The Preparation and Electrical Conductivity of TCNQ Complexes of Some Simple Stilbazoles, and of a Poly(vinylstyrylpyridine)

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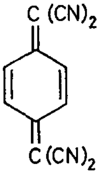
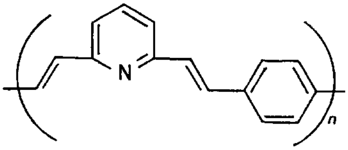
Experiments involving the condensation of 2-methyl- and 2,6-dimethylpyridine with benzaldehyde, and of 2-methylpyridine with terephthaldehyde to yield stilbazoles are described. They were used as models for the polycondensation of 2,6-dimethylpyridine with terephthaldehyde which in the presence of acetic anhydride and acetic acid gives the corresponding poly(vinylstyrylpyridine) with $\overline{M}_n \sim 10\,000$. A similar polymer is formed by self-condensation of 2-(4-formylstyryl)-6-methylpyridine, the synthesis of which is described. The electrical conductivities of TCNQ complexes of the stilbazoles and the polymer are given.

ELECTRICALLY conducting TCNQ [7,7,8,8-tetracyanoquinodimethane (I)] complexes of polycations have been described previously[1], but in all these systems the cations have been present as pendant groups on a non-conjugated polymer chain, and the backbone has therefore not contributed to the conductivity. The aim of the work now described was to study the preparation of a polymer having potential cation sites forming an integral part of a fully conjugated backbone. The necessity to achieve solubility of both the polymer and neutral TCNQ or Li^+ $TCNQ^{\bar{\cdot}}$ in a common inert solvent in order to prepare the complexes limits the type of polymer which can be used, and attention was therefore focused on the relatively little-studied poly(vinylstyrylpyridine) (II).



(I)



(II)

EXPERIMENTAL

2-Picoline and 2-formyl-6-methylpyridine were fractionally distilled. 2,6-Lutidine was purified via its urea complex[2]. Terephthaldehyde was twice sublimed under reduced pressure. Formic acid was dried by refluxing with phthalic anhydride, and was then distilled. Other reagents were purified by distillation and/or crystallization. Solvents were fractionally distilled, ethers from sodium.

Electrical conductivities were determined using the four-probe method[1] on compressed discs *in vacuo* at room temperature. Compounds were prepared as follows:

Stilbazoles

Equivalent amounts of the alkylpyridine, aldehyde, acetic anhydride and acetic acid were heated (bath at 140°C) under reflux for 16 h, the mixture was cooled, neutralized with aqueous potassium carbonate, and then extracted with chloroform. The solution was washed with water, dried, and the solvent was removed; the residue was treated as described below:

(*a*) From 2-picoline and benzaldehyde. Recrystallization from aqueous methanol gave stilbazole, (III), as white needles (30 per cent), m.pt 89°–90°C (lit.[3] 89°–90°) which had $\lambda_{max.}$ (in EtOH) 307 mμ (ϵ 27 000).

(*b*) From 2-picoline and terephthaldehyde. Two products were formed, and were separated by sublimation: (*i*) at 150°C (bath)/10^{-2} mm Hg, and (*ii*) at 190°C (bath)/10^{-2} mm Hg. Sublimate (*i*) was the mono-condensate 2-(4-formylstyryl)pyridine (5 per cent), m.pt 87°–88°C, which had $\nu_{max.}$ 1 695 cm^{-1}. Sublimate (*ii*) (yellow) was 1,4-bis-(2-pyridylvinyl)benzene (IV) (70 per cent), m.pt 239°–240°C (lit.[4] 239°–240°) which had $\lambda_{max.}$ (in EtOH) 350 mμ (ϵ 59 000) and τ (in CF_3CO_2H) 2·55 (doublet, $J = 18$ c./sec).

(*c*) From 2,6-lutidine and benzaldehyde. Recrystallization from benzene gave 2,6-distyrylpyridine (V) as white needles (65 per cent), m.pt 168°–169°C (lit.[5] 164°) which had $\lambda_{max.}$ (in EtOH) 290, 333 mμ (ϵ 37 000, 23 000).

Polymerizations

(*a*) Terephthaldehyde (1·408 g), 2,6-lutidine (1·127 g) and an equimolar mixture of acetic anhydride and acetic acid (3·415 g) were placed in a Pyrex ampoule, which was then cooled in liquid nitrogen, pumped at 10^{-5} mm Hg for 15 min, and sealed. It was then heated at 135°C (bath) for 140 h, cooled, and opened, and the contents extracted with formic acid (15 cm^3). Insoluble material was removed by filtration, and the filtrate was diluted with ethanol (30 cm^3) and then treated with freshly prepared 5N aqueous potassium hydroxide until it had pH 9. The polymer which separated was collected by centrifugation, washed with ethanol and ether, and then pumped at 20°C/10^{-2} mm Hg over P_2O_5 to give a yellow powder (1·95 g, 90 per cent) which had $\lambda_{max.}$ (in HCO_2H) 424 mμ (ϵ 15 000) and [η] (in HCO_2H) 0·079. It showed weak carbonyl absorption, $\nu_{max.}$ 1 685 cm^{-1}, and had τ (in DCO_2D) 7·18 (very weak, terminal CH_3) and 1·78 (strong singlet, protons on benzene rings) with intensities indicating $\bar{M}_n \sim 10\,000$.

(*b*) Analogous treatment of 2-(4-formylstyryl)-6-methylpyridine (VII) gave polymer which was essentially identical with that obtained from 2,6-lutidine and terephthaldehyde except that $\bar{M}_n \sim 2\,000$ was the maximum obtained.

TCNQ complexes

Filtered, boiling, solutions of stoichiometric amounts of the simple base, TCNQ and durohydroquinone in acetonitrile were mixed and boiled for 0·5 h. The products were filtered off, recrystallized from acetonitrile, and dried at 20°C/10^{-2} mm Hg over P_2O_5. They had the following properties:

(*a*) 2-Styrylpyridinium$^+$ TCNQ$^{\overline{\cdot}}$ TCNQ^0. Black needles (65 per cent), decomp. 195°–215°C (Found: C, 74·9; H, 3·5; N, 21·0. $C_{37}H_{19}N_9$ requires C, 75·3; H, 3·2; N, 21·3 per cent), with $\lambda_{\text{max.}}$ (in MeCN) 392 mμ (ϵ 57 000).

(*b*) (2-Styrylpyridinium$^+$ TCNQ$^{\overline{\cdot}}$)$_2$ TCNQ^0. Light blue amorphous solid (57 per cent) (Found: C, 75·9; H, 3·8; N, 20·1. $C_{31}H_{17}N_7$ requires C, 76·2; H, 3·6; N, 20·4 per cent) with $\lambda_{\text{max.}}$ (in MeCN) 392 mμ (ϵ 37 000).

(*c*) 2,6-Distyrylpyridinium$^+$ TCNQ$^{\overline{\cdot}}$. Greenish-blue microcrystals (72 per cent), decomp. 190°–200°C (Found: C, 81·5; H, 4·6; N, 14·2. $C_{33}H_{21}N_5$ requires C, 81·4; H, 4·3; N, 14·4 per cent), with $\lambda_{\text{max.}}$ (in MeCN) 290, 337, 408, 418, mμ (ϵ 35 000, 21 500, 21 000, 22 000).

(*d*) 1,4-Bis-(2-pyridylvinyl)benzene^{2+} (TCNQ$^{\overline{\cdot}}$)$_2$. Purple microcrystals (65 per cent) decomp. 195°–210°C (Found: C, 76·0; H, 4·1; N, 20·0. $C_{44}H_{24}N_{10}$ requires C, 76·2; H, 3·8; N, 20·2 per cent), with $\lambda_{\text{max.}}$ (in MeCN) 352, 370, 406, 418 mμ (ϵ 67 000, 63 000, 43 000, 46 500).

(*e*) Poly(vinylstyrylpyridine$^+$ TCNQ$^{\overline{\cdot}}$). This was prepared by a modified method: poly(vinylstyrylpyridine) (0·202 g) was dissolved in formic acid (20 cm^3) and the solution was diluted with ethanol (60 cm^3). Neutral TCNQ (0·606 g) and durohydroquinone (0·492 g) were dissolved in ethanol (70 cm^3). Both solutions were brought to the boil, and then mixed and boiled for 15 min. On cooling, the polymer separated as a greenish-blue solid (0·54 g, 75 per cent) (Found: C, 79·8; H, 3·8; N, 16·0 per cent. A product with 90 per cent incorporation of TCNQ would require: C, 80·3; H, 3·6; N, 16·5 per cent) with $\lambda_{\text{max.}}$ (in HCO_2H) 392 mμ (ϵ 47 000).

Wittig reactions and synthesis of 2-(4-formylstyryl)-6-methylpyridine (VII)

(*a*) 1,4-Xylylene dichloride (2·27 g) and triphenylphosphine (6·86 g) were stirred together in refluxing *N*,*N*-dimethylformamide (15 cm^3) for 15 min, and the white precipitate was collected and washed with ethanol to give the bis-phosphonium salt (8·20 g, 90 per cent). A portion (1·41 g) of this in ethanol (5 cm^3) was treated with ethanolic lithium ethoxide (35 cm^3, 0·137 M) to give the bis-Wittig reagent (VIII), and 2-formylpyridine (0·48 g) was then added, the mixture being stirred at room temperature for 2 h. The ethanol was removed by distillation, and the residue was partitioned between chloroform and water. The chloroform phase was separated, evaporated, and the residue was crystallized from methanol to give *trans, trans*-1,4-bis-(2-pyridylvinyl)benzene (0·26 g, 40 per cent) m.pt 237°–238°C, identical (i.r. spectrum and mixed m.pt) with material prepared as described above from 2-picoline and terephthaldehyde.

(*b*) (*i*) 4-Cyanobenzyl bromide (0·41 g) and triphenylphosphine (0·56 g) were refluxed together in tetrahydrofuran (10 cm^3) for 3 h, and the white precipitate was collected and washed with ethanol to give the triphenylphosphonium salt (0·83 g, 58 per cent). This salt (0·90 g) in ethanol (5 cm^3) was treated with ethanolic lithium ethoxide (17·5 cm^3, 0·137 M) giving a deep orange solution to which 2-formyl-6-methylpyridine (0·29 g) in ethanol (5 cm^3) was added dropwise with stirring: the colour became lime-green. Stirring was continued at room temperature for 16 h, and the ethanol was then removed and the residue partitioned between carbon tetrachloride and water. The organic phase was separated, and chromatographed on silica gel to give a pale yellow solid from which, by crystallization from light petroleum (b.pt 60°–80°C), 2-(4-cyanostyryl)-6-methylpyridine (IX) (0·14 g, 27 per cent) was obtained as colourless crystals, m.pt 87°–88°C (Found: C, 81·6; H, 5·6; N, 12·6. $C_{15}H_{12}N_2$ requires C, 81·8; H, 5·5; N, 12·7 per cent). It had $\nu_{max.}$ 2 230 cm^{-1} (—C≡N) and $\lambda_{max.}$ (in EtOH) 324 mμ (ε 34 500).

(*ii*) A mixture of 4-cyanobenzyl bromide (3·57 g) and triethyl phosphite (3·15 g) was stirred at 140° for 2 h and then distilled to give diethyl 4-cyanobenzylphosphonate (4·13 g, 90 per cent) as a colourless liquid, b.pt 190°–192°C/0·1 mm Hg. It had $\nu_{max.}$ 1 250 cm^{-1} (strong, P═O) and 1 170 cm^{-1} (weak, P—O), and τ (pure liquid) 6·78 (doublet, $J = 23$ c./sec, CH_2—P). A solution of this ester (1·1 g) in tetrahydrofuran (5 cm^3) was treated with a suspension of sodium hydride (0·21 g) in tetrahydrofuran (5 cm^3), and the mixture was stirred at room temperature for 1 h, when it became deep orange-brown. A solution of 2-formyl-6-methylpyridine (0·52 g) in tetrahydrofuran (5 cm^3) was then added, and the mixture was slowly heated to 60°, with stirring; it was then kept for 0·5 h at 60°, cooled, and stirred overnight at room temperature. Work-up as described in the preceding paragraph gave 2-(4-cyanostyryl)-6-methylpyridine (IX) (0·65 g, 67 per cent), m.pt 88°–89°C.

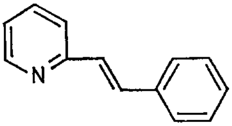
(*c*) Ethereal lithium aluminium hydride (21 cm^3, 1·2 M) was added to a solution of the foregoing nitrile (5·4 g) in lithium-aluminium hydride-dried ether (10 cm^3), and the mixture was stirred under nitrogen for two days. The solution was hydrolysed with 5N sulphuric acid, neutralized with potassium carbonate, freeze-dried, and then extracted with chloroform. Removal of the solvent, chromatography of the residue on silica gel, and crystallization from light petroleum (b.pt 30°–40°C) gave 2-(4-formylstyryl)-6-methylpyridine (VII) (1·62 g, 30 per cent) as very pale yellow needles, m.pt 87·5°–88·5°C (Found: C, 80·6; H, 5·9; N, 6·3. $C_{15}H_{13}NO$ requires C, 80·7; H, 5·8; N, 6·3 per cent). It had $\nu_{max.}$ 1 700 cm^{-1}, τ (in $CDCl_3$) 7·44 (CH_3) and 0·06 (CHO), and $\lambda_{max.}$ (in EtOH) 332 mμ (ε 30 000).

RESULTS AND DISCUSSION

Model compounds

A polymer of probable structure (II) was originally prepared[6] by condensation of 2,6-lutidine (2,6-dimethylpyridine) with terephthaldehyde in the presence of zinc chloride. However, earlier work on model compounds derived from 2- and 4-picoline (2- and 4-methylpyridine, respectively) and aromatic aldehydes suggested that byproducts are formed with zinc chloride, and indicated that condensations could be effected more cleanly with a mixture of acetic anhydride and acetic acid as catalyst[7]. Optimization of the conditions for 2-picoline and benzaldehyde to give stilbazole (III) showed that equivalent amounts of the picoline, anhydride and acid, and a slight excess of the aldehyde were required[3].

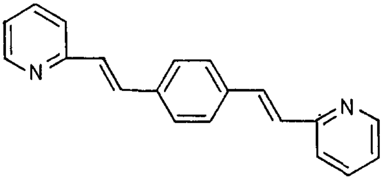
An alternative route to stilbazole involves the piperidine-catalysed condensation of 2-picolinium methiodide with benzaldehyde followed by liberation of the free base from its methiodide either thermally[8] or by treatment[9] with thiophenoxide ion. This method gives a high yield of stilbazole methiodide, but the subsequent pyrolysis or thiophenoxide reactions are



(III)

not satisfactory. Further, the methiodide has a low solubility, which could be a serious drawback for a polymeric system.

The efficacy of the acetic anhydride-acetic acid catalysed condensation was established in the present work for stilbazole (III), and the earlier assignment[10] of the *trans* stereochemistry was confirmed by proton magnetic resonance (p.m.r.) spectroscopy ($J_{trans} = 18$ c./sec; a value of about 12 c./sec would have been expected for *cis*). The method was satisfactorily used for the preparation of 1,4-bis-(2-pyridylvinyl)benzene (IV) from 2-picoline and terephthaldehyde, and of 2,6-distyrylpyridine (V) from 2,6-lutidine and benzaldehyde.



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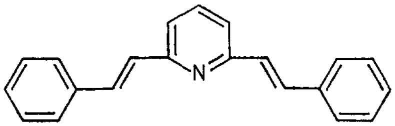
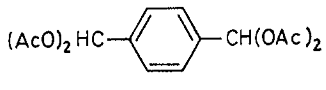


(V)

Polymerization reactions

Extension of the acetic anhydride-acetic acid condensation to a mixture of 2,6-lutidine and terephthaldehyde in equimolar amounts resulted in precipitation of a yellow polymer which was insoluble in benzene, ethanol and dimethylsulphoxide, but soluble in concentrated sulphuric acid, trifluoroacetic acid and *o*-chlorophenol. It was purified by precipitation from the latter solvent with ether, and its infra-red spectrum showed absorption assignable to carbonyl groups; its p.m.r. spectrum in trifluoroacetic acid indicated $\bar{M}_n \sim 700$, and showed the presence of an excess of formyl end-groups. The low molecular weight may have been due to precipitation of the polymer, and hence condensation in the presence of a larger quantity of acetic anhydride-acetic acid mixture was attempted: the only product isolated was the tetra-acetate (VI). An alternative reason for the low molecular weight may have been poor monomer balancing, either initially or due to loss during polymerization, which was carried out under nitrogen at normal pressure. Two methods of overcoming this were attempted: first, polymerization in a sealed, evacuated tube, and, secondly, self-condensation of 2-(4-formylstyryl)-6-methylpyridine (VII), the synthesis of which is described below.



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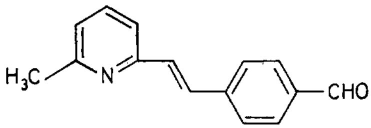


(VII)

Sealed-tube polymerization of a mixture containing equivalent amounts of 2,6-lutidine, terephthaldehyde, acetic anhydride and acetic acid gave a yellow polymer similar in appearance to that described above, but now only sparingly soluble in trifluoroacetic acid and *o*-chlorophenol; it was appreciably soluble in concentrated sulphuric acid and in formic acid, giving viscous solutions. The p.m.r. spectrum in dideuterioformic acid was consistent with structure (II), and showed poor resolution of the resonances due to the olefinic and heteroaromatic protons, but contained a sharp singlet at τ 1·78 due to the 1,4-disubstituted benzene nucleus; weak singlets at τ 0·03 and 7·12 were assigned to formyl and methyl end groups respectively. These had relative intensities of 1 : 3, indicating that the polymer contained equal numbers of the two types of end group, and comparison of these intensities with that of the singlet at τ 1·78 indicated $\bar{M}_n \sim 2\,000$. Repeated polymerizations using longer reaction times gave products with $\bar{M}_n$ up to $\sim 10\,000$ ($\overline{DP} \sim 45$), above which the p.m.r. spectroscopic method was no longer sufficiently accurate to give meaningful values. In contrast to the experiments performed under nitrogen, sealed tube condensations employing up to eight equivalents of catalyst mixture all yielded polymer.

The comparatively high solubility of the polymer in formic acid suggested that still higher molecular weights might be achieved using an acetic anhydride-formic acid catalyst, but this was unsuccessful due to decomposition[11] of the formic acid by the lutidine.

Sealed-tube polymerization of 2-(4-formylstyryl)-6-methylpyridine (VII) with the acetic anhydride-acetic acid mixture gave a polymer which was spectroscopically essentially identical with that obtained from 2,6-lutidine and terephthaldehyde except that the maximum $\bar{M}_n$ achieved was only $\sim 2\,000$.

TCNQ complexes

A particularly useful method[12] for preparing TCNQ complexes[1] of heteroaromatic compounds involves a proton-electron source such as H_2TCNQ or duroquinol, e.g.

$$\begin{tikzcd}
R_3N + H_2TCNQ \arrow[rr] & & {[R_3N^+H,\ HTCNQ^-]} \arrow[d, "TCNQ"] \\
& HTCNQ\cdot \arrow[r, phantom, "+"] \arrow[r, bend right=60, swap, "R_3N"] & {[R_3N^+H,\ TCNQ^{\overline{\cdot}}]}
\end{tikzcd}$$

Treatment of 1,4-bis-(2-pyridylvinyl)benzene (IV) with two equivalents each of TCNQ and duroquinol in acetonitrile gave the expected bis-simple salt, but this, and not the complex salt, was also formed when four equivalents of TCNQ were used. Change of solvent, use of H_2TCNQ instead of duroquinol, or treatment of the bis-simple salt with an excess of TCNQ all failed to yield a complex salt. In contrast, stilbazole (III) afforded only its complex salt except in one, unrepeatable, experiment from which a product having a stilbazole:TCNQ ratio of 2:3 was obtained.

The main problem in preparing a TCNQ complex of the polymer was to find a suitable solvent; TCNQ salts are decomposed by sulphuric acid, formic acid, and *o*-chlorophenol. However, surprisingly, a formic acid-ethanol mixture could be used. Addition of formic acid to a solution of $Li^+\ TCNQ^{\overline{\cdot}}$ in ethanol caused a progressive change of colour from green to yellow and at the yellow stage the ultraviolet-visible absorption spectrum of the solution indicated that it contained neutral TCNQ; on complete removal of the solvent, a green residue remained which, in acetonitrile, had an ultraviolet-visible spectrum identical with that of $Li^+\ TCNQ^{\overline{\cdot}}$. An equilibrium system which may be of the form:

$$2\,HCO_2H + 2\,Li^+\,TCNQ^{\overline{\cdot}} \rightleftharpoons 2\,HCO_2Li + 2\,HTCNQ\cdot \rightleftharpoons H_2TCNQ + TCNQ$$

is therefore probably set up in formic acid-ethanol, and the amount of $TCNQ^{\overline{\cdot}}$ existing at a given solvent composition can be determined from the absorption spectrum, thus potentially allowing the solution to be used for $TCNQ^{\overline{\cdot}}$ salt formation. This potentiality was realized on the model compound 1,4-bis-(2-pyridylvinyl)benzene (IV) which yielded a simple salt identical with that prepared by the conventional method. The polymer similarly yielded a simple salt containing about 90 per cent of the theoretical amount of $TCNQ^{\overline{\cdot}}$; a complex salt was not obtained.

Electrical conductivities

Conductivities are listed in *Table 1*. The values obtained are in general agreement with those to be expected[1] for TCNQ salts of heteroaromatic systems. The complex salts are better conductors than the simple ones.

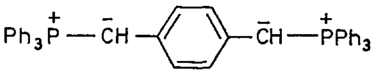
Table 1. Electrical conductivities of TCNQ salts

Compound	σ (*ohm*$^{-1}$ *cm*$^{-1}$)
2-Styrylpyridinium+ $\mathrm{TCNQ}^{\overline{\cdot}}\mathrm{TCNQ}^0$	1·55
(2-Styrylpyridinium+ $\mathrm{TCNQ}^{\overline{\cdot}})_2\mathrm{TCNQ}^0$	$1{\cdot}14\times10^{-1}$
2,6-Distyrylpyridinium+ $\mathrm{TCNQ}^{\overline{\cdot}}$	$4{\cdot}43\times10^{-6}$
1,4-Bis-(2-pyridylvinyl)benzene^{2+} $(\mathrm{TCNQ}^{\overline{\cdot}})_2$	$7{\cdot}35\times10^{-7}$
Poly(vinylstyrylpyridine+ $\mathrm{TCNQ}^{\overline{\cdot}}$)	$2{\cdot}86\times10^{-7}$
Poly(vinylstyrylpyridine)	$< 10^{-8}$

Poly(vinylstyrylpyridine) itself has a very low conductivity, of the order expected for a polymer with incomplete conjugation ('rubiconjugation', ref. 13) in the backbone; the rather drastic conditions required for the preparation of the polymer, and the less than quantitative yields of the model compounds obtained under similar conditions suggest that the polymer is unlikely to have the ideal structure indicated by formula (II). Addition of $\mathrm{TCNQ}^{\overline{\cdot}}$ to the derived polycation increases the conductivity to a value typical of those of simple TCNQ salts of related monomeric materials. The absence of further enhanced conductivity can be attributed to probable breaks in the conjugation of the backbone, and to the failure to achieve greater than 90 per cent of the theoretical incorporation of $\mathrm{TCNQ}^{\overline{\cdot}}$ required to give an exactly 1 : 1 simple salt.

Synthesis of 2-(4-formylstyryl)-6-methylpyridine (VII)

A requirement of the synthesis of this compound is that it should yield a product with a *trans* disubstituted olefinic double bond so that self-condensation will yield a polymer of the same geometry as that obtained from 2,6-lutidine and terephthaldehyde. The Wittig reaction[14] often gives mixtures of *cis* and *trans* isomers, but it has been used[4] for the preparation of stilbazoles which are identical with the *trans*-stilbazoles obtained from methylpyridines and benzaldehyde using either acetic anhydride-acetic acid or zinc chloride catalysts. This work was checked for the present series of compounds by allowing the Wittig reagent (VIII), from 1,4-xylylene-bis-(triphenylphosphonium chloride) and sodium ethoxide, to react with two equivalents of 2-formylpyridine: 1,4-bis-(2-pyridylvinyl)benzene (IV), identical with material prepared as described above, was obtained in 40 per cent yield.



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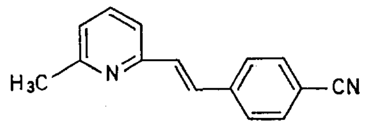

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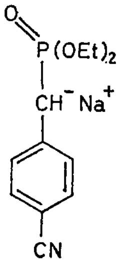

(X)

For the preparation of the aldehyde (VII), the Wittig reagent obtained analogously from 4-cyanobenzyl bromide was treated with 2-formyl-6-methylpyridine to give a 27 per cent yield of 2-(4-cyanostyryl)-6-methylpyridine (IX), the *trans* geometry being confirmed by p.m.r. spectroscopy. An improved synthesis, giving a 67 per cent yield of identical material, involved treatment of 2-formyl-6-methylpyridine with the monoanion (X) of diethyl 4-cyanobenzylphosphonate, obtained by reaction of the phosphonate, from 4-cyanobenzyl bromide and triethyl phosphite, with one equivalent of sodium hydride.

Attempts to convert the cyano group into a formyl group by Stephen's method[15], or by treatment with lithium triethoxyaluminohydride[16], were unsuccessful, but the required aldehyde (VII) was obtained in 40 per cent yield by partial reduction[17] of the nitrile with lithium aluminium hydride.

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