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POLYHALOGENOAROMATIC COMPOUNDS

XXIX*. HEXACHLORO-5,5'-DILITHIO-4,4'-BIPYRIDINE AS AN INTERMEDIATE FOR ORGANOMETALLIC AND ORGANIC SYNTHESES

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Summary

Metal—halogen exchange between octachloro-4,4'-bipyridine and two molar equivalents of n-butyllithium gives hexachloro-5,5'-dilithio-4,4'-bipyridine. On reaction with dichlorodiphenylsilane or di-π-cyclopentadienyltitanium dichloride, the dilithio compound gives products lacking a metallocyclic ring. With sulphur dichloride the expected thienodipyridine is obtained. The stereochemical features of the reactions and of the products are discussed. Thermolysis of the dilithio compound failed to yield a cyclobutadipyridine.

2,3,6-Trichloropyridine is metallated by n-butyllithium in the 4-position.

Introduction

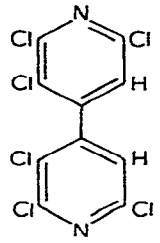
We have shown that the metal—halogen exchange reaction between n-butyllithium and octachloro-4,4'-bipyridine gives heptachloro-5-lithio-4,4'-bipyridine, which undergoes both typical reactions with electrophilic reagents and elimination of lithium chloride to form a 2-pyridine intermediate [2]. It was expected that the reaction of octachloro-4,4'-bipyridine with two molar equivalents of n-butyllithium might furnish a dilithio compound which would be a valuable intermediate for organometallic and organic syntheses.

Results and discussion

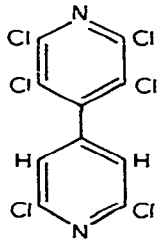
Octachloro-4,4'-bipyridine was treated with 2.3 molar equivalents of n-butyllithium at $-75°$, and the mixture was allowed to warm to room temperature before being hydrolysed. The main product (accompanied by a little 5H-heptachloro-4,4'-bipyridine) was a hexachlorobipyridine, m.p. 175-176°. The

*For part XXVIII see ref. 1.

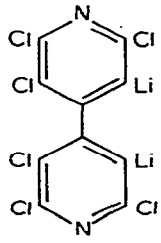
^{1}H NMR spectrum of the hexachlorobipyridine consisted of a singlet at τ 2.70, corresponding to protons at the β-position of a pyridine ring [3].



(I)

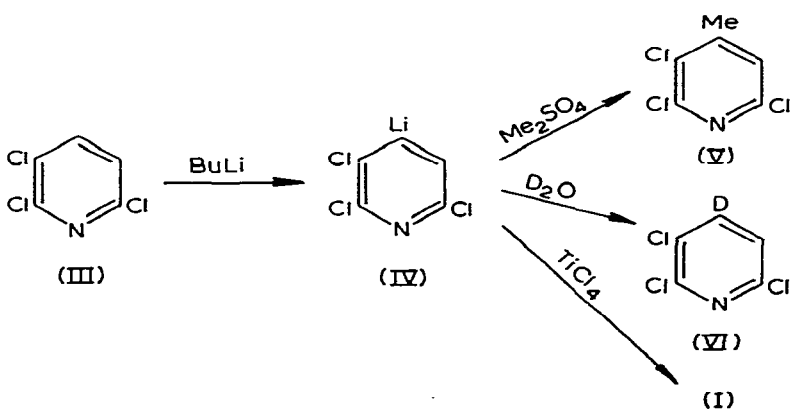


(II)



(VII)

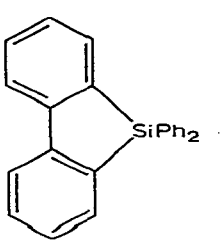
The two isomers, (I) and (II), could give this type of spectrum. The 5H,5'H-isomer (I) was considered to be more likely as the introduction of the first lithium atom would be expected to deactivate the ring concerned to further substitution. However, since the 3H,5H-isomer (II) could not be excluded, compound (I) was synthesised independently. Metallation of 2,3,6-trichloropyridine (III) by n-butyllithium gave the 4-lithio derivative (IV), whose structure was proved by reaction with dimethyl sulphate and with deuterium oxide. The derivatives, (V) and (VI) respectively, could not be freed from small amounts of starting material, but had ^{1}H NMR spectra corresponding to those of the known 4-substituted compounds; the methyl derivative (V) showed singlets at τ 2.80 and 7.54 in a ratio of 1/3 (cf. ref. 4), and the deuterio derivative (VI) showed a singlet at τ 2.71 (cf. ref. 5). The 4-lithio compound (IV) was then coupled by reaction with titanium tetrachloride [2,6] to give 5H,5'H-hexachloro-4,4'-bipyridine (I). This compound had IR and NMR spectra identical with those of the hexachlorobipyridine described above. The latter sample thus derived from hydrolysis of heptachloro-5,5'-dilithio-4,4'-bipyridine (VII).



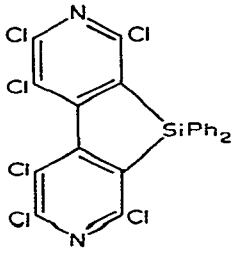
(III) (IV) (V) (VI) (I)

Despite the angle strain involved in forming the five-membered silicon-containing ring, the reaction of 2,2'-dilithiobiphenyl with dichlorodiphenylsilane gives the silafluorene (VIII) [7]. Analogous syntheses of titanium hetero-

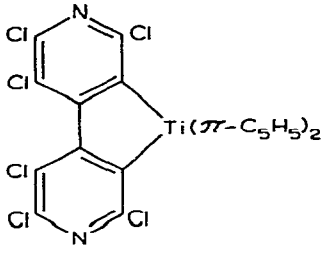
cycles have also been achieved by reactions of 2,2′-dilithiobiphenyls with di-π-cyclopentadienyltitanium dichloride [8,9]. It was thus expected that the reaction of the dilithio compound (VII) with dichlorodiphenylsilane and di-π-cyclopentadienyltitanium dichloride might give the novel heterocyclic compounds (IX) and (X). These compounds were not obtained.



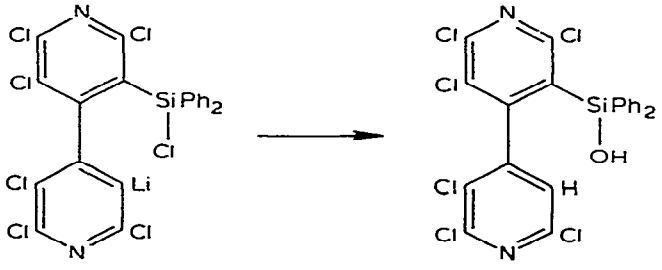
(VIII)



(IX)



(X)

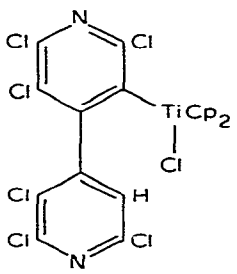


(XII) (XI)

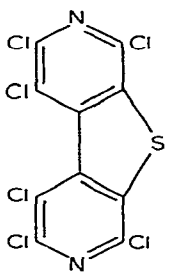
The reaction with dichlorodiphenylsilane gave a product which we formulate as the silanol (XI), and which arises from hydrolysis of the intermediate (XII). Evidence for this structure (XI) was provided by its elemental analysis, by its IR spectrum (which showed absorption attributed to O—H stretching at $\nu_{max.}$ 3340 cm^{-1} and by its ^1H NMR spectrum. The NMR assignments were as follows: τ 2.88 (m, 10 H*; Ph), 3.35 (s, 1 H; 3-pyridyl-H), 7.50 (br, 1 H, exchangeable; OH). We could not identify the molecular ion (*m/e* 558) in the mass spectrum of the compound, owing to the presence of isotopic peaks associated with the peak at *m/e* 557 (see below). However, accurate mass measurement of the peaks at *m/e* 523 and 557 showed them to correspond to ions with the composition $C_{22}H_{12}{}^{35}Cl_5N_2O^{28}Si$ and $C_{22}H_{11}{}^{35}Cl_6N_2O^{28}Si$, respectively. The former could be derived from the molecular ion by loss of chlorine (the appropriate pattern of isotopic peaks was observed), and the latter by loss of hydrogen (or possibly by cleavage of the corresponding disiloxane, whose formation in the spectrometer would not be unexpected).

*Integrations only approximate, because of presence of $CHCl_3$ in solvent.

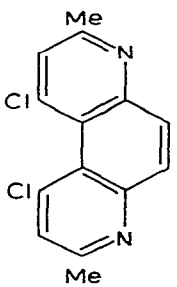
Similarly, di-π-cyclopentadienyltitanium dichloride gave a yellow product, whose elemental analysis and ^{1}H NMR spectrum corresponded to those expected for the uncyclised compound (XIII). A noteworthy feature of the NMR spectrum was the presence of two signals for the cyclopentadienyl groups. Their non-equivalence is attributed to restricted rotation about the bond joining the pyridine rings, resulting in chirality in the molecules. The mass spectrum of compound (XIII) showed no peak due to the molecular ion. The groups of peaks of highest mass corresponded to the ion resulting from loss of HCl from the molecular ion; the measured mass of the lowest of the group was 535.8431, ($C_{20}H_{10}{}^{35}Cl_6N_2{}^{48}Ti$), and the appropriate isotope pattern for six chlorines and one titanium was observed. Another fragment ion at *m/e* 499.8672 ($C_{20}H_9{}^{35}Cl_5N_2{}^{48}Ti$) corresponded to a further loss of HCl. Compound (XIII) was stable towards air and water, and could be recrystallised from ethanol.



(XIII)



(XIV)



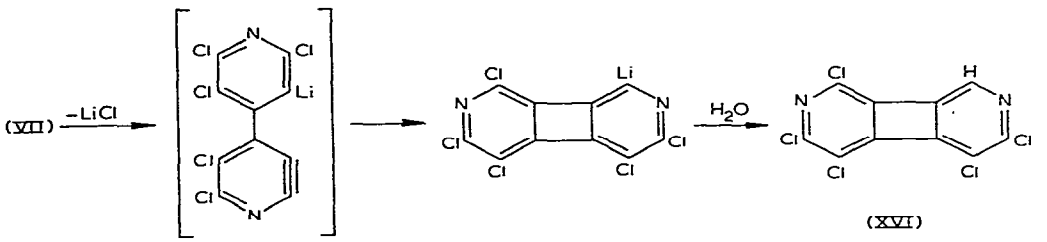
(XV)

We attribute the non-formation of metallocycles to the chlorine atoms at the 3- and 3'- positions, which hinder the pyridine rings from approaching coplanarity. The additional strain thus introduced cannot be overcome by an increase in the temperature at which the reaction is carried out since this leads to decomposition of the intermediate [e.g. (XII)] by elimination of lithium chloride from the pyridine ring (cf. ref. 2).

In contrast to the reactions with dichlorodiphenylsilane and di-π-cyclopentadienyltitanium dichloride, the reaction of the dilithio intermediate (VII) with sulphur dichloride gave the expected thienodipyridine (XIV), whose structure was confirmed by its elemental analysis and mass spectrum and by the absence of ^{1}H NMR signals.

In this case, the formation of the new ring involves less bond angle strain. Furthermore, the new ring is aromatic, and this fact too, may lead to a lower energy barrier to its formation. Nevertheless, inspection of models indicates that there is severe interference between the 5- and 6-chlorine atoms of compound (XIV). The molecular structure of 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline (XV) shows considerable deviations from coplanarity and distortions of the normal bond angles [10] and X-ray crystallographic studies now in progress reveal similar overcrowding in compound (XIV) [11]. Very few examples of thienodipyridines have been recorded [12] and compound (XIV) represents the first derivative of the thieno[2,3-*c*:5,4-*c'*]dipyridine ring system.

Thermolysis of the dilithio compound (VII) was briefly studied. By analogy with octafluoro-2,2'-dilithiobiphenyl [13], this might have given the cyclobutadipyridine (XVI) by the following route.



However, thermolysis of the dilithio compound (VII) in various solvents at various temperatures failed to yield the cyclobutadipyridine (XVI) [or any identifiable products other than the hexachlorobipyridyl (I)]. Once again, the lack of success of this synthesis may be ascribed to steric hindrance of coplanarity by the 3- and 3'-chlorine atoms.

Experimental

All experiments involving organolithium compounds were carried out under dry, oxygen-free nitrogen using scrupulously dried solvents and apparatus. n-Butyllithium was used as a commercial 2.3 *M* solution in hexane. ^{1}H NMR spectra were recorded at 60 MHz with tetramethylsilane as internal reference. Calculated *m/e* values for molecular ions are based on ^{35}Cl.

Metallation of 2,3,6-trichloropyridine

A solution of n-butyllithium (0.015 mole) was added to a solution of 2,3,6-trichloropyridine (3.1 g, 0.015 mole) in diethyl ether (150 ml) at — 70°. The solution was stirred at —60° during 45 min and —20° during 2 h, then recooled to —50°.

(*a*) Dimethyl sulphate (7.0 ml) was added, and the mixture was stirred at room temperature during 3 h. The excess of dimethyl sulphate was destroyed by aqueous ammonia. Conventional work-up, followed by chromatography on silica, gave 2,3,6-trichloro-4-methylpyridine (IV) (1.4 g), $\tau(CCl_4)$ 2.80 (s, 1 H) and 7.54 (s, 3 H) contaminated by 2,3,6-trichloropyridine, τ 2.23 (d, 1 H), 2.74 (d, 1 H).

(*b*) Deuterium oxide (1 ml) was added. Conventional work-up, followed by chromatography on silica, gave 2,3,6-trichloro-4-deuteriopyridine (VI) (1.2 g), $\tau(CCl_4)$ 2.71 (s), contaminated by 2,3,6-trichloropyridine, τ 2.23 (d, 1 H), 2.74 (d, 1 H).

5H,5'H-hexachloro-4,4'-bipyridine (I)

Titanium(IV) chloride (15 ml) was added to a solution of 2,3,6-trichloro-4-lithiopyridine, prepared as described above, at — 70°. The mixture was stirred at room temperature during 1 h. The ether solvent was distilled as methylcyclohexane (150 ml) was added, and the mixture was heated under reflux during 1 h. Hydrolysis with water, followed by conventional work-up and chromato-

graphy on silica, gave 2,3,6-trichloropyridine (eluted by benzene/light petrol 1/4) (1.3 g) and 5H,5'H-hexachloro-4,4'-bipyridine (nc) (eluted by benzene) (0.9 g), m.p. 176°, $\tau(CDCl_3)$, 2.69 (s), identical (IR, mixed m.p.) with the compound described below.

Hexachloro-5,5'-dilithio-4,4'-bipyridine

n-Butyllithium solution (4.1 ml) was added to a solution of octachloro-4,4'-bipyridine (2.0 g) in diethyl ether (100 ml) at — 75°. The mixture was stirred at — 75° during 1 h and at room temperature during 2 h.

Reactions of hexachloro-5,5'-dilithio-4,4'-bipyridine

(a) Hydrolysis. To a solution of the dilithio compound, prepared as described above, was added water (50 ml). Conventional work-up, followed by chromatography on silica (eluant light petroleum + benzene) gave 5H-heptachloro-4,4'-bipyridine (0.25 g, 14%), m.p. 171 - 172° (lit. [2] 171 - 172°) and 5H,5'H-hexachloro-4,4'-bipyridine (0.95 g, 55%), m.p. 175 - 176° (from light petroleum), $\tau(CDCl_3)$ 2.70. (Found, C, 33.0; H, 0.7; N, 7.65%; M^+ 360. $C_{10}H_2Cl_6N_2$ calcd.: C, 33.05; H, 0.55; N, 7.7%; M^+ 360.)

(b) With dichlorodiphenylsilane. To a solution of the dilithio compound in diethyl ether at — 70°, prepared as described above from octachloro-4,4'-bipyridine (4.32 g), was added dichlorodiphenylsilane (2.53 g). The mixture was stirred at room temperature during 1½ h. Ether was distilled as benzene was added, and the temperature was maintained at 55° during 1¼ h. Hydrolysis of the cooled solution with water, followed by conventional work-up and chromatography on silica, gave 5H,5'H-hexachloro-4,4'-bipyridine (1.6 g, eluted by 20% benzene in light petrol) and (3'H-hexachloro-4,4'-bipyridin-3-yl)diphenylsilanol (XI) (nc) (1.2 g, eluted by benzene), m.p. 208-9°. (Found: C, 46.4; H, 2.2; N, 4.8. $C_{22}H_{12}Cl_6N_2OSi$ calcd.: C, 47.1; H, 2.1; N, 5.0%.)

(c) With di-π-cyclopentadienyltitanium dichloride. To a solution of the dilithio compound in diethyl ether at — 40°, prepared as described above from octachloro-4,4'-bipyridine (4.32 g) was added a slurry of titanocene dichloride (2.60 g) in diethyl ether. The mixture was stirred at room temperature during 1 h and at 55° (ether + benzene solvent) during 1½ h. Hydrolysis with cold water, conventional work-up, and chromatography on silica, gave 5H,5'H-hexachloro-4,4'-bipyridine (1.1 g, eluted by 20% benzene in light petrol) and chlorodi-π-cyclopentadienyl-σ-(3'H-hexachloro-4,4'bipyridin-3-yl)titanium(IV) (XIII) (nc) (1.50 g, eluted by chloroform), m.p. 215° (decomp.), $\tau(CDCl_3)$ 2.97 (s, 1 H), 3.70 (s, 5 H) and 3.78 (s, 5 H). (Found: C, 41.8; H, 2.8; N, 4.95; $C_{20}H_{11}Cl_7N_2Ti$ calcd.: C, 41.75; H, 1.9; N, 4.9%.)

(d) With sulphur dichloride. To a solution of the dilithio compound in diethyl ether at — 40°, prepared as described above from octachloro-4,4'-bipyridine (4.32 g), was added sulphur dichloride (1.20 g). The mixture was stirred at room temperature during 1 h and at 60° (benzene + ether solvent) during 1½ h. Hydrolysis with cold water, conventional work-up and chromatography on silica gave hexachlorothieno[2,3-c:5,4-c']dipyridine (XIV) (nc) (2.1 g, 54%), m.p. 230-1°. (Found: C, 31.0; N, 7.2; M^+ 389.7911. $C_{10}Cl_6N_2S$ calcd.: C, 30.6; N, 7.1%; M^+ 389.7913.)

Acknowledgements

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