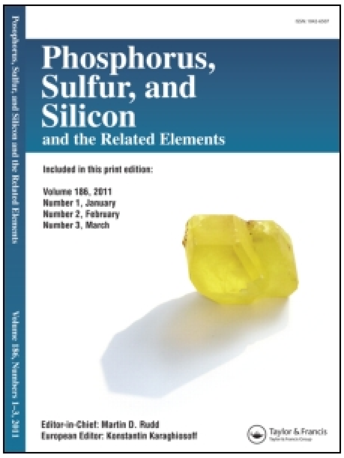

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# HYDRAZONES FROM YLIDES AND DIAZONIUM SALTS: A CONVENIENT SPOT TEST FOR STABILIZED YLIDES OF PHOSPHORUS, ARSENIC, AND SULFUR

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# HYDRAZONES FROM YLIDES AND DIAZONIUM SALTS: A CONVENIENT SPOT TEST FOR STABILIZED YLIDES OF PHOSPHORUS, ARSENIC, AND SULFUR

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The reactions of a series of stabilized ylides of phosphorus, arsenic and sulfur with 2,4-dinitrobenzenediazonium tetrafluoroborate are described. The reaction courses, leading either to azo-onium salts (**II**), azo-onium ylides (**III**), formazans (**IV**) or hydrazones (**VI**), are discussed. The formation of hydrazone, which constitutes a new reaction of stabilized ylides, is interpreted in terms of stability of the transition state and of the hydrazone carbanion formed in the hydrolytic decomposition of (**II**) and (**III**). The spot test depends on the specific colour produced by the hydrazone in basic conditions, and permits detection of many stabilized ylides in concentrations down to 0.3–0.5 $\mu g/\mu l$.

*Key words:* Stabilized ylides; spot test; synthesis; hydrazones.

## INTRODUCTION

Reactions between phosphonium ylides and diazonium salts have been reported in two papers. Ramirez and Levy[1] observed that cyclopentadienylidene triphenylphosphorane reacted with benzene- and 4-nitrobenzenediazonium salts with substitution into the 2-position of the cyclopentadienyl anion. Later Märkl[2] caused to react a series of more conventional phosphonium ylides (**I**) with diazonium salts (Scheme I) and obtained azophosphonium salts (**II**), azophosphonium ylides (**III**), and formazans (**IV**) Scheme I, which indicate attack on the carbon atom alpha to phosphorus.

Hydrazones have not been mentioned as products from any of these reactions. We now wish to report the formation of hydrazones from the reaction of 2,4-dinitrobenenediazonium tetrafluoroborate (2,4-dnbt) with a variety of stabilized ylides of phosphorus as well as arsenic, nitrogen, and sulfur.

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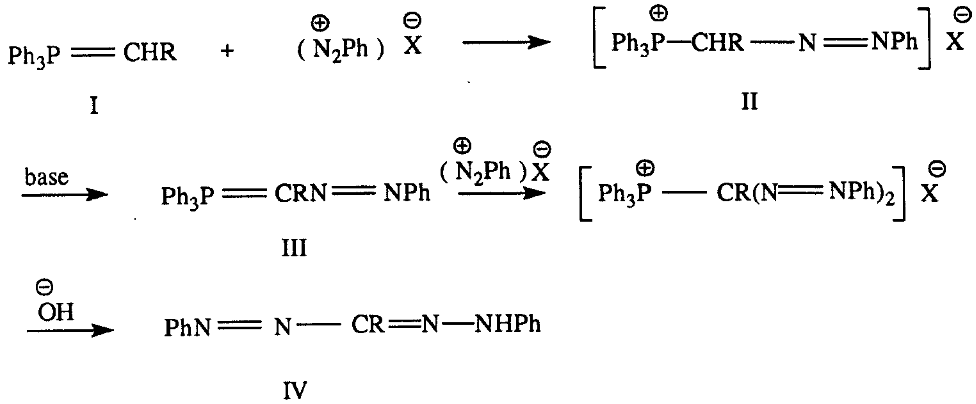


$$\underset{\mathrm{I}}{\mathrm{Ph_3P{=}CHR}} + (\overset{\oplus}{\mathrm{N_2Ph}})\,\overset{\ominus}{X} \longrightarrow \underset{\mathrm{II}}{\left[\overset{\oplus}{\mathrm{Ph_3P}}\mathrm{{-}CHR{-}N{=}NPh}\right]\overset{\ominus}{X}}$$

$$\xrightarrow{\text{base}} \underset{\mathrm{III}}{\mathrm{Ph_3P{=}CRN{=}NPh}} \xrightarrow{(\overset{\oplus}{\mathrm{N_2Ph}})\overset{\ominus}{X}} \left[\overset{\oplus}{\mathrm{Ph_3P}}\mathrm{{-}CR(N{=}NPh)_2}\right]\overset{\ominus}{X}$$

$$\xrightarrow{\overset{\ominus}{\mathrm{OH}}} \underset{\mathrm{IV}}{\mathrm{PhN{=}N{-}CR{=}N{-}NHPh}}$$

SCHEME I

## RESULTS

In connection with the purification of the ylides **5** and **16** Table I, we were in search of a convenient spot test for monitoring the ylides in the effluent from a chromatographic column. In one experiment the effluent was spotted on a silica gel TLC plate and sprayed with a freshly prepared solution of 2,4-dnbt in acetonitrile. When the TLC plate thereafter was exposed to diethylamine vapour, the spot immediately gave orange or red colour reactions characteristic of the hydrazone[3] **VI** (Scheme II) of the carbonyl compound corresponding to the carbanion portion of the ylide **V**.

Further investigation of this reaction by thin layer chromatography (TLC) with a number of stabilized phosphonium, arsonium, pyridinium and sulfonium ylides, in each case compared with the authentic hydrazone, showed it to be fairly general, although the specificity of the reaction depended strongly on the nature of the substituents $R^1$ and $R^2$ and the onium atom Y. The reaction is particularly efficient in the case of functionally disubstituted ylides, and it should be noted that many ylides usually too stable to undergo the Wittig or other characteristic ylide reactions, can be detected rapidly and with high sensitivity by the present spot test procedure (cf. Experimental part). The reaction may also be of some value for the preparation of hydrazones which are difficult to obtain by the normal procedures, e.g., those from ylides **1**, **4**, **10**, **12**. The results are summarized in Table I.

Acetonitrile proved to be the most suitable reaction medium. For preparative purposes the solid diazonium salt was added in one portion with rapid stirring to a solution of ylide in acetonitrile. The reaction mixture usually was applied directly to a preparative TLC plate in order to isolate the main products. In some cases the hydrazone occurred as a mixture of syn and anti isomers. Some ylides (**20**, **22**, **26**, **27**) gave in addition to the hydrazone a reaction product which did not move on the TLC plate, but which readily was converted to the hydrazone after treatment of the reaction mixture with liquid diethylamine. This intermediate product probably is the azo-onium salt corresponding to II (Scheme I).

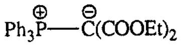
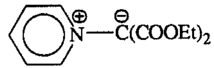
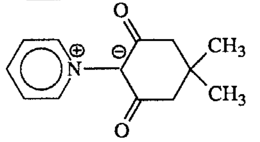
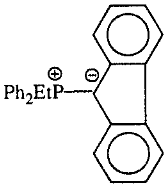
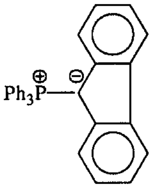
In other cases (**1**, **10**, **19**) the reaction product moved rapidly as a yellow spot,

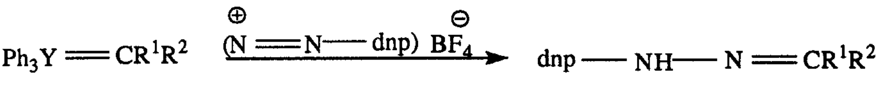
TABLE I

Reaction of some stabilized ylides with 2,4-dinitrobenzenediazonium tetrafluoroborate in acetonitrile

| No | Ylide | Primary product | $Et_2NH$ converts prim. prod. to |
|---|---|---|---|
| 1 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}HCN$ | Azophosphonium ylide | Hydrazone |
| 2 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(Me)CN$ | Hydrazone | |
| 3 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(CN)Ph$ | Hydrazone | |
| 4 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(CN)COMe$ | Hydrazone | |
| 5 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(CN)COOMe$ | Hydrazone | |
| 6 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}(CN)COOEt$ | Hydrazone | |
| 7 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(Me)COMe$ | (Hydrazone) | |
| 8 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(Me)COOMe$ | (Hydrazone) | |
| 9 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(Me)COOEt$ | (Hydrazone) | |
| 10 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}HCOMe$ | Azophosphonium ylide | Hydrazone |
| 11 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}HCOMe$ | (Formazan) + (Hydrazone) | |
| 12 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}HCOPh$ | (Formazan) + (Hydrazone) | |
| 13 | $Me_2\overset{\oplus}{S}—\overset{\ominus}{C}HCOPh$ | (Hydrazone) + (Formazan) + (Azosulfonium ylide) | |
| 14 | $Ph_2\overset{\oplus}{S}—\overset{\ominus}{C}HCOPh$ | (Hydrazone) + (Azo-ylide) | |
| 15 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}HCO\ C_6H_4Me(p)$ | (Formazan) + (Hydrazone) | |
| 16 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}HCOC_6H_4NO_2(p)$ | (Formazan) + (Hydrazone) | |
| 17 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}HCOC_6H_4Ph(p)$ | (Formazan) + (Hydrazone) | |
| 18 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}HCOOMe$ | decomposition [c] | |
| 19 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}HCOSEt$ | Azophosphonium ylide | Hydrazone |
| 20 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}(COOMe)Ph$ | (Hydrazone) + Azoarsonium salt | Hydrazone |
| 21 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}(COOMe)picryl$ | (Hydrazone) | |
| 22 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(COOEt)Ph$ | (Hydrazone) + Azophosphonium salt | Hydrazone |
| 23 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}(COOMe)COPh$ | Hydrazone | |
| 24 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(COOMe)COCOOMe$ | Hydrazone | |
| 25 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}(COOMe)C{=}NPhCOOMe$ | (Hydrazone) | |
| 26 | $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(COMe)_2$ | Hydrazone + Azophosphonium salt | Hydrazone |
| 27 | $Ph_3\overset{\oplus}{As}—\overset{\ominus}{C}(COMe)_2$ | Hydrazone | |

TABLE I (*Continued*)

| No | Ylide | Primary product | $Et_2NH$ converts prim. prod. to |
|---|---|---|---|
| 28 |  $Ph_3\overset{\oplus}{P}—\overset{\ominus}{C}(COOEt)_2$ | Hydrazone | |
| 29 |  | Azopyridinium salt<br>+<br>(Hydrazone) | Hydrazone |
| 30 |  | Azopyridinium salt<br>+<br>(Hydrazone) | Hydrazone |
| 31 |  | Azophosphonium salt<br>+<br>(Hydrazone) | Hydrazone |
| 32 |  | Azophosphonium salt<br>+<br>(Hydrazone) | Hydrazone |



$$\underset{\text{V}}{Ph_3Y{=}CR^1R^2} \xrightarrow{(\overset{\oplus}{N}{\equiv}N—dnp)\ \overset{\ominus}{BF_4}} \underset{\text{VI}}{dnp—NH—N{=}CR^1R^2}$$

dnp = 2,4-dinitrophenyl.

SCHEME II

which only slowly gave the colour reaction of the hydrazone. After several hours in contact with the silica gel, or on prolonged treatment in solution with diethylamine, or more instantaneously on treatment with sodium hydroxide solution, the hydrazone was obtained. This behaviour is consistent with an azo-onium ylide structure (cf. III).

Several of the mono-substituted ylides (**11–13**, **15–17**) yielded mixtures of hydrazone and another product which gave a blue colour reaction with bases. The latter product was shown to be the formazan (cf. IV, Scheme I) by comparison with original samples obtained by coupling the corresponding dinitrophenylhydrazones with 2,4-dnbt.

Chromatograms on fluorescent layer (exited by 254 nm light) showed, in addition to the hydrazone and other spots, a colourless, fluorescence-quenching spot at or very close to the starting point, corresponding to authentic triphenylphosphine oxide or triphenylarsine oxide. Authentic triphenylphosphine and triphenylarsine moved more rapidly.

These observations support the reaction scheme proposed by Märkl[2] as far as the formation of azo-onium salt (**II**), azo-onium ylide (**III**), and formazan (**IV**) is concerned. It should be pointed out, however, that the formazan may also arise from the hydrazone (**VI**, $R^1 = H$) by diazo coupling.

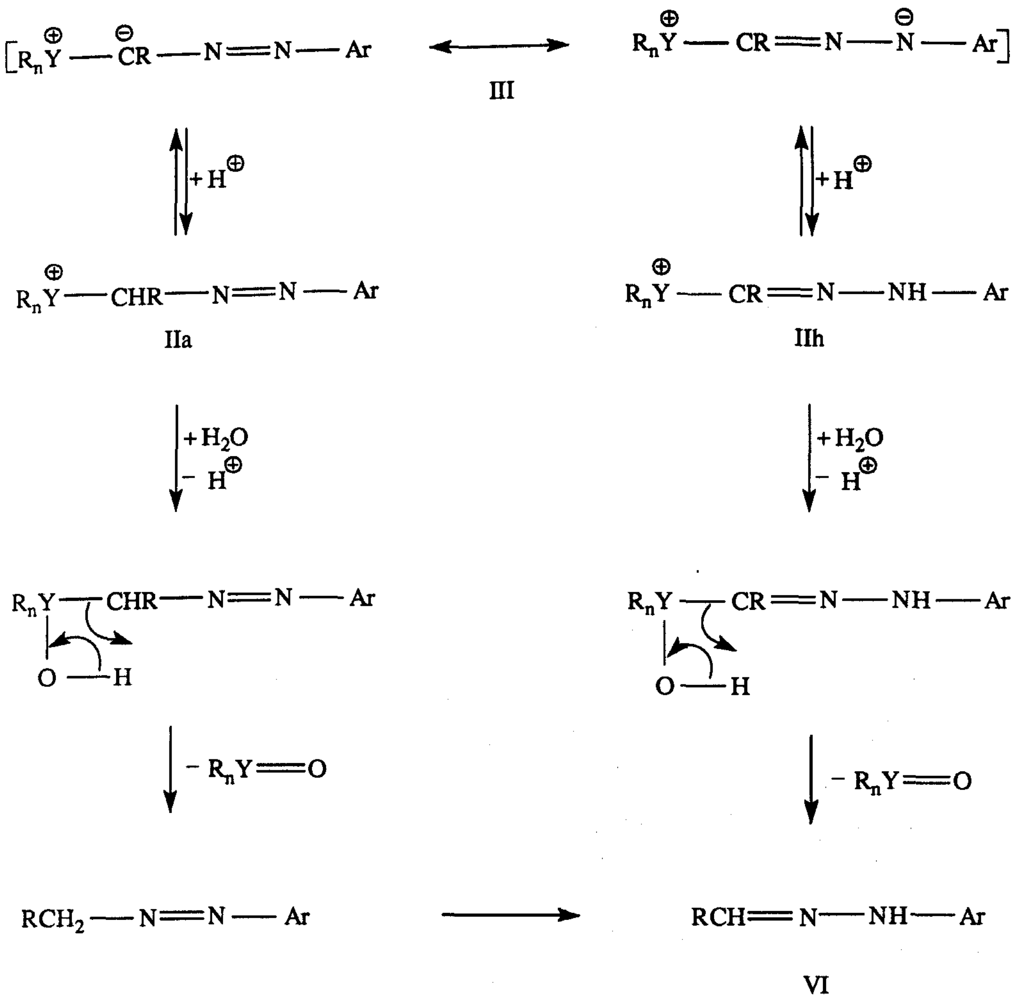
## DISCUSSION

The hydrazone-forming reaction probably occurs mainly via hydrolysis of the azo-onium salt by moisture present in the untreated acetonitrile or the TLC silica gel (cf. Scheme III).

The prototropic equilibrium between azo-onium ylide III and azo-onium salt IIa makes it reasonable to assume an initial transformation of **III** back into **IIa** before hydrolysis (Scheme III, left-hand part). Further, the occurrence of the azo-onium salt (**IIa**) in the tautomeric hydrazono-onium salt form **IIh** may indicate the right-hand part of Scheme III as an important reaction alternative. In view of the stabilizing effect of the azo group on the intermediate azo-onium ylide observed by Märkl,[2] the ready formation of hydrazone may seem surprising. However, the acidity of these strongly polar hydrazones, with pKa values in the range 4.8 (**4h**), 6.0 (**6h**), 8.8 (**1h**), to 9.2 (**2h**),[4] where **h** denotes the 2,4-dinitrophenylhydrazone obtained from the ylide indicated by the preceding number, points to a high degree of stability of the emerging hydrazone carbanion, and hence to an increased stability of the transition state itself. In accordance with this it was found that ylides with two electron withdrawing substituents on the carbon adjacent to the onium atom (e.g., **2–6**, **27**) produce hydrazone more readily and cleanly than ylides containing $\alpha$-H. Moreover it appears that alkyl substitution at the ylidic carbon, i.e., **7–9**, tends to reduce the yield of hydrazone since electron donating substituents make the carbanion a poorer leaving group, leading to a low rate of reaction.

Clearly the hydrazone formation is less dependent on the onium group than on the nature of the carbanion substituents: ylides of phosphorus as well as arsenic, sulfur, and even nitrogen undergo the reaction. It appears, however, that the present reaction is applicable only to ylides of low nucleophilicity, i.e. strongly stabilized ylides.

Already the introduction of one hydrogen atom at the carbanion constitutes a complication, partly because of the formation of **III** and **IV**, and, more importantly, because the primarily formed azo-onium salt (**II**) is less susceptible to hydrolysis. This may be inferred from the observation that **III** is the main primary product from many of the $\alpha$-H ylides, and that treatment with additional base is necessary to obtain the hydrazone end product (Table I). In some critical instances, i.e. with only one strongly stabilizing group at the carbanion, it appears that even the Ar substituent (Scheme III) has a marked effect on the reaction course. In these cases the increase in electronegative character of the Ar substituent in **II** or **III** along the series Ar = Phenyl[2] < 4-nitrophenyl[2] < 2,4-dinitrophenyl would suggest a



$R_nY$ = $Ph_3P$, $Ph_3As$, $Ph_2S$, $Me_2S$
dnp = 2.4-dinitrophenyl.

SCHEME III

corresponding increase in the amount of hydrazone formed by hydrolysis, e.g., through increasing stability of the transition state and/or the $\alpha$-C fragment anion (Scheme III).

As shown by the relative stabilities of the 4-nitro- and 2,4-dinitrophenylhydrazone tautomers of azophenols,[5] the effect of a 4-nitro substituent is probably far less than that of 2,4-dinitro. This may explain why Märkl[2] did not observe the hydrazone as an end product with Ar = Phenyl or 4-nitrophenyl, whereas it is a main product in the present series.

The observed cleavage of the azo-onium salt or azo-onium ylide by excess diethylamine or sodium hydroxide in the presence of moisture is explained by a similar hydrolysis (cf. Scheme III), initiated by hydroxide ion.

## EXPERIMENTAL

$^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Gemini-200 spectrometer operating at 200 and 50.3 MHz, respectively. Infrared spectra were measured with a Perkin Elmer 1310 spectrophotometer. The mass spectra were obtained on a VG Micromass 7070F instrument. Column chromatography was carried out using Merck No. 9385 Silica gel 60. Thin layer chromatography was performed using Merck No. 60765 silica gel GF254.

### *Spot test for stabilized ylides*

*Materials:* 2,4-dinitrobenzene tetrafluoroborate, diethylamine, silica TLC sheet (Merck alufolien).

*2,4-Dnbt reagent:* 0.02% solution of 2,4-dnbt in acetonitrile containing 0.01% of 40% $HBF_4$ as a stabilizer.

*Procedure.* A 1 μl sample of supposed ylide solution is applied to a piece of silica TLC sheet, dried, and lightly sprayed with the 2,4-dnbt reagent. After one minute the TLC sheet is held for a second in a small TLC tank containing a few ml of diethylamine. Formation of an orange, red, purple, etc., colour confirms the presence of ylide in the sample. The colour is easily observable with ylide concentrations down to 0.3–0.5 μg/μl. The particular colour produced depends on the type of carbonyl compound corresponding to the carbanion portion of the ylide, ranging from red orange (**1**) through bright red (**4**) to various dark red shades (**3**, **12**, **21**, **30**). A dark blue (**31**) colour, due to azo-onium salt anion or formazan, or golden yellow (**10**), due to azo-ylide and not influenced by the amine vapour, likewise may indicate the presence of ylide. Other colours (black, brown) may be due to mixtures and should be examined by TLC. More concentrated diazonium salt solutions than indicated above work well with ylide concentrations above about 1 μg/μl, but tend to give bluish or greyish colours with more dilute ylide samples, probably as a result of further reactions of the excess diazonium salt. Also, the more intense background colour tends to mask the colour of weaker spots. The reagent is well suited as a spray reagent in TLC analysis of ylides.

$Al_2O_3$ TLC sheets are not recommended as a spot test medium due to weaker colour response.

*Preparation of ylides.* With the exception of the synthesis of the two compounds described below, the ylides were prepared from the corresponding phosphonium, arsonium, and sulfonium salts in analogy with methods described in the literature.[6–16] The melting points, IR and NMR spectral data were compatible with the structures. The pyridinium ylides **29** and **30** were prepared by the following general procedure: To a vigorously stirred solution of 0.05 mol of the appropriate ester or ketone (diethyl malonate and 5,5-dimethyl-1,3-cyclohexanedione, respectively) in chloroform (80 ml), was added a solution of bromine (8 g, 0.05 mol) in carbon tetrachloride (50 ml) with vigorous stirring. Pyridine (12 g, 0.25 mmol) was thereafter added, and the mixture was stirred overnight at ambient temperature. The precipitated pyridinium hydrobromide was removed by filtration, the solvents evaporated in vacuo, and the remaining product extracted with ethyl acetate. Evaporation of this solvent yielded the crystalline ylide, which was purified by recrystallization from acetone-ethyl acetate (**29**) or 1,2-dichloroethane (**30**).

*Pyridinium diethoxycarbonylmethylide* (**29**) (67%) m.p. 177–179°C, lit.[17] 170–171°C; $^1H$ NMR (200 MHz, $CDCl_3$) δ 1.15 (m, 6 H, $CH_3$), δ 4.03 (m, 4H, $CH_2$), δ 7.65 (t, 2H, 3'-H), δ 8.06 (t, 2H, 2'-H), δ 8.46 (d, 1H, 4'-H); $^{13}C$ NMR (50.29 MHz, $CDCl_3$) δ 15.22 ($CH_3$), δ 59.23 ($CH_2$), δ 97.95 (C-carbanion), δ 126.26 (3'-C), δ 141.90 (4'-C), δ 150.40 (2'-C), δ 165.30 (C=O).

*Pyridinium 4,4-dimethyl-2,6-dioxocyclohexylide* (**30**) (65%) m.p. 133–136°C; $^1H$ NMR (200 MHz, $CDCl_3$), δ 1.02 (s, 6H, $CH_3$), δ 2.46 (s, 4H, $CH_2$), δ 8.15 (m, 2H, 3'-H), δ 8.60 (m, 1H, 4'-H), δ 9.99 (d, J 1.4 Hz, 2H, 2'-H); $^{13}C$ NMR (50.29 MHz, $CDCl_3$) δ 28.50 ($CH_3$), δ 32.65 ($CH_2$), δ 47.56 (4-C), δ 99.93 (C-carbanion), δ 129.18 (3'-C), δ 141.50 (4'-C), δ 147.38 (2'-C), δ 181.69 (C=O).

*Preparation of 2,4-dinitrobenzenediazonium tetrafluoroborate.*[4] 2.0 g of 2,4-dinitroaniline was dissolved by heating in a mixture of 5 ml glacial acetic acid and 0.5 ml of conc. sulfuric acid in a 20 × 150 mm test tube, mounted vertically, and then rapidly cooled to 10–20°C. Isopentyl nitrate was thereafter added slowly, drop by drop from a pipette dropper, while stirring vertically with a glass rod flattened at the end. The temperature was kept below 20°C by occasional cooling. The fine, yellowish powder of 2,4-dinitroaniline was gradually dissolved, with slight evolution of nitrous fumes. As soon as the solution was clear, 5 ml of 40% tetrafluoroboric acid was added with stirring, followed by diethyl ether up to the top of the tube. On cautious stirring the diazonium tetrafluoroborate crystallized rapidly, and was filtered and washed with ether. After short air drying, the white to slightly yellowish product (80%) was immediately put in a refrigerator. It can be kept for months at 5°C or below.

*2,3-Butanedione 2-(2,4-dinitrophenylhydrazone)* **7h** from 2,4-dinitrobenzenediazonium tetrafluoroborate and 3-(triphenylphosphoranylidene)-2-butanone **7**. 2,4-dnbt (54 mg, 0.191 mmol) in one portion was added to a vigorously stirred solution of **7** (170 mg, 0.51 mmol) in acetronitrile (5 ml) at ambient temperature.

Stirring was continued for a few seconds whereafter the acetonitrile was removed under vacuum and the resulting oily product purified by chromatography (silica gel 60, diethyl ether-ethylacetate, 2:1) to give 20 mg (39%) of **7h** m.p. 180–182°C, Lit.[18] 175°C; $^1$H NMR (200 MHz, $CDCl_3$) δ 1.62 (br.s., 1H, NH), δ 2.20 (s., 3H, $CH_3$), δ 2.57 (s., 3H, $CH_3$), δ 8.12 (d., J 9.5 Hz, 1H, 6'-H), δ 8.44–8.50 (dd., 1H, 5'-H), δ 9.83 (d., J 2.4 Hz, 1H, 3'-H).

*2-Oxopropanenitrile 2,4-dinitrophenylhydrazone* **2h**. To a vigorously stirred solution of 2-(triphenylphosphoranylidene)-propanenitrile **2** (175 mg, 0.55 mmol) in acetonitrile (5 ml) at room temperature was added 50 mg (0.177 mmol) of 2,4-dnbt in one portion. The reaction mixture was stirred for a short while whereafter the solvent was evaporated in vacuo. The resulting solid was chromatographed (silica, n-butyl chloride-acetonitrile, 4:1) to give **2h** (13 mg, 0.053 mmol, 30%) m.p. 135–137°C, Lit.[19] 140°C; $^1$H NMR (200 MHz, $CDCl_3$) δ 1.60 (br. s., 1H, NH), δ 2.33 and 2.41 (d., 3H, probably syn and anti $CH_3$, approximate ratio 1:4), δ 7.98 (d., J 9.5 Hz, 0.8 H, 6'-H), δ 8.08 (d., J 9.5 Hz, 0.2 H), δ 8.39–8.45 (m., 1H, 5'-H (syn + anti conformer)), δ 9.17 (d., J 2.4 Hz, 1 H, 3'-H).

*2,3,4-Pentanetrione 3-(2,4-dinitrophenylhydrazone)* **27h**. To a rapidly stirred solution of 0.20 g (0.5 mmol) of 3-(triphenylarsoranylidene)-2,4-pentanedione **27** in acetonitrile (5 ml) was added 0.14 (0.5 mmol) of 2,4-dnbt in one portion. Stirring was continued for a short time, whereafter the acetonitrile was removed under vacuum, and the resulting yellow oil purified by thin layer chromatography (silica gel 60, n-butyl chloride-nitromethane 4:1) to give the expected hydrazone 0.047 g (96%) as yellow plates: m.p. 185–186°C, Lit.[20] 176°C; $^1$H NMR (200 MHz, $CDCl_3$) δ 2.58 (s, 3H, $CH_3$), δ 2.66 (s, 3H, $CH_3$), δ 8.27 (d., J 9.2 Hz, 1H, 6'-H), δ 8.50–8.56 (dd., 1H, 5'-H), δ 9.18 (d., J 3.5 Hz, 1H, 3'-H). 180 mg of the analogous phosphorane (**26**) when similarly treated with an equimolar amount of 2.4-dnbt in acetonitrile, gave a product with m.p. 185–186°C and NMR data as above, albeit in much lower yield.

*Diethyl 2-oxopropanedioate 2,4-dinitrophenylhydrazone* **28h**. To diethyl 2-(triphenylphosphoranylidene)-propanedioate **28** (210 mg, 0.5 mmol) in acetronitrile (5 ml) was added 140 mg (0.5 mmol) 2,4-dnbt in one portion. The reaction mixture was vigorously stirred during the addition, whereafter the solvent was evaporated in vacuo, and the resulting oil chromatographed (silica, n-butyl chloride-acetonitrile, 4:1) to give the hydrazone **28h** 0.036 g (20%): m.p. 122–123°C, Lit.[21] 116–117°C; $^1$H NMR (200 MHz, $CDCl_3$), δ 1.35–1.43 (m., 6H, $CH_3$), δ 4.33–4.50 (m., 4H, $CH_2$), δ 8.18 (d., J 9.4 Hz, 1H, 6'-H), δ 8.40–8.41 (dd., 1H, 5'-H), δ 9.11 (d., J 2.5 Hz, 1H, 3'-H). Similar treatment of the analogous pyridinium ylide **29** gave only a minor amount of **28h**.

*5,5-Dimethylcyclohexane-1,2,3-trione 2-(2,4-dinitrophenylhydrazone)* **30h**. 0.140 g (0.5 mmol) 2,4-dnbt was added in one portion to a solution of the ylide **30** (0.11 g, 0.5 mmol) in acetonitrile (5 ml) at ambient temperature. The reaction mixture was rapidly stirred during the addition, whereafter the acetonitrile was evaporated and the resulting red oil purified twice by thin layer chromatography (silica, n-butyl chloride-dioxane, 4:1, followed by n-butyl chloride-acetonitrile, 4:1) to give the expected hydrazone **30h** (0.017g, 11%) as yellow plates: m.p. 212–214°C; $^1$H NMR (200 MHz, $CDCl_3$), δ 1.17 (s., 6H, $CH_3$), δ 2.74 (d., J 2.7, 4H, $CH_2$), δ 8.51–8.52 (m., 2H, 6'-H and 5'-H), δ 9.16 (d., 1H, 3'-H).

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