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THE TITANIUM TETRACHLORIDE INDUCED SYNTHESIS OF N-PHOSPHINOYLIMINES AND N-SULPHONYLIMINES DIRECTLY FROM AROMATIC ALDEHYDES[1]

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Abstract: The reaction of phosphinic amides or sulphonamides with an aromatic aldehyde in the presence of titanium tetrachloride and triethylamine provides a simple, one-step preparation of N-phosphinoylimines (**5a-e**) and N-sulphonylimines (**7a-g**). The extension of this reaction to ketones failed to give the desired imines, the aldol condensation products were obtained instead. The reaction of (+)-camphor with phosphinic amides or sulphonamides in refluxing toluene in the presence of titanium tetrachloride and triethylamine affords the (-)-camphorphosphinoyl- and (-)-camphorsulphonylimines in moderate yield.

The preparation of 2-diphenylphosphinoyloxaziridines (**3**, $R^3 = R^4 = Ph$) by the peroxyacid oxidation of N-phosphinoylimines has recently been reported.[2] The N-phosphinoylimines used in this study were prepared using the method reported by Krzyzanowska and Stec (Scheme 1).[3] Reaction of an oxime with a chlorophosphorus(III) compound at -40 to -45 °C gives an unstable *O*-phosphino-oxime (**1**), which rearranges *via* a radical pair mechanism[4,5] to give the N-phosphinoylimine (**2**). Whilst this reaction works reasonably well, several aspects of this reaction led us to seek an alternative route to N-phosphinoylimines (**2**). In our hands the yields were often variable and low, and in some cases the reaction failed to give any N-phosphinoylimine at all. We were also interested in preparing N-phosphinoyloxaziridines (**3**, $R^3 \neq R^4$), possessing a chiral (non-racemic) phosphorus atom. The reported methodology is unsuitable for this purpose because chlorophosphorus(III) compounds are configurationally unstable, as they can invert by chloride exchange. We now wish to report that the reaction of phosphinic amides, which are configurationally stable, with aromatic aldehydes in the presence of titanium tetrachloride and triethylamine at 0 °C gives N-phosphinoylimines (**5a-e**).

Results and Discussion

Weingarten *et al.*,[6] Moretti and Torre[7] and Boyd *et al.*[8] have shown titanium tetrachloride to be a highly efficient reagent to effect the condensation of sterically hindered and/or unreactive ketones and alkyl amines to give N-alkylimines. In view of these results, it was envisaged that a similar reaction might be possible between a phosphinic amide and carbonyl compounds.

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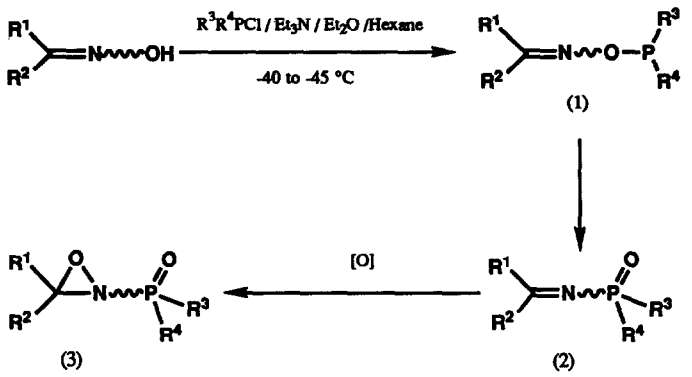


[O] = KF-MCPBA / CH_2Cl_2 / 0 °C
or = MCPBA / $CHCl_3$ / $NaHCO_3$ / 0 °C

Scheme 1

After some initial experimentation it was found that the addition of titanium tetrachloride to a mixture of an aromatic aldehyde, diphenylphosphinic amide (4) and triethylamine in dichloromethane gave the N-phosphinoylimines (**5a-e**) after *ca.* 30 min at 0 °C, in moderate to good yield (Table 1) after recrystallisation. Longer reaction times were required for benzaldehydes possessing electron donating substituents as would be expected from the reduced electrophilic character of the carbonyl group. All the compounds were characterised by ^1H and ^{31}P NMR spectroscopy and all new compounds gave satisfactory elemental analysis.

In the preparation of N-alkylimines, using titanium tetrachloride, a large excess of the amine is usually employed.[6-8] An excess of the phosphinic amide (4) was deemed to be undesirable in view of separation problems and efficiency when valuable optically active phosphinic amides are used. Thus conditions have been found where only equivalent amounts of phosphinic amide and aryl aldehyde and 0 6 equivalents of titanium tetrachloride are required by using 3.0 equivalents of triethylamine to neutralise the HCl produced.

The progress of the reaction can easily be monitored by removing a small sample of the reaction mixture and recording an infra-red spectrum of the sample after filtration and rotary evaporation. The aromatic aldehyde carbonyl peak at *ca*. 1700 cm^{-1} was replaced by the C=N stretch at a lower frequency in the region 1600-1630 cm^{-1}. The N-phosphinoylimines also show a strong absorption in the region 1200-1210 cm^{-1} attributed to the P=O stretching frequency (Table 1).[3]

Dichloromethane appears to be the best solvent for the reaction. Other solvents, toluene and petroleum, were investigated but the yields were lower and prolonged reaction times were required. This is probably due to the low solubility of diphenylphosphinic amide in toluene or petroleum. Although the yields of the recrystallised products were not as high as anticipated, ^1H NMR analysis of the indicated that the crude imines (**5a-e**) were normally sufficiently pure (>90%) to use for further transformations , for example, oxidation to the oxaziridine[2] or reduction and hydrolysis to the primary amine.[9] The impurities, if any, were unreacted aldehyde and phosphinic amide. Titanium tetrachloride is remarkably efficient in this condensation reaction as the nitrogen atom in phosphinic amides is not particularly nucleophilic due to p_π-d_π or n-σ^* bonding between nitrogen and phosphorus.[10-13]

Table 1

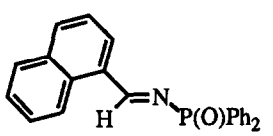
$$ArCHO + NH_2P(O)Ph_2 \xrightarrow[Et_3N/0\,^\circ C]{TiCl_4/CH_2Cl_2} ArCH{=}NP(O)Ph_2$$

(4) (5a-e)

Compound	Ar	Yield /% (%) [a]	∂_H [b]	$^3J_{PH}$/Hz	∂_P [c]	$\nu_{C=N}$/cm^{-1} [d]	$\nu_{P=O}$/cm^{-1} [d]
5a	Ph	58(54)	9.33	33.2	24.8	1627	1201
5b	1-Naphthyl	57(64)	9.93	33.1	25.0	1602	1208
5c	2-Naphthyl	52(67)	9.48	31.3	25.0	1620	1202
5d	4-ClC_6H_4	35(73)	9.20	31.8	25.0	1625	1202
5e	4-$MeOC_6H_4$	52(68)	9.23	33.1	24.8	1605	1208

a. Isolated yield of purified imine (crude yield given in parenthesis, estimated to be >90% pure by ^{1}H NMR.
b. Chemical shift of the imino proton, measured in $CDCl_3$ solution at 89.6 MHz (TMS reference).
c. Measured in $CDCl_3$ solution at 36.2 MHz (85% H_3PO_4 reference).
d. Recorded as Nujol mulls.

The most informative feature in the ^{1}H NMR spectra of compounds (**5a-e**) is the imino proton doublet at ∂ 9.2-9.5 split by a large three-bond coupling to phosphorus of *ca.* 32 Hz (Table 1).[2,3] Compound (**5b**) is anomalous in that the imino proton appears at ∂ 9.93 ($^3J_{PH}$ 33.1 Hz), some 0.45 ppm further downfield than the 2-naphthyl derivative (**5c**). The 1-naphthyl group may be orientated as depicted in (**6**) so that the imino proton lies in the deshielding region of ring B and thus is shifted downfield.

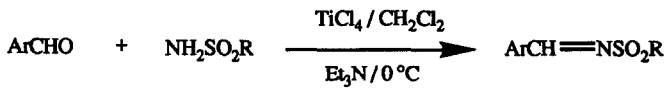
(6) 

The ^{1}H decoupled ^{31}P shifts for N-phosphinoylimines appear at *ca.* ∂ 25 relative to 85% phosphoric acid (Table 1). This is consistent with the literature values for saturated compounds of the type $Ph_2P(O)NR_2$, which lie in the range ∂ 17-29.[14]

The titanium tetrachloride reaction also works well (Table 2) for the preparation of N-sulphonylimines (**7a-g**) from aromatic aldehydes and sulphonamides. These compounds are the synthetic precursors of N-sulphonyl-oxaziridines, in which there is current interest. Davis and co-workers have recently reported an alternative preparation of N- sulphonylimines from aromatic aldehydes using molecular sieves and an ion exchange resin.[15] The N-sulphonylimines (**7a-g**) prepared by the titanium tetrachloride method have C=N stretching frequencies in the range 1595-1605 cm^{-1} (Table 2). These compounds have a characteristic imino resonance in their ^{1}H NMR spectra at *ca.* ∂ 9.1. The 1-naphthyl derivative (**7b**) is again anomalous.

As the synthesis of N-phosphinoyl- and N-sulphonylimines derived from aromatic aldehydes was achieved, an obvious extension to this work was to investigate the application of this methodology to the preparation of N-phosphinoyl- and N-sulphoylimines derived from ketones.

Table 2



(7 a-g)

Compound	Ar	R	Yield/% (%)[a]	∂_H[b]	$\nu_{C=N}$/cm^{-1} [c]
7a	Ph	4-Me-C_6H_4	58(81)	9.03	1595
7b	1-Naphthyl	4-Me-C_6H_4	68(86)	9.59	1598
7c	2-Naphthyl	4-Me-C_6H_4	70(89)	9.13	1600
7d	3-$NO_2C_6H_4$	4-Me-C_6H_4	53(77)	9.12	1605
7e	4-$MeOC_6H_4$	4-Me-C_6H_4	47(51)	8.94	1592
7f	Ph	Me	51(71)	9.04	1604
7g	2-Naphthyl	Me	50(81)	9.17	1600

a. Isolated yield of purified imine (crude yield given in parenthesis, estimated to be >90% pure by ^{1}H NMR).
b. Chemical shift of the imino proton measured in $CDCl_3$ solution at 60 MHz (TMS reference).
c. Recorded as Nujol mulls.

Acetophenone and diphenylphosphinic amide were reacted together under the standard conditions employed for the aldimine synthesis. An infra-red spectrum recorded of the reaction mixture after 30 min revealed that most of the ketone ($\nu_{C=O}$ 1680 cm^{-1}) had been consumed. There was however, no evident imine C=N stretch at *ca.* 1635 cm^{-1}.[3] Significantly, N-H stretches at 3350-3130 cm^{-1}, due to unreacted diphenylphosphinic amide, were still evident in the infra-red spectrum of the reaction mixture.

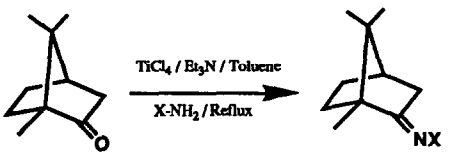
A ^{1}H NMR spectrum, of the crude reaction mixture, recorded at 270 MHz in deuteriochloroform, indicated that the desired reaction had not taken place. Three doublet signals appeared in the high field region of the spectrum at ∂ 2 32 (*J* 1.3 Hz), 2 60 (*J* 1.3 Hz) and 2.97 (*J* 2.0 Hz), in the ratio of 3:12:1 respectively. The doublet at ∂ 2.97 ($^4J_{PH}$ 2 0 Hz) is probably due to the desired imine, PhMeC=NP(O)Ph_2 (8).[3] A sample of the crude product was purified by column chromatography on silica gel. The major fraction, which was the first eluted from the column, was further purified by distillation affording two fractions; acetophenone (25%) and 1,3-diphenyl-2-buten-1-one (dypnone, 75%). Dypnone is an aldol condensation product of acetophenone. It has been demonstrated by Eisenbraun and co-workers[16] that titanium tetrachloride in the presence of triethylamine can be used to form enolates *in situ*, which can be used in subsequent aldol type condensation reactions. Brooke and Matthews noted the same type of process occurring in the preparation of imines from acetophenone and pentafluoroaniline and 1,3,4,5,6,7,8-heptafluoro-2-naphthylamine in the presence of zinc chloride.[17]

Titanium tetrachloride has been used as a condensation agent in the preparation of N-alkylimines derived from enolisable ketones. In most cases the desired imine was formed, though, the yields in these preparations were often low. The low yields may result from the formation of aldol condensation products. The fact that the imine is obtained in acceptable yield in these cases and only in *ca.* 5-10% yield (by ^{1}H NMR analysis of the crude product) in the

attempted preparation of (8) is probably a consequence of the greater nucleophilicity of the amine nitrogen atom compared with the phosphinic amide nitrogen atom.

One of the advantages of the titanium tetrachloride route is that it should allow easy access to chiral N-phosphinoyl- and N-sulphonylimines. However, when (+)-camphor was reacted with diphenylphosphinic amide or 4-methylbenzenesulphonamide under standard conditions, no imine could be detected by infra-red analysis. When the reaction was performed in refluxing toluene instead of dichloromethane, imines (9) and (10) were formed in both cases in moderate yield. Formation of these imines required heating to reflux with titanium tetrachloride in toluene for 24-48h. Infra-red spectral analysis of the reaction mixture indicated that these reactions did not proceed to completion, a carbonyl stretch at 1690 cm^{-1} was always present. Additional portions of titanium tetrachloride failed to drive the reaction significantly further towards completion.

The (-)-camphorsulphonylimine (9) and the (-)-camphorphosphinoylimine (10) were obtained in 33% yield after flash column chromatography. These N-phosphinoyl- and N-sulphonylimines (9) and (10) were the only examples prepared that could successfully be purified by column chromatography. Imines derived from aldehydes or ketones decompose on silica gel to the parent carbonyl compound and phosphinic amide or sulphonamide. Imines (9) and (10) were characterised by NMR (^1H, ^{13}C and ^{31}P) and infra-red spectroscopy and elemental or mass spectral analysis, all of which were in accord with the proposed structure.



(9): X = 4-$MeC_6H_4SO_2$-
(10): X = $Ph_2P(O)$-

Davis and co-workers[18] have recently independently reported the preparation of N-sulphonylimines derived from (+)-camphor using titanium tetrachloride methodology. These imines can be used to prepare α-substituted sulphonamides in good chemical yields but low optical yields. These workers have also oxidised related camphorsulphonylimines with *meta*-chloroperoxybenzoic acid (MCPBA) to give camphorsulphonyloxaziridines.[19]

Conclusions

The titanium tetrachloride induced preparation of N-phosphinoyl- and N-sulphonylimines clearly works well for aromatic aldehydes, and ketones which are not readily enolisable (eg (+)-camphor). In the case of acetophenone (an enolisable ketone) it appears that aldol condensation products predominate. The method outlined in this paper is probably the method of choice for the preparation of N-phosphinoylimines derived from aromatic aldehydes. In the case of N-sulphonylimines, the titanium tetrachloride method is an efficient alternative to the recently reported one-step procedure using molecular sieves and an ion exchange resin.[15] The two-step route[3,20] *via* the oxime, is superior for the preparation of N-phosphinoyl- and N-sulphonylimines from enolisable ketones.[21,22]

This methodology ought to permit the introduction of a resolved phosphorus atom into an N-phosphinoylimine and hence oxaziridine.[23] These compounds may exhibit interesting asymmetric oxygen transfer properties.[24]

Experimental

NMR spectra were recorded in deuteriochloroform (unless otherwise stated) either on a Jeol FX90Q or a Jeol GX270 spectrometer.

All reagents were used as purchased except for triethylamine, which was dried by heating at reflux over potassium hydroxide pellets for 1h, distilled and then stored over potassium hydroxide pellets. Dichloromethane was dried over molecular sieves (4Å), diethyl ether (ether) and toluene were first dried over magnesium sulphate and then stored over sodium wire. Manipulations involving potentially toxic phosphorus compounds were performed wearing protective gloves and in an efficient fume hood. All the imine syntheses were performed under dry nitrogen atmosphere but purification procedures were carried out in the air.

P,P-Diphenylphosphinic Amide (4).[26]

Recrystallised diphenylphosphinic acid, mp 198-200 °C[25] (28.9 g, 0.13 mol) in dry toluene (250 cm^3) was heated gently at reflux for 2h with freshly distilled thionyl chloride (31.4 g, 0.26 mol). The reaction mixture was allowed to cool and the solvents removed on a rotary evaporator. The resulting oily liquid was placed *in vacuo* (0.05 mmHg) for 30 min to yield crude diphenylphosphinic chloride (29.1 g); ν_{max}(liquid film) 1235 cm^{-1}.

The crude diphenylphosphinic chloride in dry dichloromethane (60 cm^3) was added dropwise with stirring to a saturated ethanolic ammonia solution (250 cm^3) and dichloromethane (100 cm^3) cooled in an ice/salt-bath. The reaction mixture was stirred overnight while attaining room temperature. The precipitated solid was filtered off and then the solvents were removed by rotary evaporation to afford an off-white solid. The solid was dissolved in chloroform (350 cm^3) and washed successively with 5% aqueous potassium carbonate (2x100 cm^3) and water (100 cm^3). The organic layer was separated, dried over magnesium sulphate, filtered and the solvent removed to give an off-white solid (34 9 g). The crude product was recrystallised from toluene to yield 23.1 g (80%) of the title compound, mp 164-166 °C (lit.,[26] 165-166 °C); ν_{max}(Nujol) 3340, 3285, 3235 and 3115 cm^{-1} (NH_2), 1175 cm^{-1} (P=O).

P,P-Diphenyl-N-arylmethylenephosphinic Amides (5a-e): General Procedure.

Titanium tetrachloride (0.7 cm^3, 6.3 mmol) in dry dichloromethane (10 cm^3) was added dropwise to a stirred ice-cooled solution of the aldehyde (11.5 mmol), diphenylphosphinic amide (2.50 g, 11.5 mmol) and anhydrous triethylamine (3.50 g, 34.7 mmol) in dry dichloromethane (50 cm^3). After the addition was complete, typically 5 min, the mixture was stirred for 25 min at 0 °C (except for compound e which was stirred at room temperature for 4h). The titanium dioxide was removed by suction filtration through Celite and washed with dichloromethane (20 cm^3). Rotary evaporation of the filtrate gave a solid mixture of the imine and triethylamine hydrochloride. The solid mixture was broken up and either heated at reflux for 5 min in dry ether (75 cm^3-compounds a,d and e) or stirred for 5-10 min at room temperature in dry toluene (75 cm^3 compounds b and c). The residual triethylamine hydrochloride was removed by suction filtration and the residue extracted a second time. Concentration of the combined ether or toluene extracts gave the crude N-phosphinoylimines.

P,P-Diphenyl-N-(phenylmethylene)phosphinic Amide (5a). The crude product (2.23 g, 64%)was precipitated from dichloromethane with hexane to afford 2.00 g (58%) of a colourless powder, mp 139-141 °C (lit.,[3] 140-141 °C).

P,P-Diphenyl-N-(1-naphthylmethylene)phosphinic Amide (5b). The crude product (2.61 g, 64%) was precipitated from dichloromethane with hexane to afford 2.33 g (57%) of a colourless powder. A sample was further purified by recrystallisation from benzene/hexane, mp 120-122 °C (Found: C, 77 4; H, 5.0; N, 4,2 $C_{23}H_{18}NOP$ requires C, 77.4; H, 5.11; N, 3.94%).

P,P-Diphenyl-N-(2-naphthylmethylene)phosphinic Amide (5c). The crude imine (2.70 g, 67%) was recrystallised from benzene to afford 2.09 g (52%) of a colourless powder, mp 172-174 °C (Found: C, 77.7; H, 5 2; N; 3 8. $C_{23}H_{18}NOP$ requires C, 77.74; H, 5.11; N, 3.94%).

P,P-Diphenyl-N-(4-chlorophenylmethylene)phosphinic Amide (5d). The crude product (2.36 g) was precipitated three times from dichloromethane with hexane to afford 1 14 g (35%) of a colourless powder, mp 127-130 °C (Found. C, 67.0, H, 4.5; N, 4.3. $C_{19}H_{15}ClNOP$ requires C, 67.17; H, 4.45; N, 4.12%).

P,P-Diphenyl-N-(4-methoxyphenylmethylene)phosphinic Amide (5e). The crude imine (2.50 g, 68%) was recrystallised from chloroform/hexane to afford 1.90 g (52 %) of a colourless, crystalline solid, mp 147-149 °C (Found: C, 71.9; H, 5.6; N, 4.5. $C_{20}H_{18}NO_2P$ requires C, 71.63; H, 5.41; N, 4.18%).

N-Arylmethylenesulphonamides (7a-g)

Titanium tetrachloride (1.05 cm^3, 9.5 mmol) in dry dichloromethane (10 cm^3) was added dropwise to a stirred ice-cooled solution of the aldehyde (19 mmol), sulphonamide (19 mmol) and anhydrous triethylamine (5.76 g, 57 mmol) in dry dichloromethane (40 cm^3). After the addition was complete, typically 5 min, the mixture was stirred at 0 °C for 25 min (except for compound e which was stirred at room temperature for 4h). The titanium dioxide was removed by suction filtration through Celite and washed with dichloromethane (20 cm^3). Rotary evaporation of the filtrate gave a solid mixture of the imine and triethylamine hydrochloride which was broken up and either heated at reflux in dry ether (75 cm^3 - compounds a,e and f) or stirred at room temperature for 5-10 min in dry toluene (75 cm^3 - compounds b,c,d and g) The residual triethylamine hydrochloride was removed by suction filtration and the residue extracted a second time Concentration of the ether or toluene extracts gave the crude N-sulphonylimine.

4-Methyl-N-(phenylmethylene)benzenesulphonamide (7a). The crude product (3.98 g, 81%) was placed in a Soxhlet extraction thimble and extracted for 7h with light petroleum (40-60 °). The resulting solution obtained was evaporated to dryness and then the pure imine was obtained by precipitation from dichloromethane with light petroleum (60-80 °) affording 2.87 g (58%) of a colourless powder, mp 109-111 °C (lit.,[27] 109 °C).
4-Methyl-N-(1-Naphthylmethylene)benzenesulphonamide (7b). The crude product (5.01 g, 86%) was precipitated from dichloromethane with hexane affording 4.00 g (68%) of a yellow powder. A sample was further purified by recrystallisation from chloroform/hexane to afford yellow rhombic crystals, mp 139-141 °C (Found: C, 69.9; H, 4 9; N, 4.7; S, 10.1. $C_{18}H_{15}NO_2S$ requires C, 69.88; H, 4.89; N, 4.53; S, 10.36%).
4-Methyl-N-(2-Naphthylmethylene)benzenesulphonamide (7c). The crude product (5.20 g, 89%) was precipitated from dichloromethane with light petroleum (40-60 °) to afford 4.10 g (70%) of a pale yellow powder. A sample was further purified by recrystallisation from chloroform/hexane to afford yellow needles, mp 114-116 °C (Found: C, 69.8, H; 4.8; N, 4.7; S, 10.7. $C_{18}H_{15}NO_2S$ requires C, 69.88; H, 4.89; N, 4.53; S, 10.36%).
4-Methyl-N-(3-Nitrophenylmethylene)benzenesulphonamide (7d). The crude product (4.47 g, 77%) was recrystallised from benzene/light petroleum (60-80 °) to afford 3.04 g (53%) of a colourless crystalline solid, mp 143-145 °C (lit.,[28] 139-140 °C).
4-Methyl-N-(4-methoxyphenylmethylene)benzenesulphonamide (7e). The crude product (2.81 g, 51%) was precipitated from from dichloromethane with hexane to afford 2.62 g (47%) of a white crystalline solid (which yellowed on standing), mp 126-129 °C (lit.,[27] 128.5 °C).
N-(Phenylmethylene)methanesulphonamide (7f). The crude product (2.47 g, 71%) was recrystallised from toluene/hexane to afford 1.76 g (51%) of colourless needles, mp 90-91 °C (lit.[28] 90-92 °C).
N-(2-Naphthylmethylene)methanesulphonamide (7g). The crude imine (3.57 g, 81%) was precipitated from dichloromethane with hexane to afford 2.22 g (50%) of a yellow powder. A sample was further purified by recrystallisation from chloroform/hexane, mp 119-121 °C (Found: C, 61 5; H, 4.8; N, 6.0; S, 14.0 $C_{12}H_{11}NO_2S$ requires C, 61.78; H, 4.75; N, 6.00; S, 13.74%); ν_{max}(Nujol) 1600 cm^{-1} (C=N), 1302 and 1150 cm^{-1} (SO_2); ∂_H (60 MHz) 3.16 (3H, s, Me), 7.48-8.41 (7H, m, aromatic), 9.17 (1H, s, HC=N).

The Attempted Preparation of P,P-Diphenyl-N-(phenylethylidene)phosphinic Amide (8).

Titanium tetrachloride (0.7 cm^3, 6.3 mmol) in dry dichloromethane (10 cm^3) was added dropwise to a stirred ice-cooled solution of acetophenone (1.38 g,11.5 mmol), diphenylphosphinic amide (2.50 g, 11.5 mmol) and anhydrous triethylamine (3.50 g, 34.7 mmol) in dry dichloromethane (50 cm^3). After the addition was complete, *ca.* 5 min, the mixture was stirred for 25 min at 0 °C. The titanium dioxide was removed by suction filtration through Celite and washed with dichloromethane (20 cm^3). Rotary evaporation of the filtrate gave a solid mixture of the product and triethylamine hydrochloride. The solid mixture was broken up and heated at reflux for 5 min in dry ether (75 cm^3) The residual triethylamine hydrochloride was removed by suction filtration and the residue extracted a second time. Concentration of the combined ether extracts gave the crude product (1.92 g) as a brown semi-solid. Tlc analysis (ether) of the crude product indicated that the product was a complex mixture containing at least seven components. A sample of the crude product (1.07 g) was purified by column chromatography on silica gel eluting with ether/hexane (1·1) until the first component was eluted from the column, and then 100 cm^3 portions of the following solvent mixtures were used as eluants ether/hexane (3:1 and 1:0), chloroform/ether (1.3, 1:1, 3:1 and 1.0), dichloromethane/chloroform (1:3, 1:1, 3:1 and 1.0) and methanol/dichloromethane (5:95, 1:9, 1.3, 1.1 and 1:0). Two fractions were isolated (i) 0.71 g of a brown liquid,which was shown by ^1H NMR spectroscopy to be a mixture of two components, infra-red spectroscopy indicated the presence of two carbonyl containing compounds and (ii) 0.30 g of a colourless solid which ^1H NMR spectroscopy indicated to be largely unreacted diphenylphosphinic amide. A portion (0.50 g) of the first fraction from the column was further purified by reduced pressure distillation, two fractions were obtained (i) 0.05 g, bp 76-78 °C at 74 mmHg and (ii) 0 20 g, bp 182-186 °C at 6 mmHg (lit.,[29] bp 155 °C at 1 mmHg) Fraction (i) was.shown by infra-red and ^1H NMR spectroscopy to be unreacted acetophenone and also by comparison with an authentic sample. Fraction (ii) was shown by infra-red and ^1H and ^{13}C NMR spectroscopy and ms to be a mixture (82:18)[29] of E- and Z-1,3-diphenyl-2-buten-1-one. ν_{max}(liquid film) 1663 cm^{-1} (C=O), 1600 cm^{-1} (C=C), ∂_H (270 MHz) 2.32 (3H, d, *J ca.* 1 Hz, Z-Me), 2.62 (3H, d, *J ca.* 1 Hz, E-Me), 6 70 (1H, d, *J ca.* 1 Hz, Z-alkenyl H), 7.15-7.63 (11H, m, aromatic and E-alkenyl H), 7.81-7.88 (2H, m, Z-aromatic), 7.93-8.06 (2H, m, E-aromatic); ∂_C (67.8 MHz) 18.86 (E-Me), 26.50 (E-Me), 116.5-155.0 (alkenyl and aromatic), 191.79 (E-C=O), 193.12 (Z-C=O); LREI-MS 222 (M^+, 80), 221 (100), 145 (11), 105 (12), 77 (11), 31 (45), HREI-MS Found: 222.1038 $C_{16}H_{14}O$ requires 222.1045.

4-Methyl-N-(1*R*)-(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)benzenesulphonamide (9).

Titanium tetrachloride (3.0 cm^3, 28.0 mmol) in dry toluene was added dropwise to a stirred cooled solution of (+)-camphor (7.63 g, 50.0 mmol), 4-methylbenzenesulphonamide (8.56 g, 50.0 mmol) and anhydrous triethylamine (15.15 g, 150 mmol) in dry toluene (100 cm^3). On completion of the addition the mixture was allowed to warm up to room temperature for 60 min and then heated to reflux for 24 h. The reaction mixture was allowed to cool and the precipitated solids were removed by suction filtration through a Celite pad, which was washed with a small amount of toluene. The solvent was removed on a rotary evaporator to give a brown oil. The oil was dissolved in dichloromethane (200 cm^3) and washed with water (2x100 cm^3), dried ($MgSO_4$) and concentrated on a rotary evaporator to afford a brown liquid (12.15 g). The product was then purified by flash column chromatography (ether/hexane 1:1 as eluant) which on combination of the appropriate fractions gave 10 19 g of a brown semi-solid Crystallisation of this product from hexane afforded 5.22 g (34%) of a colourless crystalline solid, mp 87-89 °C (Found:

C, 66.55; H, 7.6; N, 4.6. $C_{17}H_{23}NO_2S$ requires C, 66.85; H, 7.59; N, 4.59%); $[\alpha]_D$ -29.8 ° (*c* 0.1, $CHCl_3$); ν_{max}(Nujol) 1631 cm^{-1} (C=N), 1319 and 1158 cm^{-1} (SO_2); ∂_H (270 MHz) 0.77 (3H, s, Me), 0.93 (3H, s, Me), 0.95 (3H, s, Me), 1.25-1.48 (2H, m, CH_2), 1.70-1.96 (2H, m, CH_2), 2.03-2.10 (1H, m, CH), 2.43 (3H, s ,4-Me), 2.51-2.54 and 2.95-3.10 (2H, m, CH_2), 7.31 (2H, d, $^3J_{HH}$ 7.9 Hz, aromatic), 7.85 (2H, d, $^3J_{HH}$ 8.3 Hz, aromatic); ∂_C (22.5 MHz) 10.62 (q, Me-$C_{10'}$), 18 89 (q-Me-$C_{9'}$), 19.46 (q, Me-$C_{8'}$), 21.53 (q, tolyl methyl), 26.63 (m, CH_2-$C_{5'}$), 31.41 (m, CH_2-$C_{6'}$), 40.92 (t, CH_2-$C_{3'}$), 43.92 (d, CH-$C_{4'}$), 47.90 (s, $C_{7'}$), 57.92 (s, $C_{1'}$), 127.10, 129.35, 129.35 and 143.46 (aromatic), 201.30 (C=N).

P,P-Diphenyl-N-(1*R*)-(1,7,7,-Trimethylbicyclo[2.2.1]hept-2-ylidene)phosphinic Amide (10).

Titanium tetrachloride (3.0 cm^3, 28.0 mmol) *in dry toluene* (10 cm^3) was added dropwise with stirring to a solution of (+)-camphor (7.63 g, 50.0 mmol), diphenylphosphinic amide (10.85 g, 50.0 mmol) and triethylamine (15.15 g, 0.15 mol) in toluene (100 cm^3) cooled in an ice-bath. On completion of the addition the mixture was stirred at room temperature for 1h and then heated to reflux for 48h. After cooling the reaction the precipitated solids were removed by suction filtration through Celite and washed with toluene. The toluene was removed on a rotary evaporator to afford a brown oil. The oil was dissolved in dichloromethane (200 cm^3) and washed with water (2x100 cm^3), dried ($MgSO_4$), filtered and evaporated to afford a brown semi-solid The oil was purified by flash column chromatography using ether as eluant to afford the title compound 5.72 g (33%) as an oil $[\alpha]_D$ -28.6 ° (c 0.022 $CHCl_3$); ν_{max}(liquid film) 1665 cm^{-1} (C=N), 1208 cm^{-1} (P=O); ∂_H (270 MHz) 0.70 (3H, s, Me), 0.96 (3H, s, Me), 1.09 (3H, s, Me),1.20-1.42 (2H, m, CH_2), 1.67-1.92 (2H, m, CH_2), 1.94- 2.01 (1H, m, CH), 2.43-2.55 and 2.74-2.84 (2H, m, CH_2), 7.31-7.52 (6H, m, aromatic), 7.83-7.99 (4H, m, aromatic); ∂_C (22.5 MHz) 10.93 (Me-$C_{10'}$), 19.12 (Me-$C_{8'}$), 19.51 (Me-$C_{9'}$), 26.83 (CH_2-$C_{5'}$), 31.64 (d, $^4J_{PC}$ 1.5 Hz, CH_2-$C_{6'}$), 42.54 (d, $^3J_{PC}$ 12.5 Hz, CH_2-$C_{3'}$), 43.99 (CH-$C_{4'}$), 47.25 ($C_{7'}$), 58.01 (d, $^3J_{PC}$ 19.1 Hz, $C_{1'}$),127.9-137.7 (aromatic), 204.44 (d, $^2J_{PC}$ 11.0 Hz, C=N); ∂_P 19.5; LREI-MS 351 (M^+,54), 323 (58), 201 (100), 150 (51), 77 (48), HREI-MS Found 351.1764 $C_{22}H_{26}NOP$ requires 351 1744.

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