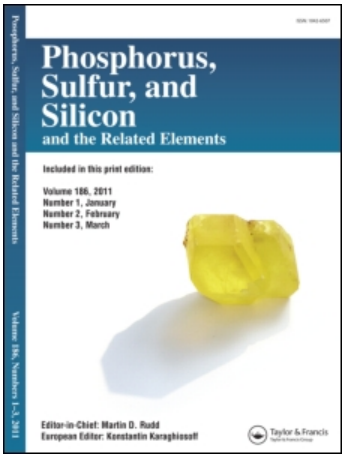

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A PARTICULARLY CONVENIENT ONE-POT SYNTHESIS OF *N*-ALKOXYCARBONYL, *N*-ACYL AND *N*-AROYL SUBSTITUTED IMINOPHOSPHORANES; IMPROVED PREPARATION OF AZIDOFORMATES, AROYL AND ALKANOYL AZIDES; AN ALTERNATIVE ROUTE TO COMPLEX AMIDES

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A PARTICULARLY CONVENIENT ONE-POT SYNTHESIS OF *N*-ALKOXYCARBONYL, *N*-ACYL AND *N*-AROYL SUBSTITUTED IMINOPHOSPHORANES; IMPROVED PREPARATION OF AZIDOFORMATES, AROYL AND ALKANOYL AZIDES; AN ALTERNATIVE ROUTE TO COMPLEX AMIDES

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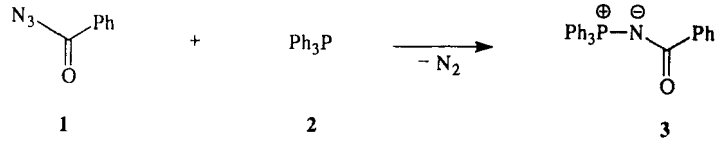
Chloroformates and acid chlorides react smoothly with sodium azide in acetone at 0°C, forming azidoformates, aroyl and alkanoyl azides in very high yield. With triphenylphosphine or other phosphines present in the reaction mixture, the forming azides are intercepted, leading directly to the corresponding *N*-alkanoyl, *N*-aroyl, *N*-alkoxycarbonyl, and *N*-aryloxycarbonyliminophosphoranes. *N*-acylliminophosphoranes react with *n*-butyllithium forming anions which react readily with electrophiles, e.g., carbonyl compounds, forming highly substituted iminophosphoranes. The phosphonium group is effortlessly removed from the latter compounds by acid hydrolysis forming the corresponding amides in high yield.

Key words: Synthesis; iminophosphoranes; aroyl azides; alkanoyl azides; complex amides.

N-alkyl and *N*-arylsubstituted iminophosphoranes are valuable reagents, e.g. in the aza-Wittig (Staudinger-Meyer-Hauser)[1,2] reaction and enjoys broad application in contemporary organic chemistry. Far less interest has been focused on the less nucleophilic *N*-aroyl, *N*-alkanoyl and *N*-alkoxycarbonyliminophosphoranes since the latter compounds for many years were considered unreactive towards electrophiles.[3] As shown by Plieninger[4,5] and other workers,[6] however, they react readily with activated carbonyls, e.g. with glyoxalates, keto malonates, and ketenes.[7] Another potentially useful application of *N*-alkanoyl iminophosphoranes would involve metallation of the *C*-atom alpha to the carbonyl group. The resulting highly nucleophilic species (Scheme VIII) react smoothly with a variety of electrophiles to yield a multitude of new iminophosphoranes, applicable in the aza-Wittig reaction of activated carbonyl compounds. Furthermore, and perhaps of greater importance, since the P—N bond is easily cleaved in dilute mineral acid, these elaborate iminophosphoranes can be hydrolysed to compounds, i.e. highly substituted amides which may otherwise be difficult to prepare.

Methods for the Preparation of N-alkoxycarbonyl, N-aroyl and N-acyl Iminophosphoranes

The first iminophosphorane, *N*-phenyltrianilinophosphinimine, was prepared by Lemoult[8] from the reaction of phosphorus pentachloride with aniline. Later, and



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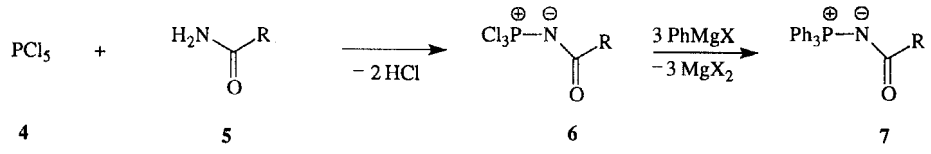
SCHEME I



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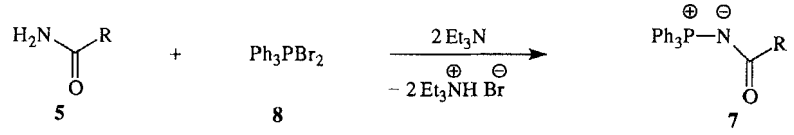


5 8 7

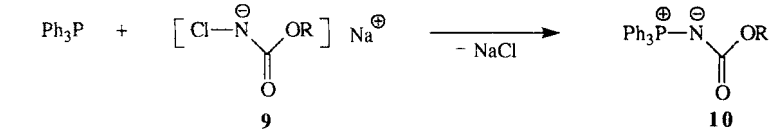
SCHEME II

independent of the work of Lemoult, Staudinger in a succession of classical investigations prepared a long series of these compounds and studied their reactions. Staudingers group obtained iminophosphoranes in excellent yields from what became later known as the Staudinger reaction, i.e., the reaction of a phosphine with an organic azide. Thus the first *N*-aroyl iminophosphorane, *N*-benzoyltriphenylphosphinimine[2] **3** was prepared by mixing benzoyl azide **1** with triphenylphosphine **2** in ether (Scheme I).

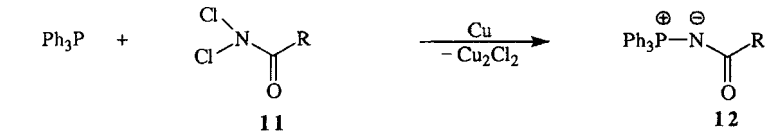
Kirsanov[9] apparently unaware of Lemours work developed his method, utilizing phosphorus pentachloride **4** and certain amino-derivatives, usually those containing strongly electron withdrawing groups. Thus, acylamides **5** afford the corresponding *N*-acyl iminotrichlorophosphoranes **6**, which, as shown by the same workers,[10,11] can be arylated by organometallic reagents, e.g., phenylmagnesium chloride, to *N*-acyl iminotriphenylphosphorane **7** as indicated in Scheme II.

Horner[12] found that the intermediate trichlorophosphorane in many cases could be dispensed with and made iminotriphenylphosphoranes directly from the amino-derivative and dibromo-triphenylphosphorane **8**, usually in the presence of two equivalents of triethylamine (Scheme II).

N-Halogenoamides and *N*-halogenocarbamates provide yet another starting point for the preparation of α-carbonyl stabilized iminophosphoranes. For example the sodium salts of *N*-chlorocarbamates **9** react readily with triphenylphosphine yielding alkoxycarbonyltriphenylphosphoranes **10** (Scheme III) in excellent yields.[3] Also *N*-dichloroamides **11** react under mild conditions with phosphines in the presence of a halogen scavenger to form *N*-acyl and *N*-aroylsubstituted iminophosphoranes[13] **12**. As a rule finely divided copper powder is used as the halogen scavenger (Scheme III).

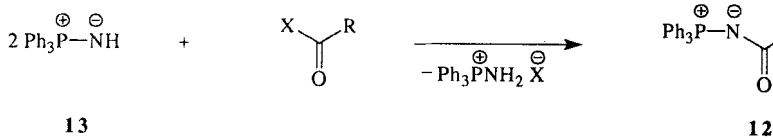


9 10



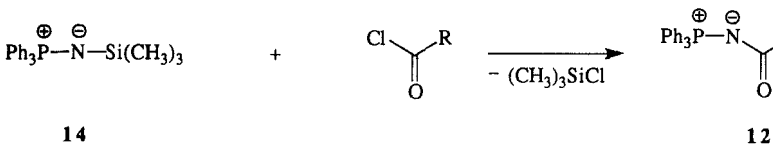
11 12

SCHEME III



13 12

SCHEME IV



14 12

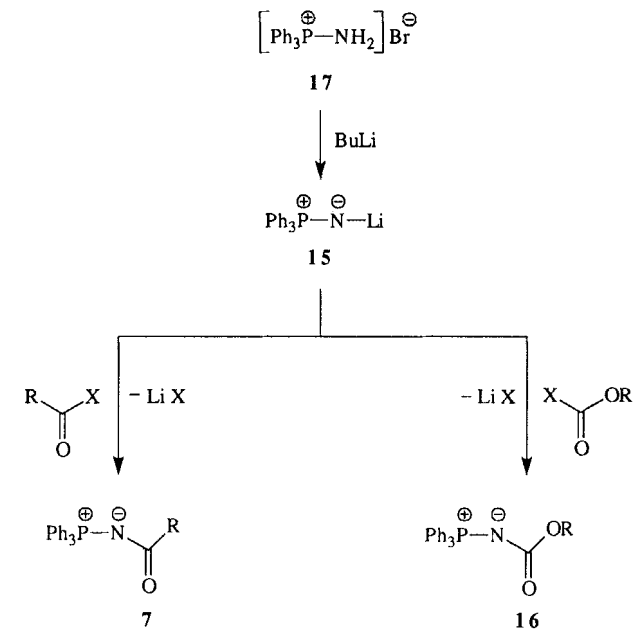
SCHEME V

The reaction between triphenylphosphine and *N*-bromoamides takes another course, however, yielding nitriles and triphenylphosphine oxide hydrobromide.[14]

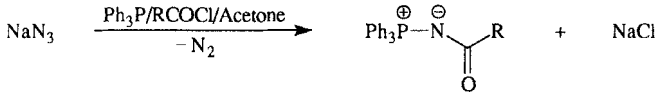
Another preparative route starting with iminotriphenylphosphorane[15] **13** and then acylating this very reactive compound with the appropriate reagents, has been applied by several workers[15–17] (Scheme IV). As pointed out,[18] however, **13** is prone to hydrolysis and rigorously anhydrous conditions are required for its preparation and use.

Kricheldorf[19] found that the *N*-silylated iminophosphorane **14** made from triphenylphosphine and trimethylsilyl azide,[20] can be acylated with acid chlorides or anhydrides, giving amidotriphenylphosphoranes **12** in nearly quantitative yields as shown in Scheme V.

Each of the abovementioned preparative routes requires at least two stages from an acid chloride or a chloroformate, some of them rather cumbersome, or utilises some premade iminophosphorane as starting material. Recently, Christau *et al.*[21] reported on the application of the *N*-lithiated triphenylphosphine imide **15**, initially prepared by Schmidbaur and Jonas,[22] for the synthesis of *N*-acyliminotriphenylphosphoranes **7** and *N*-alkoxycarbonyltriphenylphosphoranes **16** (Scheme VI). The method has some drawbacks, however. The yields are erratic, varying from zero (R = CH_3) to 77% (R = CF_3), and the key precursor, aminotriphenylphosphonium bromide **17** requires tedious preparation from triphenylphosphine, bromine and



SCHEME VI



SCHEME VII

ammonia followed by treatment of this reagent (**17**) by BuLi in an anhydrous solvent (THF).

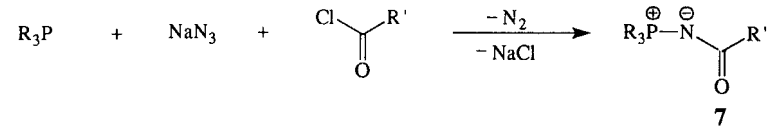
During our continued studies of iminophosphoranes we have investigated various methods with a view of finding a more convenient synthetic route for the preparation of α-carbonyl stabilized iminophosphoranes.

For the last two years we have made use of a very rapid, efficient, and as it appears, general one-pot preparation of *N*-alkoxycarbonyl, *N*-alkanoyl and *N*-aroyl substituted iminophosphoranes from readily available reagents. We now describe the synthesis of a series of these compounds from just mixing the appropriate acid halide or haloformate with sodium azide and triphenyl phosphine (or any other phosphine) in acetone (Scheme VII). The yields are close to 100 per cent. The results are summarized in Table I.

Without the addition of phosphines to the reaction mixture, the method presents a very convenient route to azidoformates, alkanoyl and aroyl azides.[23] The reaction seems to work equally well with alkanoyl halides and aroyl halides containing electron-withdrawing as well as electron-releasing substituents. Thus it appears that any available acid halide or haloformate by this simple method, rapidly and effortlessly can be transformed into the corresponding azide in almost quantitative yield.

TABLE I

Preparation of iminophosphoranes **7** in acetone



7

R'	R	Temp.°C	Time m.	Product	(%) Yield[a]
methyl	Ph	0	20	1	85
ethyl	Ph	0	30	2	93
chloromethyl	Ph	0	30	3	98
isobutyl	Ph	20	30	4	90
ethoxy	Ph	0	30	5	97
phenyl	Ph	0	30	6	96
4-methylphenyl	Ph	20	60	7	90
4-methylphenyl	n-butyl	0	30	8	85[b]
3,5-dinitrophenyl	Ph	0	30	9	94
4-nitrophenyl	Ph	20	30	10	91
benzyl	Ph	20	30	11	80[b]
thenyl	Ph	0	30	12	85[b]

[a] Yields refer to isolated products after crystallization.
[b] Lower yields due to the oily character of these compounds and losses during the chromatographic purification.

RESULTS AND DISCUSSION

Acid chlorides and chloroformates react exothermically with equivalent amounts of sodium azide in acetone to afford excellent yields of the appropriate azidoformates and aroyl and alkanoyl azides. In order to secure a rapid and quantitative reaction, it is advisable, however, to use a little excess (1.1–1.5 molar equivalents) of sodium azide. With triphenylphosphine or any other aryl or alkyl substituted phosphine present in the reaction mixture, the Staudinger reaction is usually initiated very rapidly, as can be seen from the vigorous evolution of nitrogen which starts after a few seconds. A yellow colour appears immediately and then fades at the end of the reaction. This colour, due to the formation of a phosphazide complex containing the azide and phosphine in equal proportions, is marking the onset of the first step of the Staudinger reaction. The reaction mixture is cooled with ice-water during the exotherm, whereafter it is left at ambient temperature for 15 min., or until the yellow colour of the phosphazide complex fades.

It appears that the scope of this reaction for the synthesis of α-carbonyl stabilized iminophosphoranes is limited only by the availability of the requisite reactants, i.e., haloformate, alkanoyl or aroyl halide and phosphine.

Isolation of Azides

Acyl and aroyl azides are valuable synthetic intermediates, e.g., for the preparation of isocyanates (from which amines, urethanes, thiourethanes, ketenimines, car-

bodiimides, ureas, amides etc.) can be easily made. Alkoxycarbonyl azides which do not readily undergo the Curtius rearrangement play on the other hand an important role in peptide chemistry and have a rich triazolidine and nitrene chemistry.[24] Alkoxycarbonyl azides together with the relatively stable aroyl azides can be isolated from the present reaction in close to quantitative yields.

Because of their instability and high tendency for explosions no attempt was made to prepare in a pure state the lower members of the intermediate alkanoyl azides. Acetyl azide and propionyl azide were nevertheless prepared in solution from the corresponding chlorides in 100% yield as determined by NMR. One of the higher members, hexadecanoyl azide which akin to the aroylazides is relatively stable could be isolated directly in a very pure state, however.

The method works equally well with aroyl halides. Thus 4-nitrobenzoyl chloride with sodium azide at 0°C provided the corresponding nitrobenzoyl azide in 100% yield (90% isolated) within half an hour.

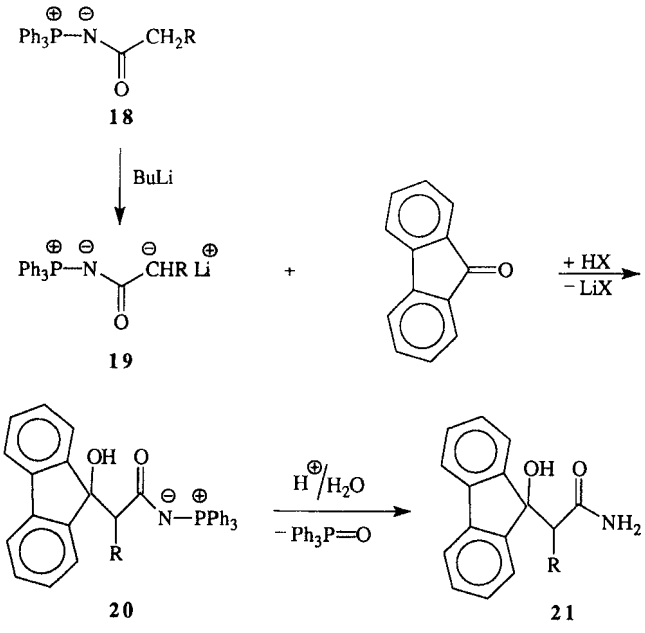
This very rapid reaction of two perfectly stable, commercially available and unexpensive reactants, should be compared with the 72 h reaction time required by the otherwise attractive preparative route to aroyl azides reported by Olah *et al.*[23] In the latter method aroyl chlorides are reacted with trimethylsilyl azide under zink iodide catalysis in dichloromethane. We believe the present method to be more convenient, more widely applicable and perhaps the safest and most attractive yet devised for the preparation of these compounds. The results are summarized in Table II.

TABLE II

Preparation of azidoformates, alkanoyl and aroyl azides in acetone

Entry	Substrate	Product	(%) Yield
1	acetyl chloride	acetyl azide	100
2	propionyl chloride	propionyl azide	100
3	chloroacetyl chloride	chloroacetyl azide	100
4	isobutyryl chloride	isobutyryl azide	100
5	trimethylacetyl chloride	trimethylacetyl azide	100
6	hexadecanoyl chloride	hexadecanoyl azide	100 (95)
7	ethyl chloroformate	ethyl azidoformate	100
8	isobutyl chloroformate	isobutyl azidoformate	100
9	phenyl chloroformate	phenyl azidoformate	100
10	benzoyl chloride	benzoyl azide	100 (91)
11	4-methylbenzoyl chloride	4-methylbenzoyl azide	100 (92)
12	4-nitrobenzoyl chloride	4-nitrobenzoyl azide	100 (91)
13	4-chlorobenzoyl chloride	4-chlorobenzoyl azide	100 (90)

Yields in parentheses refer to isolated products. Other yields as determined by ^{13}C NMR.



SCHEME VIII

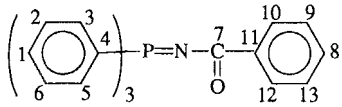


FIGURE 1 Structure formula of *N*-aroylphosphinimines showing the numbering of C-atoms in the experimental part.

Application of N-alkanoyl Iminophosphoranes in Syntheses of Complex Amides

The utility of iminophosphoranes as reagents to effect C=N double bonds via the aza-Wittig (Staudinger-Meyer-Hauser) reaction is clearcut, and enjoys broad application in contemporary synthetic chemistry. Very little effort has been expended, however, in attempts to broaden the range of applications of these compounds to other reactions, for example as reagents to effect carbon–carbon bond formation.

One alternate and potentially very useful route to highly substituted amides for instance, would involve reacting the anion **19** of the appropriate *N*-alkanoyl iminophosphorane **18** with a suitable carbonyl compound, e.g., fluorenone in a first step, followed by hydrolysis of the resulting hydroxy-substituted iminophosphorane **20** to β-hydroxyamides **21** (Scheme VIII). We have demonstrated the feasibility of this method as described below.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer operating at 200 and 50.29 MHz, respectively. Infrared spectra were measured with a Perkin Elmer 1310 spectrophotometer.

The mass spectra were obtained on a VG Micromass 7070 instrument. Column chromatography was carried out using Merck No. 9385 Silica gel 60. Thin layer chromatography was performed using Merck No. 60765 silica gel GF 254.

Preparation of N-alkanoyl, N-aroyl, N-alkoxy and N-aryloxycarbonyliminophosphoranes. The iminophosphoranes were prepared from the corresponding acid chlorides or chloroformates by the following general procedure. To a suspension of 11–15 mmol sodium azide in 50 ml of acetone is added 10 mmol of the appropriate acid chloride, followed by 10 mmol of triphenylphosphine. The reaction mixture is vigorously stirred during the addition and cooled by means of an ice-bath.

Despite the cooling the Staudinger reaction sometimes tends to become rather vigorous, especially with aliphatic phosphines like tributyl phosphine. These phosphines should therefore be added dropwise or in small portions. In a slightly modified version we have added the acid chlorid to a likewise cooled mixture of sodium azide and the appropriate phosphine in acetone with no discernible alteration in product yields. The reaction is usually completed in a few minutes. The cooling-bath is thereafter removed and the reaction mixture stirred for another 20–30 min. The solvent is evaporated in vacuo, and the iminophosphorane dissolved in dichloromethane or ethyl acetate. The salts, sodium chloride and excess sodium azide, are removed by filtration and the remaining product purified either by crystallization or column chromatography. In many cases the iminophosphorane crystallizes readily and in a fairly pure state from the dichloromethane solution by addition of a little ether. In other cases where the iminophosphoranes are oils, they are preferably freed from impurities (usually an excess either of phosphine or acid chloride) by chromatography through a short column of silica gel. Yields as deemed by NMR are quantitative. Yields of isolated products varies from 85 to 95% (Table I).

Preparation of azides. The more sensitive alkanoyl azides were prepared from the appropriate alkanoyl chlorides by the following general procedure: To a well stirred suspension of 1.5 mmol (0.195 g) sodium azide in 2 ml deuteroacetone were added 1.0 mmol alkanoyl chloride. The temperature was held at approximately 0°C by means of an ice-water bath during the reaction and the reaction mixture stirred vigorously for about half an hour. The reaction mixture was thereafter filtered through cotton wool and used directly for the NMR analyses. As a rule no trace of unreacted alkanoyl chloride could be detected either by ^1H or ^{13}C NMR analysis. The more stable azidoformates and the aroyl azides were usually prepared at room temperature in ordinary acetone and at a larger scale by the same procedure. But in the latter case the solvent was evaporated in vacuo and the resulting azide taken up in a small volume of pentane or dichloromethane. The undissolved salts were filtered off and the product isolated along two routes. In the case of aroyl azides like benzoyl azide the concentrated pentane solutions were cooled until the aroyl azides crystallized. Some aroyl azides, like 4-nitrobenzoyl azide, are only slightly soluble in acetone and crystallize very readily from this solvent during the reaction. In these cases more acetone should be added to the reaction mixture until the azide redissolves.

In the case of the azidoformates, the dichloromethane was evaporated under vacuum and the liquid product isolated directly, usually in a very pure state (depending on the purity of the starting chloroformate).

N-Acetyltriphenylphosphinimine m.p. 179°C, lit.[21] 169.2°C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.21 (d, J 2.9 Hz, 3H, CH_3), δ 7.25–7.55 (m, 9H, Ph-p and Ph-o), δ 7.60–7.90 (m, 6H, Ph-m); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 29.08 and 29.47 (CH_3), J P—CH_3 19.7 Hz, δ 127.59 and 127.59 (C_4), J P—C_4 97 Hz, δ 192.45 and 200.00 (C_2 and C_6), J P—C_6 12 Hz, δ 132.35 (C_1), δ 133.20 and 133.40 (C_3 and C_5), J P—C_3 9.7 Hz, δ 182.51 (d, J 9 Hz, CO).

N-Chloroacetyltriphenylphosphinimine m.p. 170–171°C; ^1H NMR (200 MHz, $CDCl_3$) δ 4.28 (s, 2H, CH_2), δ 7.46–7.65 (m, 9H, Ph-p and Ph-o), δ 7.65–7.90 (m, 6H, Ph-m); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 48.34 and 48.85 (CH_2), J P—CH_2 25.7 Hz, δ 126.78 and 128.74 (C_4), J P—C_4 98.5 Hz, δ 128.95 and 129.19 (C_2 and C_6), J P—C_6 12.4 Hz, δ 134.74 (C_1), δ 133.24 and 133.44 (C_3 and C_5), J P—C_5 10 Hz, δ 176.20 (d, CO).

N-Propionyltriphenylphosphinimine m.p. 138–139°C, lit.[25] 133–134°C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.19 (t, J 7.5 Hz, 3H, CH_3), δ 2.48–2.60 (q, J 7.5 Hz, 2H, CH_2), δ 7.40–7.65 (m, 9H, Ph-o and Ph-p), δ 7.65–7.85 (m, 6H, Ph-m); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 12.71 (CH_3), δ 34.91 and 35.29 (CH_2), J P—CH_2 19.1 Hz, δ 127.83 and 129.76 (C_4), J P—C_4 97.4 Hz, δ 128.75 and 128.99 (C_2 and C_6), J P—C_2 11.9 Hz, δ 132.27 and 132.33 (C_1), J P—C_1 2.8 Hz, δ 133.20 and 133.40 (C_3 and C_5), J P—C_3 9.7 Hz, δ 185.48 and 185.68 (CO), J P—C_7 10.3 Hz.

N-(2-Methylpropionyl)triphenylphosphinimine m.p. 115–116°C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.23 (d, J 6.9 Hz, 6H, CH_3), δ 2.72 (m, 1H, CH), δ 7.35–7.60 (m, 9H, Ph-p and Ph-o), 7.65–7.90 (m, 6H, Ph-m); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 22.26 (CH_3), δ 40.05 and 40.42 (CH), J, P—C_2 18.3 Hz, δ

128.07 and 130.01 (C_4), J P—C_4 97.1 Hz, δ 128.72 and 128.96 (C_2 and C_6), J P—C_2 12 Hz, δ 132.21 and 132.28 (C_1), J P—C_1 2.8 Hz, δ 133.19 and 133.38 (C_3 and C_5), J P—C_3 9.6 Hz, δ 188 (CO), J P—C_7 9 Hz.

N-Benzoyltriphenylphosphinimine m.p. 196°C, lit.[2] 193–194°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35–7.65 (m, 12H, $H_{aromatic}$), δ 7.80–8.20 (m, 6H, $H_{aromatic}$), δ 8.40–8.55 (m, 2H, $H_{aromatic}$); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 127.54, 127.59, 127.79, 128.00, 128.26, 128.44, 128.64, 128.89, 129.13, 129.58, 129.75, 129.85, 129.90, 130.98, 132.21, 132.55, 132.83, 133.05, 133.34, 133.54, 133.92, δ 138.74 and 139.14 (C_{11}), J P—C_{11} 20.4 Hz, δ 175.89 and 176.04 (CO), J P—C_7 7.8 Hz.

N-*p*-Methylbenzoyltripenylphosphinimine m.p. 159–160°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.40 (s, 3H, CH_3), δ 7.19–8.27 (m, 19H, $H_{aromatic}$); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 23.14 (CH_3), δ 127.90, 128.03, 128.15, 128.20, 128.25, 128.38, 128.44, 128.70, 128.85, 129.09, 129.92, 129.96, 132.42, 132.47, 133.34, 133.53, δ 136.07 and 136.47 (C_8) J P—C_8 9.9 Hz, δ 140.94 (C_{11}), δ 176.0 (d, CO).

N-*p*-Methylbenzoyltributylphosphinimine oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, 9H, CH_3), δ 1.30–1.80 (m, 18H, CH_2), δ 2.40 (s, 3H, CH_3—Ph), δ 7.20–7.74 (m, 4H, $H_{aromatic}$); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 15.15 (CH_3), δ 23.02 (CH_3—Ph), δ 25.28–25.91 (CH_2), δ 28.53 and 28.81 (CH_2—P), J P—CH_2 64 Hz, δ 127.80 (Ph-o), δ 129.37 (Ph-m), δ 130.94 (Ph-i), δ 142.29 (Ph-p), δ 169.27 (d, CO).

N-*p*-Nitrobenzoyltriphenylphosphinimine m.p. 186°C, lit.[17] 187°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55–7.67 (m, 9H, H(1,3,5)), δ 7.75–7.95 (m, 6H, H(2,6)), δ 8.21–8.50 (q, 4H, H(9,10,12,13); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 123.24 (C_{10} and C_{12}), δ 127.02 (C_4), δ 129.01 and 129.26 (C_2 and C_6), J P—C_2 12.4 Hz, δ 130.67 and 130.72 (C_1), J P—C_1 2.6 Hz, δ 132.80 and 132.85 (C_9 and C_{13}), J P—C_9 2.7 Hz, δ 133.26 and 133.45 (C_3 and C_5), J P—C_3 9.9 Hz, δ 144.45 and 144.87 (C_{11}), J P—C_{11} 21.3 Hz, δ 149.32 (C_8), δ 173.63 (d, CO).

N-*m*-Dinitrobenzoyltriphenylphosphinimine m.p. 193–194°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45–7.70 (m, 9H, H(1,3,5)), δ 7.75–8.00 (m, 6H, H(2,6)), δ 9.09 (d, J 0.9 Hz, 1H, H(8), δ 9.45 (d, J 2.1 Hz, 2H, H(10,11)); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 120.48, δ 126.39 and 128.36 (C_4), J P—C_4 99.9 Hz, δ 128.62, 128.70, 128.85, 128.92, δ 129.17 and 129.42 (C_3 and C_5), J P—C_3 12.3 Hz, δ 129.69, 132.89, 133.10, 133.15, δ 133.25 and 133.45 (C_2 and C_6), J P—C_2 10.1 Hz, δ 133.74, δ 142.82 and 143.27 (C_{11}) J P—C_{11} 22.4 Hz, δ 148.24 (C_8), δ 170.61 and 170.75 (CO), j P—C_7 6.8 Hz.

N-Phenylacetyltriphenylphosphinimine oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.02 (d, J 10 Hz, 2H, CH_2), δ 6.9–7.0 (m, 2H), δ 7.12–7.20 (m, 1H, CH), δ 7.40–7.60 (m, 9H, H(1,3,5)), δ 7.65–7.85 (m, 6H, H(2,6)); ^{13}C NMR (50.29 Hz, $CDCl_3$) δ 43.12 and 43.52 (CH_2), J P—CH_2 20.1 Hz, δ 124.24, 125.91, 126.49, 127.32, δ 128.80 and 129.04 (C_3 and C_5), J P—C_3 11.1 Hz, δ 129.26, 132.43, δ 132.27 and 133.46 (C_2 and C_6), J P—C_2 9.7 Hz, δ 180.82 (d, CO).

N-(2-Thienylacetyl)triphenylphosphinimine oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.81 (d, J 2.6 Hz, 2H, CH_2), δ 7.15–7.80 (20H, $H_{aromatic}$); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 48.96 and 49.35 (CH_2), J P—CH_2 19.4 Hz, δ 126.17, 127.55, 128.32, 128.68, 128.75, 128.92, 129.99, 129.49, 129.83, 132.17, 132.25, 132.33, 132.39, 133.20, 133.40, 138.62, δ 182.27 and 182.47 (CO), J P—C_7 10.1 Hz.

N-Ethoxycarbonyltriphenylphosphinimine m.p. 140°C, lit.[19] 135–137°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.11 (t, J 7.1 Hz, 3H, CH_3), δ 3.96 (q, J 7.1 Hz, 2H, CH_2), δ 7.55–8.70 (m, 9H, Ph-o and Ph-p), δ 8.20–8.80 (m, 6H, Ph-m); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 16.35 (CH_3), δ 62.12 and 62.19 (CH_2), J P—CH_2 3.3 Hz, δ 127.42 and 129.41 (C_4), J P—C_4 100.1 Hz, δ 128.71 and 128.96 (C_2 and C_6), J P—C_2 12.4 Hz, δ 132.49 and 132.54 (C_1), J P—C_1 2.6 Hz, δ 133.12 and 133.32 (C_3 and C_5), J P—C_5 10 Hz), δ 162.00 (d, CO).

Acetyl azide ^{13}C NMR (50.29 MHz, acetone-d_6) δ 24.92 (CH_3), δ 177.80 (CO).

Propionyl azide ^{13}C NMR (50.29 MHz, acetone-d_6) δ 10.44 (CH_3), δ 31.92 (CH_2), δ 180.94 (CO).

Chloroacetyl azide ^{13}C NMR (50.29 MHz, acetone-d_6) δ 44.72 (CH_2), δ 174.51 (CO).

Isobutyryl azide ^{13}C NMR (50.29 MHz, acetone-d_6) δ 20.23 (CH_3), δ 38.25 (CH), δ 183.83 (CO).

Trimethylacetyl azide oil; ^{13}C NMR (50.29 MHz, acetone-d_6) δ 28.33 (CH_3), δ 42.57 (C_2), δ 185.68 (CO).

Hexadecanoyl azide oil; ^{13}C NMR (50.29 MHz, acetone-d_6) δ 15.82 (CH_3), δ 24.70, 26.70, 30.34, 30.72, 30.90, 31.10, 31.27, 31.36, 31.47, 31.62, 31.86, 32.24, 33.91, 38.71 (CH_2), δ 180.21 (CO).

Ethyl azidoformate oil; ^{1}H NMR (200 MHz, acetone-d_6) δ 1.28 (t, J 7.1 Hz, 3H, CH_3), δ 4.22 (t, J 7.1 Hz, 2H, CH_2); ^{13}C NMR (50.29 MHz, acetone-d_6) δ 15.72 (CH_3), δ 66.14 (CH_2), δ 157.69 (CO).

Isobutyryl azidoformate oil; ^{1}H NMR (200 MHz, acetone-d_6) δ 0.93 and 0.96 (d, J 6.7 Hz, 6H, CH_3), δ 2.82 (br. s, 1H, CH), δ 3.99 and 4.02 (d, J 6.6 Hz, 2H, CH_2); ^{13}C NMR (50.29 Hz, acetone-d_6) δ 20.35 (CH_3), δ 29.78 (CH), δ 75.69 (CH_2), δ 157.78 (CO).

Phenyl azidoformate oil; ^{13}C NMR (50.29 MHz, acetone-d_6) δ 122.15 (C_3 and C_5), δ 127.53 (C_4), δ 130.59 (C_2 and C_6), δ 151.72 (C_1), δ 156.67 (CO).

Benzoyl azide m.p. 26°C; lit.[23] 25–27°C; ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 128.91 (C_3 and C_5), δ 129.72 (C_2 and C_6), δ 134.48 (C_4), δ 172.20 (CO).

4-Methylbenzoyl azide m.p. 33°C; lit.[23] 32–33°C; ^{13}C NMR (50.29 MHz, acetone-d_6) δ 23.09 (CH_3), δ 129.06 (C_1), δ 130.43 (C_3 and C_5), δ 130.49 (C_2 and C_6), δ 146.35 (C_4), δ 172.21 (CO).

4-Nitrobenzoyl azide m.p. 70°C; lit.[23] 65°C; ^{13}C NMR (20 MHz, $CDC1_3$) δ 124.36 (C_3 and C_5), δ 130.78 (C_2 and C_6), δ 135.88 (C_1), δ 151.25 (C_4), δ 170.59 (CO).

4-Chlorobenzoyl azide m.p. 42°C; lit.[23] 39–42°C; ^{13}C NMR (50.29 MHz, acetone-d_6) δ 130.07 (C_3 and C_5), δ 130.36 (C_1), δ 131.77 (C_2 and C_6), δ 171.57 (CO).

N-(9-Hydroxy-9-fluorenylacetyl) triphenylphosphinimine **20** (R=H). To a vigorously stirred solution of acetyltriphenylphosphinimine (0.5 g, 1.56 mmol) in anhydrous THF (15 ml) at −78°C was added 1.0 ml (approximately 1.60 mmol) of BuLi (1.6 N in hexane). After the addition was complete, the reaction mixture was stirred for 15 m, during which time the temperature was raised to about 0°C.

To the yellow solution of the phosphinimine anion was henceforth added an equivalent amount (1.60 mmol, 0.29 g) of 9-fluorenone, and the reaction mixture was stirred for 30 m. at ambient temperature.

An aqueous solution of ammonium chloride was thereafter added and the aqueous layer extracted with chloroform. The organic layer was washed with a little water and dried over $MgSO_4$. The solvent was removed in vacuo, leaving the phosphinimine as a yellow oil (0.95 g), which was purified by column chromatography to give 0.33 g of **20** (R=H); m.p. 214–215°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.99 (s, 2H, CH_2), δ 7.08–7.15 (t, 2H, $H_{aromatic}$), δ 7.25–7.29 (t, 2H, $H_{aromatic}$), δ 7.70–7.70 (m, 13H, $H_{aromatic}$), δ 7.74–7.90 (m, 6H, $H_{aromatic}$), δ 7.99 (s, 1H, OH); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 49.24 and 49.58 (CH_2), J P—CH_2 16.7 Hz, δ 81.18 (C_9), δ 120.12, 124.81, 126.60, 127.90, 128.66, 129.29, 132.94, 133.33, 133.53, 139.44, 149.68, δ 182.55 (CO).

2-(9-Fluorene-9-ol)-acetamide) **21** (R=H). To a stirred solution of **20** (140 mg 0.28 mmol) in ethanol (10 ml) was added 3 ml of 0.1 N HCl. The solution was heated at gentle reflux for 3 h, whereafter the solvents were evaporated in vacuo. Chromatography (Merck 60765 silica gel GF 254, acetone-chloroform, 1:5) yielded **21** (0.60 g, 0.25 mmol, 90%); m.p. 151–153°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.49 (s, 2H, CH_2), δ 4.1–5.3 (s, 1H, OH), δ 5.7–6.05 and 6.15–6.35 (2H, NH_2), δ 7.10–7.60 (m, 8H, $H_{aromatic}$); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 45.25 (CH_2), δ 80.54 (C_9), δ 120.41, 124.075, 128.33, 129.44, 138.08, 147.86, δ 174.60 (CO).

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