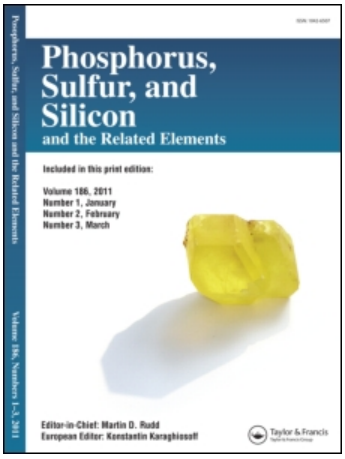

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THE FORMATION OF PYRAZINES FROM N-β-KETO IMINOTRIPHENYLPHOSPHORANES; IMINOPHOSPHORANE-MEDIATED SYNTHESES OF 2,2,4,4-TETRAPHENYL-N,N' -BIS(2-PENTANE-3-ON)- CYCLOBUTANE-1,3-DIIMINE; 1,3,4-OXADIAZOLES; 2-AMINO-3,5-DIHYDROIMIDAZOL-4-ONES; AND 2-DIPHENYLMETHYL-I,5-DIHYDROIMIDAZOL-4-ONE

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THE FORMATION OF PYRAZINES FROM N-β-KETO IMINOTRIPHENYLPHOSPHORANES; IMINOPHOSPHORANE-MEDIATED SYNTHESES OF 2,2,4,4-TETRAPHENYL-N,N'-BIS(2-PENTANE-3-ON)-CYCLOBUTANE-1,3-DIIMINE; 1,3,4-OXADIAZOLES; 2-AMINO-3,5-DIHYDROIMIDAZOL-4-ONES; AND 2-DIPHENYLMETHYL-1,5-DIHYDROIMIDAZOL-4-ONE

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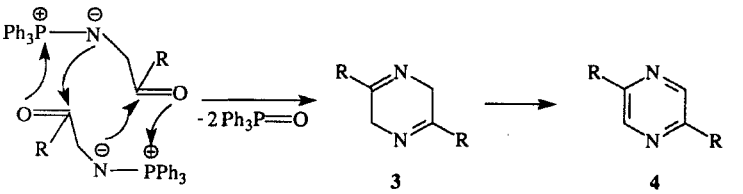
The aza-Wittig reaction has been applied to the synthesis of the unstable N-β-keto ketenimine (**18**), which dimerize spontaneously, forming the very sterically hindered 2,2,4,4-tetraphenyl-N,N'-bis (2-pentane-3-on)-cyclobutane-1,3-diimine (**21**). Iminophosphoranes (**33**) and (**38**) are used for the preparation of some novel 1,5 and 3,5-dihydroimidazol-4-ones (**36**), (**41a–b**), (**42**). N-acylamino iminotriphenylphosphoranes (**2a–d**) are applied for the syntheses of a series of 1,3,4-oxadiazoles (**32**). The mechanism of the decomposition of the unstable N-β-keto iminotriphenylphosphoranes (**1**) into pyrazines and triphenylphosphine oxide has been investigated.

Key words: Iminophosphoranes; β-keto carbodiimides; N-β-keto ketenimines; heterocycles.

INTRODUCTION

In a preceding paper[1] we have shown that iminophosphoranes (**1**), when generated in the presence of active carbonyl compounds, e.g., isocyanates and isothiocyanates, readily take part in the aza-Wittig (Staudinger-Meyer-Hauser)[2,3] reaction to yield heterocycles via some very reactive β-keto carbodiimides. It has also been found[4] that N-acylamino iminotriphenylphosphoranes (**2**) are applicable to the synthesis of the previously unknown N-acylamino carbodiimides and N-acylamino



1 **3** **4**

SCHEME I

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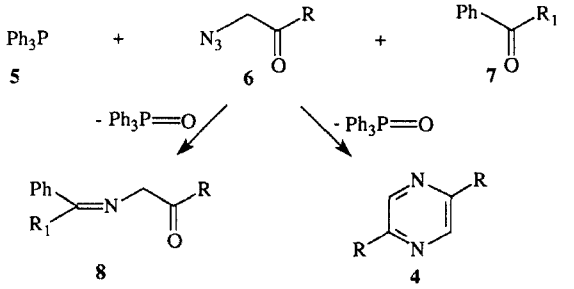
isothiocyanates which undergo spontaneous cyclization to 2-amino-1,3,4-oxadiazoles and 2-mercapto-1,3,4-oxadiazoles, respectively. It seemed worthwhile to examine more generally the reactions of these ylides (**1** and **2**), in particular the aza-Wittig reactions and the rearrangements of the intermediate heterocumulenes. Moreover, since all attempts to isolate iminophosphoranes (**1**) were frustrated by their thermodynamic instability, i.e., the surprisingly facile decomposition into pyrazines (**4**), we have made an investigation into the mechanism of this intriguing reaction.

Zbiral and Stroh,[5] who gave the first account of the transformation, attributed the smooth pyrazine formation to an intermolecular aza-Wittig reaction via the mechanism depicted in Scheme I.

Although the proposed reaction mechanism[5] does account for the products, it appears unsatisfactory for various reasons. An intermolecular head to tail aza-Wittig reaction would depend critically on the interrelationship of several factors, e. g., the nucleophilicity of the ylide nitrogen, the electrophilicity of the carbonyl carbon, and the distance between the two groups. Assuming that the reaction occurs as indicated in Scheme I, the ylides (**1**) should react with ketones, for example with the closely related (**7**). In the case of (**1**), the electrophilicity of the carbonyl carbon should be decreased (due to the negatively charged ylide nitrogen), and hence the carbonyl of (**7**) should in fact be more reactive in the aza-Wittig reaction than that of (**1**). Iminophosphoranes do not generally react with ketones, however, and under the rather mild conditions of the reaction in question, a nucleophilic attack of the ylide nitrogen of (**1**) on the carbonyl carbon of another ylide molecule is unlikely to occur. Furthermore, if the proposed intermolecular reaction course is correct, yields would be expected to be very low, due to the adverse entropy factor, and certainly less than the fair to good yields reported.[5]

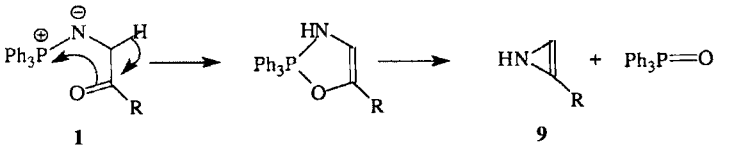
In order to test the postulate of an intermolecular reaction mechanism (Scheme I), we allowed iminophosphorane (**1**), R = Me or Ph, respectively, to react with acetophenone in methylene dichloride at room temperature. The iminophosphoranes were generated in situ from triphenylphosphine and one mol. equivalent of the appropriate azide at ambient temperature. The Staudinger reaction went to completion in a few minutes, but since no appreciable reaction occurred with the ketone, stirring was continued and the reaction mixture left at room temperature for several days. The subsequent workup yielded 2,5-diphenyl- and 2,5-dimethyl pyrazine, respectively. No trace were obtained of ketimines (**8**) (Scheme II). Similarly, performing the Staudinger reaction of (**6**) and triphenylphosphine in the



SCHEME II

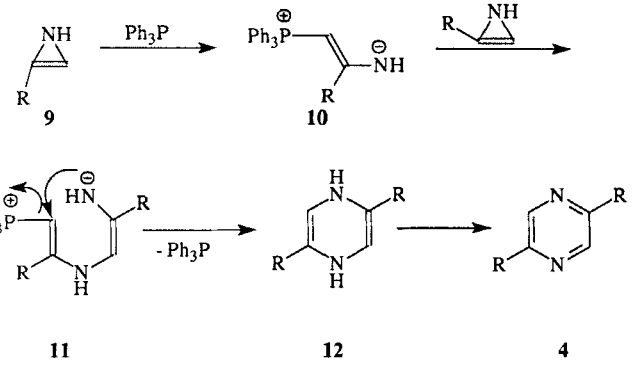
presence of a three-fold excess of benzophenone, failed to yield detectable quantities of (**8**), R_1 = Ph. Thus the present control experiments give no support for the proposal that the formation of pyrazines (**4**) proceed via an intermolecular aza-Wittig reaction.

Although there is some evidence available in favour of Wittig reactions of the type suggested,[6,7] we believe the present reaction of iminophosphoranes (**1**) follow another course. The fact that (**1**) do not react appreciably with ketones more susceptible than the ylidic carbonyl to nucleophilic attack, and the rather high yields of pyrazine, suggest that the reaction proceeds via an intramolecular first step, forming the presumably very unstable, and as yet unknown, 2-azirine (**9**) (Scheme III). Dimerization, either spontaneously, or more probably, by the catalytic influence of (**1**) or triphenylphosphine (**5**) present in the reaction mixture, converts (**9**) to the appropriate pyrazine (Scheme IV).



1 **9**

SCHEME III

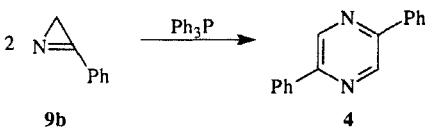


9 **10** **11** **12** **4**

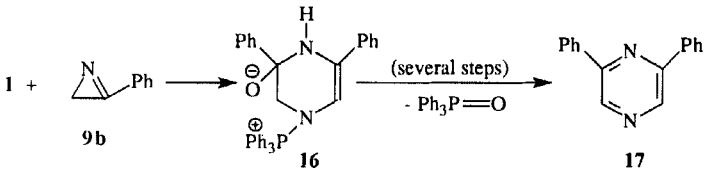
SCHEME IV

As (**9**) cannot be isolated, we have been unable to study the postulated catalytic influence of (**5**), or of thermodynamically stable analogues of (**1**) on its dimerization. However, the results from control experiments with the isolable 2-phenyl-1-azirine (**9b**) appear to confirm the expectations, and show, at least in case of the comparatively stable (**9b**), the catalytic influence of triphenylphosphine on the formation of 2,5-diphenyl pyrazine (Scheme V). Further control experiments also confirm the earlier report[5] that pyrazine formation from 2-phenyl-1-azirine is not catalyzed by triphenylphosphine oxide.

At first sight it would appear that the formation of pyrazine could also proceed via an addition of (**9**) to the intermediate iminophosphorane (**1**), followed by elimination of triphenylphosphine oxide. A closer scrutiny shows, however, that

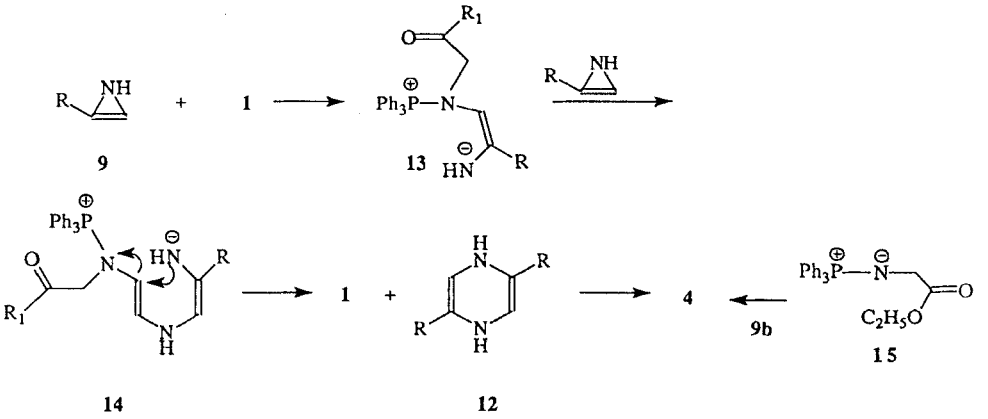


SCHEME V



SCHEME VI

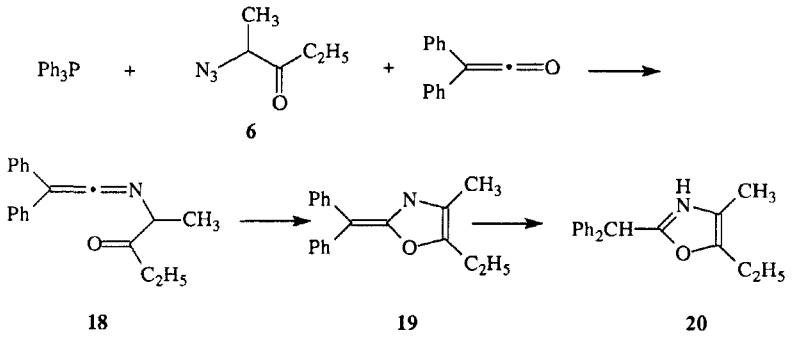
this reaction would lead to the intermediate (**16**), affording ultimately 2,6-pyrazines (**17**), instead of the 2,5-derivatives actually isolated (Scheme VI). An initial nucleophilic attack at the 2-position of (**9**) would lead to 2,5-pyrazines though, but the latter reaction course is considered less likely. Control experiments show, however, that the isolable ylide (**15**) rapidly transforms (**9b**) into 2,5-diphenyl pyrazine (**4**). This suggests a catalytic mechanism analogous to that proposed for triphenylphosphine. On account of the catalytic activity of (**15**) being superior to that of (**5**), it is concluded that pyrazine formation mainly proceeds through interaction of (**1**) with the intermediate 2-azirine (**9**) to afford (**4**) via the dihydropyrazine (**12**) as shown in Scheme VII.



SCHEME VII

Reactions with Diphenylketene, 2,2,4,4-Tetraphenyl-N,N'-bis(2-pentane-3-on)-cyclobutane-1,3-diimine (**21**)

Staudinger phosphorylation of the 2-azido-3-pentanone (**6**) (Scheme VIII) in the presence of an equimolar amount of diphenylketene gave, even under the mildest



SCHEME VIII

conditions, no trace of the ketenimine (**18**) or the 1,3-oxazole (**20**), expected in analogy with the reaction products when the same phosphorylation is performed in the presence of isocyanates or isothiocyanates.[1] Workup of the crude product led to isolation of a compound with molecular weight 554. Apparently the ketenimine (**18**) was generated initially, and then immediately consumed in a ($2\pi + 2\pi$) cycloaddition, yielding a product which could be (**21**), (**22**), (**23**), or (**24**) as depicted in Fig. 1.

The dimer, which was purified by column chromatography, exhibited a strong IR absorption at 1725 cm^{-1} Evidence for structures (**21**) and (**22**) were provided by mass spectrometry. Fragmentation of (**23**) and (**24**) would in the first place give rise to three different fragments, m/z 265, 277, and 289, whereas the symmetrical structures (**21**) and (**22**) would give rise to one fragment, m/z 277, only. Chemical

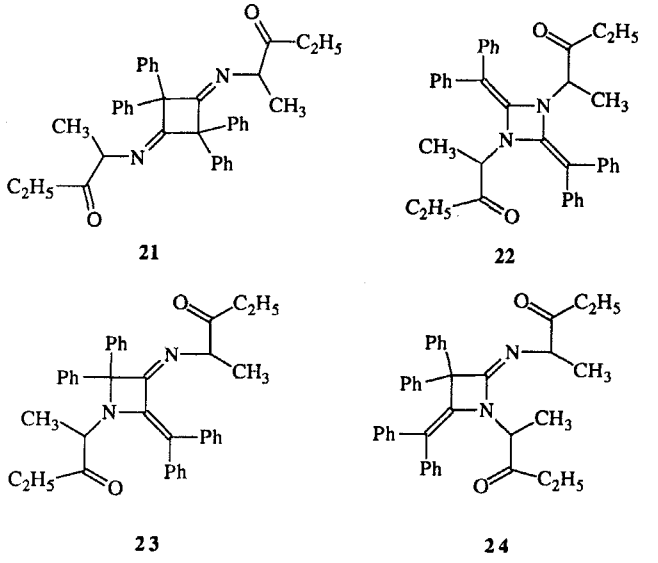
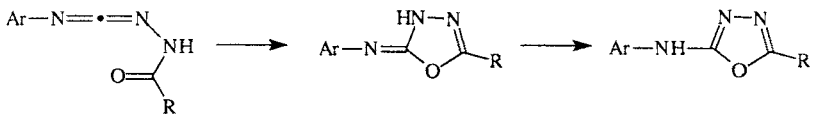


FIGURE 1

ionization mass spectrometry gave a low intensity molecular ion peak ($M^+ + 1$) at m/z 555, whereas other mass spectra (EI, 70 eV) showed $M^+/2$ at m/z 277 and no trace of m/z 265 and m/z 289. Thus structures (**23**) and (**24**) can be discarded. Structures (**21**) and (**22**) both account for IR, ^1H NMR, and MS data. Conclusive evidence for structure (**21**) was provided by ^{13}C NMR spectroscopy where the absorptions at δ 121.46 and δ 56.22 eliminate (**22**) (see under experimental).

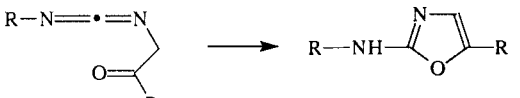
The Reaction between Diphenylketene and N-acylamino Iminotriphenylphosphoranes (**2**)

In a preceding paper[4] a new route to a wide range of 1,3,4-oxadiazoles was described, involving reaction of (**2**) with various isocyanates, isothiocyanates, and with carbon disulfide. The experimental results appeared to give strong support for the conclusion that the reaction proceed via the intermediate formation of a β-keto carbodiimide (**25**), which undergoes cyclization to afford (**27**) (Scheme IX). Similarly, it was found[1] that iminophosphoranes (**1**) reacted smoothly with isocyanates and isothiocyanates to give the likewise very reactive carbodiimides (**28**), which rearrange spontaneously to the 2-amino-oxazole (**29**) (Scheme X).



25 **26** **27**

SCHEME IX

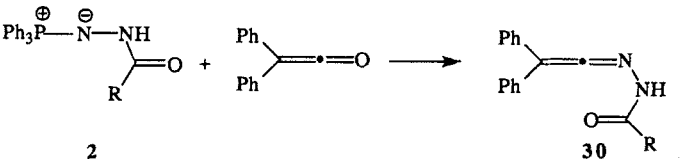


28 **29**

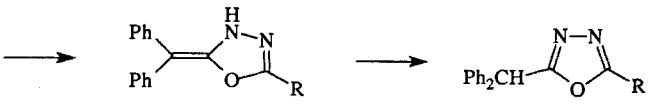
SCHEME X

In view of the surprisingly easy formation of the highly strained cyclobutane (**21**) in the reaction of (**1**) with diphenylketene, it was of interest to investigate the reaction of the N-acylamino iminotriphenylphosphoranes (**2**) with ketenes, to see if the intermediate ketenimine (**30**) preferred a reaction course analogous to that of (**18**), or if the iminophosphorane-based synthesis of 1,3,4-oxadiazoles could be extended. Reacting a solution of (**2a–d**) with one mol. equivalent of diphenylketene immediately gave the crystalline 2-diphenylmethyl-5-Ar-1,3,4-oxadiazoles (**32**) in excellent yield (Scheme XI). Contrary to the behaviour of (**1**) with the same reagent, no trace of dimerization products could be detected in the reaction mixture of (**2**) and diphenylketene.

Reactions of N-(2-acetamido) iminotriphenylphosphoranes (**33, 38**). In contrast to (**1**) which undergo a rapid intramolecular reaction, the amides (**33**) and (**38**) can be isolated and are quite stable, although somewhat more reactive than (**1**) in the aza-Wittig reaction. In one experiment a solution of (**33**) was allowed to react with



2 30

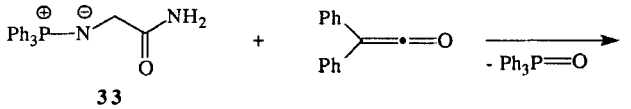


31 32

32a R = C_6H_5
32b R = 4-CH_3-C_6
32c R = 4-$NO_2C_6H_4$
32d R = 4-Cl-C_6H_4

SCHEME XI

one mol. equivalent of diphenylketene at room temperature. The reaction mixture became warm and subsequent cooling gave the crystalline (**36**), presumably via the intermediate ketenimine (**34**) (Scheme XII). That the final product is the conjugated isomer (**36**) and not (**37**), or the apparent precursor (**35**), is demonstrated by the ^{1}H NMR absorptions at 5.03 (s, 1H), 4.20 (d, 2H, J = 5.5 Hz) and 9.03 (t, 1H, J = 5.5 Hz). The reactions of (**33**) and (**38**) with isocyanates and isothiocyanates follow similar routes. Substitution at the amide nitrogen as in (**38**), prevents formation of the conjugated isomer, and (**42**) is here the sole product (Scheme XIII). Rather surprisingly, this is also the case with the unsubstituted amide (**33**), however. In striking contrast to the reaction of diphenylketene, reactions of isocyanates and isothiocyanates with the same reagent (**33**), give exclusively the 1,5-dihydroimidazol-4-one (**41**).



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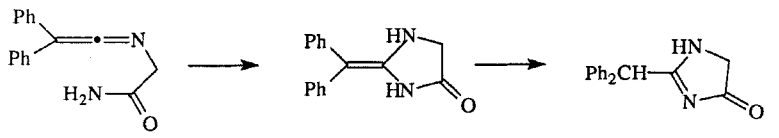
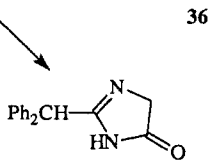
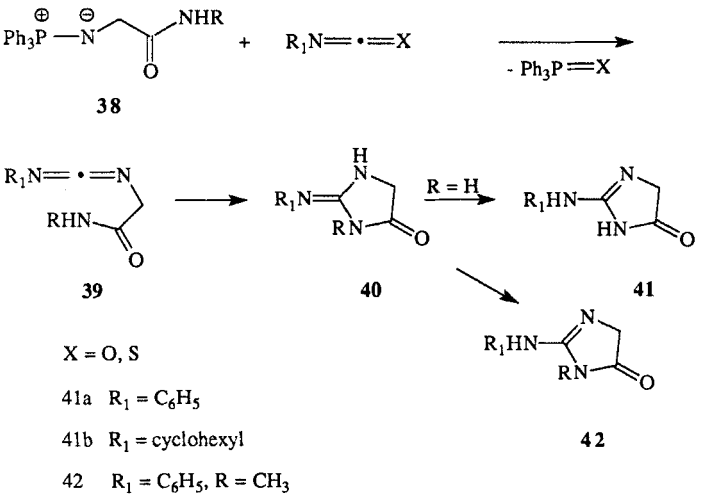


34 35 36



37

SCHEME XII



SCHEME XIII

EXPERIMENTAL

Starting materials. 2-Azido-N-methyl acetamide (**6e**). Reacting ethyl chloroacetate with sodium azide in methanol gave ethyl azidoacetate which was treated with methylamine to afford the desired amide. 2-Azido acetamide (**6d**) was prepared as described by Foster.[8] Azidoketones. ω-azidoacetophenone (**6a**), azidoacetone (**6b**), and 2-azido-3-pentanone (**6c**) were made from the corresponding chloroketones by treatment with two molar equivalents of sodium azide in methanol. The latter solvent was found to be more convenient and yields were consistently better than in DMSO. Iminophosphoranes (**33**) and (**38**) were prepared in excellent yields from triphenylphosphine by treatment with (**6d**) and (**6e**), respectively, in dichloromethane solution. 2-Phenyl-1-azirine was synthesized according to the method of Smolinsky.[9] The iminophosphoranes (**2a–d**) were prepared via the phosphonium salts, made from triphenylphospine dibromide and the appropriate acylhydrazide together with an equimolar amount of triethylamine in dichloromethane solution. The phosphonium salts were collected by filtration, freed from triethylammonium bromide with a little cold water, washed with ether and dried. The salt was thereafter dissolved in DMSO and added to an ice-cooled aqueous solution of sodium carbonate. The crystalline product was separated by filtration, washed with water and crystallized to give the desired iminophosphorane.

Attempted reaction of (1, R = Ph) with acetophenone. Triphenylphosphine (0.26 g, 1.0 mmol) was added to a stirred solution of ω-azido acetophenone (0.15 g, 1.0 mmol) and acetophenone (0.36 g, 3.0 mmol) in 3 ml dichloromethane. After 12 h at room temperature, the separated yellow crystals were filtered off, washed with ether and recrystallized from ethanol to give colourless leaves of 2,5-diphenylpyrazine, m.p. 196–202°C. Lit[5]. m.p. 190–196°C. Gc analysis of the filtrate showed the presence of three compounds. These were identified by gc/ms as unreacted acetophenone, 2,5-diphenylpyrazine, and triphenylphosphine oxide.

The experiement was thereafter repeated, this time without the acetophenone, but with 3.0 mmol of benzophenone present in the reaction mixture. Gc/ms analysis showed in addition to unreacted benzophenone, the presence of triphenylphosphine oxide, and 2,5-diphenylpyrazine (**4**). MS (70 eV):m/z (%) 232 (30.8, M^+), 103 (100, PhCN).

Attempted reaction of (1, R = CH_3) with acetophenone. To a mixture of triphenylphosphine (0.26 g, 1.0 mmol) and acetophenone (0.36 g, 3.0 mmol) in 3 ml chloroform was added azidoacetone (0.1 g, 1.0 mmol). The reaction mixture was left with vigorous stirring at ambient temperature for 2 h, whereafter the temperature was raised to 50°C for 16 h. Analysis of the reaction mixture showed, in addition to unreacted acetophenone, only two products. These were identified as triphenylphosphine oxide and 2,5-dimethylpyrazine by comparison of retention times and mass spectra of authentic samples.

Reaction of 2-phenyl-1-azirine (**9b**) *with* (**15**). Triphenylphosphine (**5**) (0.26 g, 1.0 mmol) was added to a stirred solution of ethyl azidoacetate (0.13 g, 1.0 mmol) in 2 ml chloroform. After completion of the Staudinger reaction, 2-phenyl-1-azirine (0.12 g, 1.0 mmol) was added in one portion. After 10 d at room temperature, the separated crystals of 2,5-diphenylpyrazine were filtered off (0.10 g), m.p. 202°C. Lit. 190–196°C; MS (70 eV): m/z (%) 234 (26.6), 233 (73.4), 232 (100, M^+), 103 (49.8, PhCN), 102 (99.3), 76 (13.6).

Reaction of 2-phenyl-1-azirine (**9b**) *with* (**5**). Triphenylphosphine (**5**) (0.26 g, 1.0 mmol) in 1 ml benzene was heated with 2-phenyl-1-azirine (0.12 g, 1.0 mmol) at 70°C for one week. The red colour of the dihydropyrazine (**12**) could be observed after 2–3 h. After cooling, the reaction mixture was analyzed by gc/ms and found to contain (**5**) and unreacted (**9b**) as the major components and 2,5-diphenylpyrazine (**4**) together with (**12**) as the minor products.

2,2,4,4-Tetraphenyl-N,N'-bis(2-pentane-3-on)-cyclobutane-1,3-diimine (**21**) *was prepared by adding triphenylphosphine (0.26 g, 1.0 mmol) to a vigorously stirred solution of diphenylketene (0.19 g, 1.0 mmol) and 2-azido-3-pentanone (0.14 g, 1.0 mmol) in 3 ml dichloromethane.* The reaction went to completion in a few minutes at ambient temperature. The dichloromethane was evaporated, to give a yellow oil which was chromatographed on silica gel. Elution with a mixture of petroleum ether and ether (**4:1**) gave 0.11 g, 39.7 % of (**21**), m.p. 135–137°C (from ether/pentane).

General procedure for the preparation of 1,3,4-oxadiazoles (**32a–d**). To a solution of 3.0 mmol iminophosphorane (**2**) in 10 ml of dichloromethane is added dropwise with vigorous stirring a solution of 3.0 mmol of diphenylketene in 1 ml of the same solvent. The reaction is completed in a few minutes at ambient temperature, and the reaction mixture is stirred at room temperature for another 30–40 min. The reaction mixture is thereafter concentrated in vacuo, and the product either crystallized directly, or purified by column chromatography (silica gel, 1:5 ethylacetate/ether) to afford (**32**) in excellent yield. 1,5- and 3,5-dihydroimidazol-4-ones (**36**), (**41a–b**), and (**42**) are likewise prepared in virtually quantitative yields on reacting a dichloromethane solution of iminophosphorane (**28**) or (**33**) with an equimolar amount of diphenylketene or isocyanate, respectively. As the iminophosphoranes are sparingly soluble in most organic solvents, they are best generated in situ from triphenylphosphine and the appropriate azide, whereafter the heterocumulene is added to the vigorously stirred reaction mixture. In some cases the resulting product is practically insoluble in dichloromethane and can be crystallized directly. In other cases the products are more conveniently isolated by column chromatography.

(**6a**): m.p. 17°C. Lit.[10] 17°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.75 (s, 2H, CH_2), δ 7.45–7.67 (m, 3H, $H_{arom.}$), δ 7.88–7.93 (m, 2H, $H_{arom.}$).

(**6b**): b.p. 36°C/3 mm Hg. Lit.[8] 54°C/2 mm Hg; ^{1}H NMR (20 MHz, $CDCl_3$) δ 2.15 (s, 3H, CH_3), δ 3.94 9s, 2H, CH_3).

(**6c**): b.p. 38°C/3 mm Hg. Lit.[11] 45°C/2 mm Hg; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.05 (m, 3H, ethyl-CH_3), δ 1.38 (m, 3H, N_3-C-CH_3), δ 2.55 (m, 2H, CH_2), δ 3.91 (q, 1H, CH);

(**6d**): m.p. 57°C. Lit[8] 58°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.94 (s, 2H, CH_2), δ 6.47 and δ 6.83 (2H, NH_2) IR (film) ν 3360 (NH), 3180 (NH), 2120 (N_3), 1625 (C=O), 1410, 1312 cm^{-1}.

(**6e**): m.p. 41°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.80 (d, J 5.7 Hz, 3H, CH_3), δ 3.91 (s, 2H, CH_2), δ 6.61 (br.s., 1H, NH); IR (film) ν 3280 (NH), 3080 (NH), 2100 (N_3), 1660 (C=O), 1560, 1416, 1290, 1260 cm^{-1}.

(**2d**): m.p. 208°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27 (d, J 8.6 Hz, 2H), δ 7.33–7.46 (m, 15H,), δ 7.63 (d, J 8.6 Hz, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 127.39 (m-benzoyl), δ 128.29 and δ 128.55 (P-Ph-m), δ 128.73 (o-benzoyl), δ 130.03 and δ 130.8 (P-Ph-p), δ 131.64 and δ 131.84 (P-Ph-o), δ 135.59 (P-Ph-i), δ 160.11 (C=O); IR (film) ν_{max} 1640 cm^{-1} (C=O).

(**21**): m.p. 135–137°C; ^{1}H NMR (200 MHz, acetone-d_6) δ 0.84 (t, J 7.1 Hz, 6H, ethyl-CH_3), δ 1.29 (d, J 7.1 Hz, 6H, CH_3), δ 2.23–2.43 and δ 2.58–2.78 (m, J 7.2 Hz, 4H, CH_2), δ 4.25 (*q*, J 7.2 Hz, 2H, CH), δ 7.20–7.68 (m, 20H, $H_{arom.}$); ^{13}C NMR (50.3 MHz, acetone-d_6) δ 8.49 (CH_3), δ 15.57 (CH_3), δ 36.69 (CH_2), δ 52.33 (CH), δ 56.22 (CPh_2, δ 121.46 (C=N), δ 127.60, 127.89 (Ph-o), δ 128.66, 128.97 (Ph-p), δ 129.92, 130.13 (Ph-m), δ 210.63 (C=O); IR (film) ν 3010, 2970, 1725 (C=O), 1600, 1495, 1450, 1405, 744, 700 cm^{-1}; MS (70 eV): m/z (%) 277 (6.0, $M^+/2$), 220 (10.3, M/2-EtCO), 193 (20.7, M/2-C_5H_8N), 192 (97.9, M/2-C_5H_9O), 190 (11.9), 165 (44.9, $C_{13}H_9$), 115 (14.6); MS (CI, CH_4): m/z (%) 555 (0.8, $M^+ + 1$), 334 (1.8), 278 (12.6), 277 (15), 220 (21.2), 194 (14.8), 193 (61.0), 192 (100), 167 (15.0), 165 (26.1).

(**32a**): m.p. 137°C. Lit[12] 134°C. Ms (70 eV): m/z (%) 312 (77.8, M^+), 311 (100), 167 (41.9, Ph_2CH), 166 (19.8), 165 (36.4), 152 (12.7), 145 (14.5), 105 (38.5, PhCO).

(**32b**): m.p. 127°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3), δ 5.79 (s, 1H, $CHPh_2$), δ 7.27 (d, 2H, 5-Ar-m), δ 7.30–7.35 (m, 10H, Ph), δ 7.90 (d, 2H, 5-Ar-o); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.58 (CH_3), δ 48.87 ($CHPh_2$), δ 127.00, 127.64, 128.71, 128.88, 129.72, 138.73, 142.21; IR (film) ν_{max} 1635 (C=N); MS (70 eV): m/z (%) 327 (13.4), 326 (68.2, M^+), 325 (100, M-H), 180 (10.4), 167 (60.6, M-$C_9H_7N_2O$), 166 (22.7, Ph_2C), 165 (49.0), 159 (31.3), 152 (19.4), 119 (59.1, C_8H_7O).

(**32c**): m.p. 146°C; ^{1}H NMR (300 MHz, acetone-d_6) δ 6.03 (s, 1H, $CHPh_2$), δ 7.28–7.49 (m, 10H, Ph), δ 8.30 (m, 2H, 5-Ar-m), δ 8.39–8.44 (m, 2H, 5-Ar-o); ^{13}C NMR (75.4, acetone-d_6) δ 48.75 ($CHPh_2$), δ 123.45–130.16 (m, o,m,p-$C_{arom.}$), δ 139.31, 163.80, 168.44; IR (film) ν_{max} 1635 cm^{-1}; MS (70 eV): m/z (%) 358 (9.6), 357 (48.3, M^+), 356 (100, M-H), 180 (17.4), 179 (26.9), 178 (19.5), 167 (66.9), 166 (58.5), 165 (88.1), 152 (28.5), 150 (13.8).

(**32d**): m.p. 123°C; ^{1}H NMR (300 MHz, acetone-d_6) δ 5.90 (s, 1H, $CHPh_2$), δ 7.28–7.49 (m, 10H, Ph), δ 7.58–7.64 (m, 2H, 5-Ar-m), δ 7.99–8.50 (m, 2H, 5-Ar-o); ^{13}C NMR (75.4 MHz, acetone-d_6) δ 49.29 ($CHPh_2$), δ 128.35, 128.79, 129.17, 129.52, 129.63, 130.12, 130.34, 140.09, 164.8, 168.2; IR (film) ν_{max} 1635 cm^{-1} (C=N); MS (70 eV): m/z (%) 348 (17.1), 347 (40.7), 346 (53.3, M^+), 345 (100, M-H), 180 (15.8), 179 (19.9, M-$C_7H_4ClN_2O$), 178 (13.4), 168 (11.1), 167 (84.5, Ph_2CH), 166 (41.5), 165, (72.2), 152 (25.5), 141 (15.6), 136 (50.3).

(**33**): m.p. 194°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 3.42 (d, $^3J_{PNCH}$ 13.8 Hz, 2H, CH_2), δ 7.10–7.40 (br.s., 2H, NH_2), δ 7.49–7.69 (m, 15H, $H_{arom.}$); ^{13}C NMR (50.3 MHz, DMSO-d_6) δ 49.40 (CH_2), δ 128.82–129.04 (m, p-$C_{arom.}$), δ 131.53–132.19 (o-$C_{arom.}$), δ 133.94 (i-$C_{arom.}$), δ 175.96 and 176.42 (C=O); IR (film) ν 3380 (NH_2), 1670 (C=O), 1655 (C=O), 1430, 1315 (P=N), 1210, 1110, 950, 725, 714, 694 cm^{-1}; MS (70 eV): m/z (%) 334 (0.8, M^+), 304 (13.8), 290 (22.8), 278 (40.2, Ph_3P=O), 277 (100), 276 (13), 262 (10.0, Ph_3P), 201 (15), 199 (19.6), 183 (25.7), 77 (20.9).

(**38**): m.p. dec. from about 120°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 2.68 (d, J 4.7 Hz, 3H, CH_3), δ 3.44 (d, $^3J_{PNCH}$ 13.1 Hz, 2H, CH_2), δ 7.52–7.79 (m, 15H, $H_{arom.}$), δ 8.04 (br., 1H, NH); ^{13}C NMR (50.3 MHz, DMSO-d_6) δ 26.04 (CH_3), δ 49.20 (CH_2), δ 128.78–129.29 (m-$C_{arom.}$), δ 131.20–132.28 (o, p-$C_{arom.}$), δ 133.94 (i-$C_{arom.}$), δ 173.34 and δ 173.84 (C=O); IR (film) ν 3315 (NH), 3040, 2920, 2860, 2790, 1660 (C=O), 1520, 1432, 1315 (P=N), 1250, 1210, 1110, 920, 750, 720, 695 cm^{-1}.

(**36**): m.p. 158–159°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 4.20 (d, J 5.5 Hz, 2H, CH_2), δ 5.03 (s, 1H, $CHPh_2$), δ 7.32 (m, 10H, $H_{arom.}$), δ 9.02 (t, J 5.5 Hz, 1H, NH); ^{13}C NMR (50.3 MHz, DMSO-d_6) δ 28.17 ($CHPh_2$), δ 56.74 (CH_2), δ 117.69 (C=N), δ 126.99 (p-$C_{arom.}$), δ 128.47, 128.58 (o,m-$C_{arom.}$), δ 139.70 (i-$C_{arom.}$), δ 171.55 (C=O); IR (film) ν_{max} 1650 cm^{-1} (C=O); MS (70 eV): m/z (%) 250 (1.6, M^+), 168 (19.3), 167 (100, Ph_2CH), 165 (20.1), 152 (10.5).

(**41a**): m.p. 256°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.73 (s, 2H,CH_2), δ 7.09 (t, 1H, p-$H_{arom.}$), δ 7.33 (t, 2H, m-$H_{arom.}$), δ 7.48 (d, 2H, o-$H_{arom.}$), δ 7.60 (br.s., 1H, NHPh), δ 9.97 (br.s., 1H, ring-NH); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 48.97 (CH_2), δ 120.34 (o-$C_{arom.}$), δ 123.25 (p-$C_{arom.}$), δ 128.77 (m-$C_{arom.}$), δ 138.87 (i-$C_{arom.}$); IR (film) ν 3300 (NH), 1730 w, 1665, 1585, 1460, 1335, 1110, 750, 700 cm^{-1}; MS (70 eV): m/z (%) 176 (11.4), 175 (100, M^+), 119 (11.8), 118 (62.5, M-C_2H_3NO), 91 (13.1), 77 (20.3).

(**41b**): m.p. 269–270°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 1.03–1.45 (m, 3H), δ 1.50–2.30 (m, 5H), δ 2.54 (m, 1H), δ 3.40–3.57 (m, 2H), δ 3.63 (s, 2H, N-CH_2), δ 6.80–8.40 (br.d., 2H, NH); ^{13}C NMR (50.3 MHz, DMSO-d_6) δ 25.73, 26.25, 33.81, 50.49 (N-CH_2), δ 120.04 (C=N), δ 170.10 (C=O); IR (film) ν 2900, 1700w (C=O), 1625 (C=N), 1510, 1282, 1215, 1070 cm^{-1}; MS (70 eV): m/z (%) 181 (26.6, M^+), 138 (21.3, M-HNCO), 126 (16.6), 100 (100), 81 (14.6), 72 (14.4), 67 (21.2).

(**41c**): m.p. 198°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 2.99 (s, 3H, CH_3), δ 3.37 (br.s., 1H, NH), δ 3.86 (s, 2H, CH_2), δ 6.89 (m, 3H, o,p-$H_{arom.}$), δ 7.29 (t, 2H, m-$H_{arom.}$); ^{13}C NMR (50.3 MHz, DMSO-d_6) δ 26.27 (CH_3), δ 48.10 (CH_2), δ 122.05 (o-$C_{arom.}$), δ 122.41 (p-$C_{arom.}$), δ 128.94 (m-$C_{arom.}$), δ 150.80 (i-$C_{arom.}$), δ 171.58 (C=O); IR (film) ν 3310 (NH), 1740, 1665, 1588, 1465, 1340, 1235, 1110, 960, 750, 700 cm^{-1}; MS (70 eV): m/z (%) 190 (12.7), 189 (100, M^+), 188 (21.7), 160 (32.6), 133 (14.1, M-C_2H_2NO), 132 (75.4, M-CH_3NCO), 131 (32.3), 106 (10.3), 104 (25.8, PhNCH).

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REFERENCES

1. P. Frøyen, *Phosphorus, Sulfur, and Silicon*, **60,** 81 (1991).
2. H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2,** 635 (1919).
3. H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4,** 861 (1921).
4. P. Frøyen, *Phosphorus, Sulfur, and Silicon*, **57,** 11 (1991).
5. E. Zbiral and J. Stroh, *Ann. Chem.*, **727,** 231 (1969).
6. C. E. Griffin and G. Witschard, *J. Org. Chem.*, **27,** 3334 (1962).
7. C. E. Griffin and J. A. Peters, *J. Org. Chem.*, **28,** 1715 (1963).
8. M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93,** 72 (1908).
9. G. Smolinsky, *J. Org. Chem.*, **27,** 3557 (1962).
10. J. H. Boyer and D. Straw, *J. Am. Chem. Soc.*, **75,** 1642 (1953).
11. M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93,** 669 (1908).
12. H. Aspelund, *Acta Acad. Abo.*, **5**, 1 (1928).