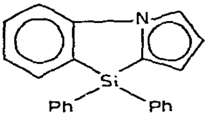

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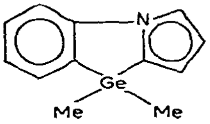

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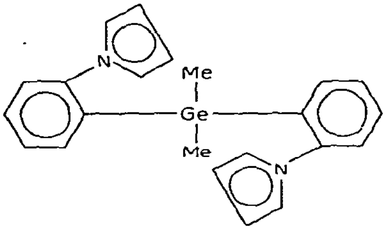

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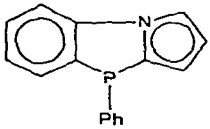

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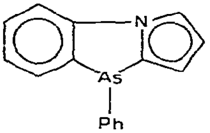

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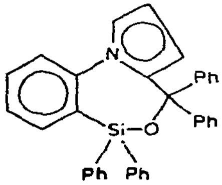

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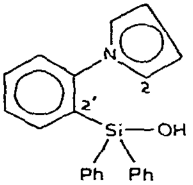

(XVIII)

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* A similar stepwise reaction was observed in the reaction of 2,2′-dilithiobiphenyl with diphenyldichlorosilane [13].

Selectivity of reaction site

The unsuccessful characterisation attempts described above illustrate the higher reactivity of the benzenoid lithium relative to the pyrrolic lithium. This selectivity was utilised in the preparation of the oxazasilepine XVII: treatment of IV with one equivalent of diphenyldichlorosilane followed by one equivalent of benzophenone resulted in the desired sequential addition, followed by loss of lithium chloride and formation of the silicon—oxygen bond. That the addition proceeded according to this sequence was indicated by the isolation of the 2′-silanol XVIII (cf. ref. 3a); none of the corresponding pyrrole-substituted silanol was isolated. Some of the bisbenzophenone adduct VI was also obtained, thus clearly indicating the unusually low reactivity of even the benzenoid lithium.

Conclusions

2,2′-Dilithio-1-phenylpyrrole is a readily available reagent for the synthesis of tricyclic compounds. The selectivity of reaction can be used to prepare asymmetrically-substituted 1-phenylpyrroles.

Experimental

Melting points were determined with a Gallenkamp melting point apparatus, and are uncorrected. Boiling points are uncorrected. Infrared spectra were recorded on a Unicam SP200 spectrometer, with Nujol mulls, liquid films or solutions in chloroform (d_0 or d_1). Ultraviolet spectra were recorded on a Unicam SP800A spectrometer, using 96% ethanol as solvent. Nuclear magnetic resonance spectra were recorded at 60 MHz on a Perkin—Elmer R12B spectrometer, using deuterochloroform as solvent, and are quoted in parts per million downfield from internal TMS. Mass spectra were recorded at 70 eV on an AEI MS30, MS50 or MS902 mass spectrometer; peak abundances are quoted as a percentage of the base peak. No attempts were made to optimise reaction conditions for yield.

Preparation of 1-(2′-bromophenyl)pyrrole (V)

To a refluxing solution of *o*-bromoaniline (124 g, 0.72 mol) in glacial acetic acid (150 ml) was added dropwise, over 5 min, neat *cis,trans*-2,5-dimethoxytetrahydrofuran (100 g, excess); TLC (chloroform) monitoring showed the reaction to be complete within 1 min of completion of addition. The mixture was allowed to cool and solvent was distilled off at atmospheric pressure. The residue was distilled from dinonyl phthalate under vacuum, the fraction distilling at 100—140°C/1 mmHg being collected. The distillate (140.5 g, 88%) was redistilled under vacuum from dinonyl phthalate; b.p. ca. 110°C/1.5 mmHg; n_D^{14} = 1.618. The product, a colourless liquid, was stored under dry nitrogen, in the dark, to minimise decomposition. Anal.: found: C, 53.4; H, 3.4; N, 6.3; $C_{10}H_8BrN$ calcd.: C, 54.1; H, 3.6; N, 6.3%. ν_{max} (film): 3100—3050m, 1700m, 1590s, 1550m, 1500vs, 1440s, 1335vs, 1240m, 1120s, 1075vs, 1055s, 1030s, 1020s, 925s, 760vs, 725vs (br) cm^{-1}. λ_{max}: 243 nm. δ: 6.2—6.4 (2H, m, H-3,4), 6.7—6.9 (2H, m, H-2,5), 6.9—7.8 (4H, m, H-3′ to 6′). *m/e*: 221 (100%, M^+[^{79}Br]). Found: 220.9836, $C_{10}H_8{}^{79}BrN$ calcd.: 220.9840.

General reaction procedure

All reactions involving organolithium reagents were performed under dry nitrogen. A 3-necked, round-bottomed flask was equipped with a magnetic stirrer, nitrogen inlet, pressure-equalising dropping funnel and condenser. The condenser outlet was connected via a mercury outlet valve to a silicone oil bubbler.

A solution of 2,2'-dilithio-1-phenylpyrrole (0.01 mol) was prepared by the addition, in one portion, of a standard solution of n-butyllithium (0.02 mol) in n-hexane to a stirred, ice-cooled solution of 1-(2'-bromophenyl)pyrrole (2.22 g, 0.01 mol) in diethyl ether (25—50 ml). A yellow colour was immediately formed. The solution was stirred at 0°C for 5 min. At this stage, Gilman Test I [8] was positive and Test II [9] was negative, i.e., the aryllithium reagent was present, but the butyllithium had been consumed. The formation of the dilithiophenylpyrrole is probably almost instantaneous.

A solution of a difunctional electrophile (0.01 mol) or a monofunctional electrophile (0.02 mol) in diethyl ether (25—50 ml) was added dropwise, over 5—30 min, to the stirred, ice-cooled organolithium solution. When addition was complete, the mixture was stirred at 0°C for 5 min, then a Gilman Test I was performed on the mixture. If a positive result was obtained, stirring was continued at 0°C until the test was negative or only very weakly positive (5—30 min, occasionally overnight). The mixture was then hydrolysed by the dropwise addition of water or saturated ammonium chloride solution (20—50 ml), which was added until any precipitate formed had redissolved and two clear layers were obtained. In some cases, the product precipitated out after hydrolysis, or during washing etc., and was filtered off and purified. The filtrate was treated as for the normal hydrolysis mixture.

The aqueous layer was separated off and extracted with diethyl ether or dichloromethane. The combined organic extracts were washed with water or saturated sodium chloride solution until the washings were neutral to pH paper, dried ($MgSO_4$) and evaporated. The residue was purified by distillation, crystallisation, sublimation or chromatography, as appropriate. Very often, when solvent was removed from the crude product, a small quantity of white sublimate was obtained. This was identified as 1-phenylpyrrole, which presumably is formed by hydrolysis of unreacted dilithiophenylpyrrole.

Characterisation of 2,2'-dilithio-1-phenylpyrrole (IV) with deuterium oxide

A solution of IV (0.005 mol) was prepared by the general procedure and hydrolysed with deuterium oxide (4 ml, 97%, large excess). Subsequent work-up gave a residue which was sublimed in vacuo to give a white crystalline sublimate (0.57 g, 79%), m.p. 60—62°C (1-phenylpyrrole has m.p. 62°C [14a]). The product was shown by NMR to consist predominantly of the 2,2'-dideuterated species; however, mass spectral analysis also showed the presence of monodeuterated and non-deuterated 1-phenylpyrroles. δ: 6.3—6.45 (m, 2H, H-3,4), 7.1—7.2 (m, 1.1 H, H-2), 7.25—7.6 (m, 4.8H, benzenoid H). δ (1-phenylpyrrole, d_0): 6.35—6.5 (m, 2H, H-3,4), 7.0—7.2 (m, 2H, H-2,5), 7.25—7.55 (m, 5H, H-2' to 6'). *m/e*: 145 (100%, $M^+[d_2]$), 144 (39%, $M^+[d_1]$), 143 (25%, $M^+[d_0]$). *m/e* (1-phenylpyrrole, d_0): 145 (0.6%, $M^+ + 2$), 144 (13%, $M^+ + 1$), 143 (100%, M^+). From the mass spectra, the sublimate was found to consist of 61, 23 and 16% of d_2-, d_1-, and d_0-1-phenylpyrroles, respectively.

Characterisation of 2,2'-dilithio-1-phenylpyrrole (IV) with benzophenone

Dilithiophenylpyrrole (IV) (0.005 mol) was treated with benzophenone (1.86 g, 0.012 mol) by the general procedure. A white precipitate was formed on addition of water. The precipitate was filtered off, and the solid and filtrate treated separately.

Solid. The white solid (1.29 g, 67%) was crystallised from a mixture of acetone, dichloromethane and ethanol, recrystallised from dichloromethane/methanol and dried in vacuo at room temperature, to give white crystals of the diol VI; m.p. 202—203° C (rapid heating; the behaviour of this material on heating is described below in more detail). Anal.: Found: C, 85.1; H, 5.7; N, 2.6. $C_{36}H_{29}NO_2$ calcd.: C, 85.2; H, 5.8; N, 2.8%. ν_{max} ($CHCl_3$): 3500m (OH), 3400m (OH) cm^{-1}. λ_{max}: 219 nm. δ: 2.8 br (OH, exchangeable), 5.0—7.6 (m, aromatic H) (a satisfactory integral was not obtained). *m/e*: 507 (6%, M^+), 489 (65%, $M^+ - H_2O$), 105 (100%, $[PhCO]^+$).

Filtrate. The filtrate from the reaction mixture was separated into two layers. The aqueous layer was extracted with diethyl ether, and the combined ether layers were washed with water, dried and evaporated. The residue (1.07 g) was dissolved in dichloromethane and adsorbed onto silica gel, and chromatographed on a pentane-packed silica gel column. Elution was carried out with mixtures of pentane and dichloromethane of increasing dichloromethane content, and finally with a mixture (1/1) of dichloromethane and ethyl acetate. Two main fractions were obtained:

(1) The more mobile component (TLC with dichloromethane) was obtained as a very pale yellow powder (0.28 g, 15%), which was crystallised from dichloromethane/methanol to give an off-white powder, m.p. 255—257° C. The product was identified as the cyclic ether VII. Anal.: Found: C, 87.8; H, 5.5; N, 3.1; $C_{36}H_{27}NO$ calcd.; C, 88.3; H, 5.55; N, 2.9%. ν_{max} (Nujol): 1600w, 1500m, 1340w, 1150m, 1015m, 760m, 700s cm^{-1}. λ_{max}: 212, 258, 271.5(sh) nm. δ: 5.5—5.95 (m, pyrrolic H), 6.4—8.2 (m, benzenoid H) (a satisfactory integral was not obtained). *m/e*: 489 (48%, M^+), 105 (100%, $[PhCO]^+$).

(2) The less mobile component was obtained as an oil (0.48 g) which was identified as benzophenone (labile form). Note: The calculated yields of VI and VII are based on the benzophenone consumed.

Melting behaviour of the diol VI. Rapid heating of the diol VI led to the observed m.p. of 202—203° C; a deep red colour appeared at ca. 188° C. When the material was inserted into an apparatus preheated to 205° C, no melting occurred until 215° C. Slow heating gave the same red colour, but the material melted at 245—250° C, i.e. just below the m.p. of the ether VII (255° C). Also, when a sample of VI was rapidly heated to the m.p. and then allowed to solidify, the subsequent m.p. was ca. 250° C. These observations suggest that heating of VI induces cyclodehydration to VII. Indeed, before melting, VI appeared on TLC (dichloromethane) as a single spot (yellow with Ehrlich's reagent); after melting, two spots were present, the less mobile corresponding to VI, the more mobile to VII (yellow, then rapidly red with Ehrlich's reagent).

Cyclodehydration of VI to VII was also found to occur when attempts were made to purify VI by chromatography on silica gel using chloroform or dichloromethane as eluent.

Preparation and characterisation of 2,2'-dilithio-1-phenylpyrrole (IV) from 1-phenylpyrrole (I)

To a stirred, ice-cooled solution of freshly sublimed I (1.43 g, 0.01 mol) in diethyl ether (25 ml) was added a solution of n-butyllithium (0.02 mol) in hexane; a very pale yellow colour appeared. Dry, freshly-distilled TMED * (3 ml, 0.02 mol) was added; a deep yellow colour immediately appeared (of the same appearance as the dilithiophenylpyrrole solution prepared from bromophenylpyrrole). A solution of benzophenone (3.68 g, 0.02 mol) in diethyl ether (25 ml) was added; Gilman Test I was then negative. Water (5 ml) was added dropwise, followed by a large excess of water. The white solid formed was filtered off, washed with water, dried (yield 4.15 g, 82%) and crystallised from dichloromethane/methanol (an insoluble residue was discarded). The white crystalline solid was washed with acetone and dried under high vacuum; m.p. 215—216°C (decomp.). The product was identified as the diol VI (for data, see above).

Attempted reaction of 2,2'-dilithio-1-phenylpyrrole (IV) with 1,2-dibromoethane

Dilithiophenylpyrrole (IV) (0.005 mol) was treated with an excess of 1,2-dibromoethane by the general procedure. The mixture was hydrolysed after 1 h at 0°C; subsequent work-up gave a crystalline product (0.69 g, 97%), which was identified as 1-phenylpyrrole; i.e., no reaction with dibromoethane had occurred.

Similar results were obtained using iodomethane, 1,3-di-iodopropane, and bis(chloromethyl) ether.

Reaction of 2,2'-dilithio-1-phenylpyrrole (IV) with trimethylchlorosilane

Dilithiophenylpyrrole (IV) (0.01 mol) was treated with freshly distilled trimethylchlorosilane (10 ml, large excess) by the general procedure. After 30 min at 0°C, the Gilman Test I was still positive **, and the mixture was allowed to reach room temperature, with stirring, overnight, after which the test was negative ***. After the usual work-up, an oil (1.77 g) was obtained. The crude product was vacuum-distilled to give two fractions, b.p. 75—80°C/ca. 0.5 mmHg (colourless) and b.p. 80—85°C/0.5 mmHg (yellow, viscous), which had essentially the same composition. The first fraction was redistilled under vacuum from dinonyl phthalate to give a colourless liquid, b.p. 88—90°C/0.5 mmHg. This material was examined by gas-liquid chromatography (Pye 104 GC gas chromatograph with flame-ionisation detector, 1.5 m × 3 mm i.d. column, 10% PEG 20M on celite support, nitrogen carrier, flow rate 30 ml min^{-1}, initial temperature 135°C increasing by 1.5° min^{-1}) and found to consist of three components, with peak areas in the ratio 3, 78 and 19% in order of elution; retention

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[*] TMED was dried over solid sodium hydroxide, then over calcium hydride. The dried liquid was distilled under nitrogen from calcium hydride, to give a colourless liquid, b.p. 120°C (lit. [14b]: 121—121.5°C).

[**] A positive test was obtained immediately following the hydrolysis step of the test (before addition of iodine/acetic acid); this is presumably due to the presence of acid liberated on hydrolysis of excess trimethylchlorosilane.

[***] Presumably, unreacted organolithium species were removed by slow reaction with the solvent ether.

times t_R = 6.2, 15.6 and 17.0 min, respectively. The second and third components were identified by combined GLC — mass spectrometry (using the above GLC conditions) as 1-(2'-trimethylsilylphenyl)pyrrole (VIII) and 1-phenylpyrrole (I), respectively. The minor component was not identified. ν_{max} (film): 1250s ($SiMe_3$), 850s ($SiMe_3$) cm^{-1}. λ_{max}: 213,239 nm (1-phenylpyrrole λ_{max} 207,253nm). δ (relative to the $SiMe_3$ group, no TMS): 0 (s, 9H, 3 × CH_3), 6.25—6.45 (m, 2.3H, H-3,4), 6.75—6.95 (m, 2.3H, H-2,5), 7.1—7.9 (m, 4.9H, H-3' to 6'). The integration corresponds to a mixture of VIII and 1-phenylpyrrole with ca. 19% of the latter. *m/e* of second (major) component (VIII): 215 (56%, M^+), 200 (100%, $M^+ - CH_3$), 184 (21%, $M^+ - 2CH_3 - H$); overall yield ca. 1.38 g, 64%. *m/e* of third component (I): 143 (100%, M^+) (the mass spectrum was identical with that of an authentic sample of 1-phenylpyrrole); (overall yield ca. 0.34 g, 24%).

Preparation of bis(2-[1'-pyrryl]phenyl)mercury (IX)

Dilithiophenylpyrrole (IV) (0.005 mol) was treated with mercuric chloride (99.5%, 1.31 g, <0.005 mol) by the general procedure. After work-up, a semisolid residue (1.21 g) was obtained. The product was treated with carbon tetrachloride, and the mixture was filtered. The white solid was washed with carbon tetrachloride and sucked dry. The filtrate was evaporated, and the residue dissolved in carbon tetrachloride, and pentane added to precipitate more solid. This process was repeated until no more solid was obtained (combined yield ca. 0.46 g, 38%). The final filtrate gave a mixture of oil and solid; the NMR spectrum of this material corresponded to a mixture of 1-phenylpyrrole and IX in a molar ratio of about 2/1.

The solid obtained as described above was crystallised from dichloromethane/methanol to give an off-white, crystalline solid, which was dried in vacuo at room temperature; m.p. 189.5—191.5°C. Anal.: Found: C, 49.7; H, 3.3; N, 5.85. $C_{20}H_{16}HgN_2$ calcd.: C, 49.5; H, 3.3; N, 5.8%. ν_{max} (Nujol): 1580w, 1310m, 1060m, 755m, 730s, 710s cm^{-1}. δ: 6.25—6.4 (4H, m, H-3,4,3', 4'), 6.85—7.0 (4H, m, H-2,5,2',5'), 7.15—7.5 (8H, m, benzenoid H). *m/e*: 484 (35%, $M^+[^{200}Hg]$), 284 (100%, $M^+ - Hg$).

Reaction of 2,2'-dilithio-1-phenylpyrrole (IV) with N,N-dimethylformamide

Dilithiophenylpyrrole (IV) (0.01 mol) was treated with molecular-sieve-dried *N,N*-dimethylformamide by the general procedure. After hydrolysis, a clear yellow solution was initially formed. Subsequently a cloudy bottom layer was formed, then the whole mixture became cloudy, and some tar was formed. The liquid was decanted off and subjected to the usual work-up to give a brown oil (1.35 g, 79%). The product was identified as 1-(2'-formylphenyl)pyrrole (XI) by comparison of its infrared and NMR spectra with those of an authentic sample, prepared as described below.

Preparation of 1-(2'-formylphenyl)pyrrole (XI)

In the conventional Grignard apparatus, a solution of 1-(2'-bromophenyl)-pyrrole (V) (43.1 g, 0.194 mol) in dry diethyl ether (50 ml) was added, over 1 h, to magnesium turnings (4.9 g) and diethyl ether (200 ml). The mixture was heated under reflux for 1 h and allowed to cool, a slow flow of nitrogen being maintained. Dry diethyl ether (100 ml) was added, and a solution of molecular-sieve-dried *N,N*-dimethylformamide (16.5 ml, 0.21 mol) in diethyl ether (55 ml) was added dropwise over 50 min. The mixture was then heated under reflux for 40 min and allowed to cool. Dilute sulphuric acid (5% v/v, 200 ml) was added dropwise, and the mixture was stirred at room temperature overnight. The organic layer was separated and the aqueous phase was extracted with dichloromethane. The combined extracts were washed with saturated sodium chloride solution, dried and evaporated, and the residue (29.3 g, 88%) was distilled in vacuo to give a light yellow liquid (20.6 g, 62%), b.p. 95—97°C/1 mmHg (lit. [10] 70—72°C/0.05 mmHg). Redistillation gave the product as a colourless liquid, $n_{\mathrm{D}}^{13.5^\circ} = 1.612$. The product was stored under dry nitrogen, in the dark, to minimise decomposition. A colourless crystalline condensate, obtained during distillation, was identified as 1-phenylpyrrole, which is presumably formed by hydrolysis of residual Grignard reagent. Anal.: Found: C, 76.7; H, 5.2; N, 8.25. $C_{11}H_9NO$ calcd.: C, 77.2; H, 5.3; N, 8.2%. ν_{max} (film): 2850m (CH), 2750m (CH), 1690 vs(br) (CO) cm^{-1}. λ_{max}: 237.5, 257 (sh), 305 nm. δ: 6.25—6.4 (2H, m, H-3,4), 6.8—6.95 (2H, m, H-2,5), 7.25—8.1 (4H, m, H-3′ to 6′), 9.75 (1H, s, CHO). *m/e*: 171 (33%, M^+), 143 (100%, $M^+ - CO$): m^* 119.9 (171 → 143): found 171.0686, $C_{11}H_9NO$ calcd.: 171.0684.

Preparation of 4H-4,4-diphenylpyrrolo[1,2-a]benz[d][1,3]azasilole (XII)

Dilithiophenylpyrrole (IV) (0.005 mol) was treated with freshly distilled diphenyldichlorosilane (1.43 g, 0.006 mol) by the general procedure. The Gilman Test I was still positive after 1 h [The observation of the usual precipitate (presumably lithium chloride) coupled with the subsequent unusual Gilman Test observation (positive result prior to iodine/acetic acid addition) suggests that the reaction proceeds in two stages: (1) the rapid displacement of one chlorine, followed by (2) the slow displacement of the second chlorine.] Diethyl ether (50 ml) was added, and the mixture was heated under reflux overnight, after which the test was negative. After cooling and subsequent work-up, the semi-solid residue (1.8 g) obtained was treated with dichloromethane. The insoluble residue (0.1 g, m.p. ca. 160°C) was removed, and the filtrate evaporated to give a dark brown oil which crystallised on standing. The product was purified by chromatography on a pentane-packed silica gel column, which was eluted with pentane/dichloromethane (4/1). Evaporation of the eluate gave beautiful colourless crystals (0.83 g, 51%). The product was twice recrystallised in the cold from pentane/dichloromethane; m.p. 109—109.5°C. Anal.: Found: C, 81.5; H, 5.3; N, 4.3. $C_{22}H_{17}NSi$ calcd.: C, 81.7; H, 5.3; N, 4.3%. ν_{max} (Nujol): 1600m, 1520w, 1430m (Si—Ph), 1330s, 1310w, 1280w, 1100s (Si—Ph), 1080m, 740m, 730w, 710s, 690s cm^{-1}. λ_{max} (ϵ): 210(32800), 226(40200), 263(16100), 279(inf) (8650), 286(sh) (7750)nm. δ: 6.4—6.55 (m, 1H, H-2), 6.7—6.85(m, 1H, H-3), 7.0—7.9 (m, 15H, H-1, benzenoid H). *m/e*: 323 (100%, M^+): found 323.1125, $C_{22}H_{17}NSi$ calcd.: 323.1130.

Preparation of 4H-4,4-dimethylpyrrolo[1,2-a]benz[d][1,3]azagermole (XIII)

Dilithiophenylpyrrole (IV) (0.028 mol) was treated with dimethyldichlorogermane (5 g, 0.029 mol) by the general procedure. After the usual work-up, a mobile liquid (3.02 g) was obtained, which was distilled under vacuum. Two fractions were obtained, together with a small quantity of white crystalline sublimate (probably 1-phenylpyrrole).

The first fraction, a colourless, mobile liquid (b.p. ca. 30°C/0.5 mmHg; $n_{\mathrm{D}}^{25.5^\circ}$ 1.443), was identified as di-n-butyldimethylgermane *. Anal.: Found: C, 56.7; H, 10.85; $C_{10}H_{24}Ge$ calcd.: C, 55.4; H, 11.1%. ν_{max} (film): 2900vs (CH), 1600w, 1515m, 1465s (CH), 1380m (CH), 1230s, 1080m, 880s, 820s, 790s cm^{-1}. δ: 0.6 (s, 6H, 2 × CH_3), 1.0—2.2 (m, 18H, 2 × C_4H_9). The second fraction, a colourless liquid (b.p. 88—110°C/0.5 mmHg), partially crystallised on standing. [The liquid and solid products were indistinguishable by film infrared or TLC (pentane or dichloromethane).] The liquid (ca. 1 g, 18%) was pipetted off and identified as dimethylbis[2-(1′-pyrryl)phenyl]germane (XIV). Anal.: Found: C, 67.3; H, 6.7; N, 6.3; $C_{22}H_{22}GeN_2$ calcd.: C, 68.3; H, 5.7; N, 7.2%. ν_{max} (film): 3050w, 2950m, 1590s, 1515s, 1470s, 1455s, 1330s, 1280m, 1080s, 800m, 755s, 720s cm^{-1}. λ_{max}: 213, 221, 250, 278(inf) nm. δ: 0.6 (s, 6H, 2 × CH_3), 6.2—6.5 (m, 4H, H-3,4,3′,4′), 7.0—7.6 (m, 12H, H-2,5,2′,5′, benzenoid H). *m/e*: 246 (100%, $M^+[^{74}Ge] - C_{10}H_8N$) ($M^+$ not observed).

The residual crystalline solid (0.55 g, 8%) was purified by vacuum sublimation, to give white crystals of the title azagermole (XIII); m.p. 70.5—73°C (softens 67°C). Anal.: Found: C, 59.8; H, 5.5; N, 5.7; $C_{12}H_{13}GeN$ calcd.: C, 59.1; H, 5.4; N, 5.7%. ν_{max} (Nujol): 1590m, 1330s, 1080s, 750s, 710s, 700s cm^{-1}. λ_{max} (ϵ): 220.5(22500), 256(12850), 278(13675) nm. δ: 0.6 (s, 6H, 2 × CH_3), 6.3—6.65 (m, 2H, H-2,3), 7.0—7.7 (m, 5H, H-1, 5 to 8). *m/e*: 241 (33%, $M^+[^{70}Ge]$), 226 (100%, $M^+[^{70}Ge]-CH_3$). Found 241.0288; $C_{12}H_{13}{}^{70}GeN$ calcd.: 241.0291.

Preparation of 4H-4-phenylpyrrolo[1,2-a]benz[d][1,3]azaphosphole (XV)

All operations involved in the preparation and manipulation of this compound were performed under an inert atmosphere, to avoid oxidation to the phosphine oxide.

Dilithiophenylpyrrole (IV) (0.01 mol) was treated with freshly distilled phenyldichlorophosphine (1.57 g, 0.009 mol) by the general procedure. The mixture was stirred at 0°C for 50 min, then filtered through a sinter which had been packed with a filter aid; the residue was washed with dry diethyl ether. Solvent was removed from the filtrate by gentle water bath heating to give a viscous, dark brown oil.

Methanol was added to the crude product; a solid was immediately formed. The supernatant liquid was removed, and the residue was triturated with fresh methanol. This process was repeated until a cream solid was obtained. The product was purified by repeated crystallisation from chloroform/methanol, and dried in vacuo (yield ca. 0.5 g, 23%); m.p. 111—112°C. The product had a characteristic phosphine odour. Anal.: Found: C, 77.0; H, 4.9; N, 5.9; $C_{16}H_{12}NP$ calcd.: C, 77.1; H, 4.85; N, 5.6%. ν_{max} ($CDCl_3$): 1600s, 1500vs, 1440s (P—Ph),

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* Di-n-butyldimethylgermane has been obtained as one of several products from the redistribution reaction between tetramethylsilane and tetra-n-butylgermane, and from the alkylation of tetrachlorogermane with a mixture of alkyl Grignard reagents [15]. However, no physical properties (other than retention time) were reported

1360s, 1330s, 1300s, 1135s cm^{-1}. λ_{max} (ϵ): 212(inf) (24600), 229.5(29800), 265(inf) (11000), 282.5(12800) nm. δ: 6.5—6.8 (m, 2H, H-2,3), 7.1—7.9 (m, 10H, H-1, benzenoid H). *m/e*: 249 (100%, M^+). Found: 249.0712; $C_{16}H_{12}NP$ calcd.: 249.0708.

Preparation of 4H-4-phenylpyrrolo[1,2-a] benz[d][1,3]azarsole (XVI)

Preparation of phenyldichloroarsine [16] (by a slight modification of the literature method). (*Caution!* phenyldichloroarsine is toxic and vesicant.)

Sulphur dioxide (excess) was passed for 10 min through a solution of phenylarsonic acid (10.0 g) and iodine (54 mg) in concentrated hydrochloric acid (17 ml) contained in a dropping funnel. An oil was deposited and formed a lower layer, which was filtered directly through phase separating paper onto molecular sieves (4A) and dried overnight. The product (7.1 g, 64%) was filtered into a distillation flask and distilled in vacuo, to give a colourless liquid, b.p. 66°C/1 mmHg (lit. [16]: 115—117°C/10 mmHg).

Preparation of XVI. Dilithiophenylpyrrole (IV) (0.007 mol) was treated with freshly distilled phenyldichloroarsine (1.57 g, 0.007 mol) by the general procedure. After work-up an oil (2.03 g) was obtained, together with a small quantity of white sublimate (1-phenylpyrrole) and a white deposit. The product was adsorbed onto a preparative TLC plate, which was developed three times with dichloromethane. The upper quarter of the plate was removed, and the material desorbed with dichloromethane; evaporation of the solvent gave an oil (1.49 g, 73%). The product was dissolved in dry pentane and diethyl ether, and the solution filtered through a silica gel pad and evaporated. This process was repeated until a pentane-soluble, almost colourless oil (0.49 g, 24%) was obtained. ν_{max} (film): 3050w, 2950m, 2850w, 1590m, 1510w, 1480s, 1460m, 1440m, 1340m, 1320m, 1290m, 1120m, 1080m, 1020m, 780w, 750s, 735s, 715s, 700s cm^{-1}. λ_{max}: 212, 226, 271.5 nm. δ: 6.25—6.65 (m, 2H, H-2,3), 6.9—7.7(m, 10H, H-1, benzenoid H). *m/e*: 293 (14%, M^+), 216 (100%, M^+ — Ph). Found: 293.0190, $C_{16}H_{12}AsN$ calcd.: 293.0186.

Preparation of 4,4,6,6-tetraphenylpyrrolo[1,2-a]benz[f][4,1,5]oxazasilepine (XVII)

Dilithiophenylpyrrole (IV) (0.01 mol) was treated with freshly distilled diphenyldichlorosilane (2.57 g, 0.01 mol) by the general procedure. A white precipitate was formed after about 2 min, and the Gilman Test I was positive. Ethereal benzophenone (1.825 g, 0.01 mol) was then added, after which the test was negative. After hydrolysis, the aqueous layer (colourless, alkaline) was extracted twice with diethyl ether. The combined organic extracts were washed with water, and a yellow, acidic aqueous layer was formed. This suggests that hydrolysis of carbon- and oxygen-bound lithiums occurred first to give an alkaline solution, followed by hydrolysis of the silicon — chlorine bond to give an acidic solution. Further washing with water caused a white precipitate to be deposited. The mixture was filtered, and the solid washed with water and diethyl ether, and dried. The solid and filtrate were treated separately.

Solid. The solid (1.16 g, 23%) was crystallised from dichloromethane/methanol to give beautiful colourless needles, which were dried under high vacuum. The product was identified as the title oxazasilepine (XVII); m.p.

226—228.5°C (softens at 225.5°C). Anal.: Found: C, 83.0; H, 5.5; N, 2.9. $C_{35}H_{27}NOSi$ calcd.: C, 83.1; H, 5.4; N, 2.8%. ν_{max} (Nujol): 1600w, 1490m, 1430m, 1320m, 1100m, 1030m, 1020m, 850m, 760m, 735m, 720m, 700m, 680s cm^{-1}. λ_{max}: 220, 256 nm. δ: 5.9—6.4 (m, pyrrolic H), 6.5—8.6 (m, benzenoid H) (a satisfactory integration was not obtained). *m/e*: 505 (95%, M^+), 307 (100%, $M^+ - Ph_2SiO$). The product gave a mauve colouration with Ehrlich's reagent.

Filtrate. The filtrate was separated into two layers. The organic layer was washed with water, dilute ammonium hydroxide, and water, dried and evaporated. Dry pentane was added to the residue, the mixture was stirred and the solid filtered off, washed with pentane and dried. The solid and filtrate were treated separately.

Solid. The solid (1.36 g, 27%) was crystallised twice from dichloromethane/methanol. The product, m.p. 217—219°C(decomp.), was identified as the diol VI (for data, see above). The product gave a yellow, then orange, colouration with Ehrlich's reagent.

Filtrate. The filtrate was evaporated in vacuo to give a yellow oil (1.84 g, ca. 54%) which was distilled in vacuo to give a brown oil, b.p. 167°C/ca. 1 mmHg. The distillate was a mixture containing the silanol (XVIII). ν_{max} (film: 3550m, 3400m (br) (SiOH), 3030m, 2900s, 2830m, 2100w (Si—H impurity?), 1600m, 1500s, 1430vs, 1230vs, 1100vs, 1070s, 860—820s (br), 750s, 720vs, 690vs cm^{-1}. λ_{max}: 210, 221.5(sh), 253 nm. δ: 0.6—1.65 (m, aliphatic impurity), 2.3(br) (1H, OH, exchangeable), 6.35—6.45 (m, 2H, H-3,4), 7.1—7.2 (m, 2H, H-2,5), 7.2—7.9 (m, 20H, benzenoid H + impurity). *m/e*: 341 (2%, M^+), 199 (100%, $[Ph_2SiOH]^+$). (Calculated yields are based on the amount of IV consumed.)

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