Iminophosphorane-Mediated Synthesis of Mesoionic 1,3,4-Oxadiazolo-[3,2-*a*]pyridinylium-2-aminides

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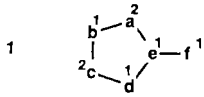
Reaction of iminophosphorane 2 with methyl isocyanate yields the mesoionic 1,3,4-oxadiazolo[3,2-*a*]pyridinylium-2-methylaminide 3, which undergoes *N*-methylation with $CF_3SO_3CH_3$ to give the 1,3,4-oxadiazolo[3,2-*a*]pyridinium cation 4. The structure of compound 4 has been established by means of X-ray crystallography. Mesoionic aminide 3 undergoes rearrangement by the action of base to give the isomeric mesoionic compound 1,3,4-triazolo[3,2-*a*]pyridinylium-2-olate 11. Compound 3 by the action of (arylimino)triphenylphosphoranes is converted into the corresponding 1,3,4-oxadiazolo[3,2-*a*]pyridinylium-2-arylaminides 12, which can be also prepared from iminophosphorane 2 and hydroximoyl chlorides.

Iminophosphoran-vermittelte Synthese von mesoionischen 1,3,4-Oxadiazolo[3,2-*a*]pyridinylium-2-aminiden

Das Iminophosphoran 2 reagiert mit Methylisocyanat zu dem mesoionischen 1,3,4-Oxadiazolo[3,2-*a*]pyridinylium-2-methylaminid 3, das durch $CF_3SO_3CH_3$ zum 1,3,4-Oxadiazolo[3,2-*a*]-pyridinium-Kation 4 methyliert wird. Struktur 4 wurde durch Röntgenstrukturanalyse gesichert. Durch Einwirkung von Base lagert das mesoionische Aminid 3 zum isomeren mesoionischen 1,3,4-Triazolo[3,2-*a*]pyridinylium-2-olat 11 um. Verbindung 3 wird durch (Arylimino)triphenylphosphorane in die entsprechenden 1,3,4-Oxadiazolo[3,2-*a*]pyridinium-2-arylaminide 12 umgewandelt, die auch aus Iminophosphoran 2 und Hydroximoylchloriden zugänglich sind.

Mesoionic compounds of the general formula 1 are an interesting family of heterocycles because of their unique structure, reaction behaviour, and pharmaceutical activity[1]. In spite of much work on the synthesis of mesoionic compounds possessing 6 π electrons in a heterocyclic five-membered ring and with the negative charge associated with a nitrogen atom (f = NAr; NCOR; NSO_2Ar), no methods for the preparation of this kind of compounds, in which the exocyclic nitrogen atom is attached to an alkyl group (f = NR) has hitherto been reported. This fact could be due to the unstability of these compounds associated with the high negative charge density on the exocyclic nitrogen atom. As a part of our study on the chemistry of fused mesoionic compounds[2] we describe here the first synthesis of the mesoionic 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]-pyridinylium-2-methylaminide (3) and its unusual reactivity.



The first reported synthesis of 1,3,4-oxadiazolium-2-arylaminides involves sequential treatment of *N*-benzoyl-*N*-methylhydrazine with isocyanide dichlorides and diazomethane[3]. Recently we have found that the reaction products of iminophosphoranes derived from *N*-aminoheterocycles with isocyanates are strongly dependent on the nature both of the heteroaromatic ring and the isocyanate[4].

Results and Discussion

Iminophosphorane 2, readily available from 1-amino-4,6-diphenyl-2(1*H*)-pyridinone and triphenylphosphane dibromide[4a], reacts with methyl isocyanate in dry benzene at room temperature to give crystalline 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridinylium-2-methylaminide (3) in 64% yield. A similar result is obtained with methyl isothiocyanate. We believe that the **2** → **3** conversion involves an initial aza-Wittig reaction between the iminophosphorane 2 and the isocyanate to give a carbodiimide as a highly reactive intermediate which cyclizes spontaneously to the valence tautomer 3. Reaction of 2 with ethyl and *tert*-butyl isocyanate failed to give the corresponding mesoionic aminides, and only complex mixtures were obtained in which the mesoionic compounds could not be detected.

The IR spectrum of 3 shows a strong absorption band at 1687 cm^{-1} which can be attributed to the exocyclic C=N stretching, this value being in good agreement with those reported for the monocyclic systems[3]. The absence of carbodiimide bands provides support for its formulation as a cyclic mesoionic structure rather than the alternative valence tautomer. The ^{1}H-NMR spectrum shows a singlet at δ = 3.20 due to the *N*-methyl protons; in the ^{13}C-NMR spectrum the *N*-methyl signal appears at δ = 12.0. The electron impact mass spectrum shows the expected molecular ion peak as base peak.

Compound 3 undergoes *N*-methylation on the exocyclic nitrogen atom by the action of methyl trifluoromethanesulfonate to give 2-(dimethylamino)-5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridinium trifluoromethanesulfonate (4). The ^{1}H-NMR spectrum of 4 shows, among others, two doublets for the pyridinium ring protons at δ = 8.55 and 8.90 (J = 2 Hz) and one singlet for the two *N*-methyl groups at δ = 3.30.

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To identify unambiguously this compound, an X-ray structure determination has been performed (Tables 1, 2 and Figure 1).

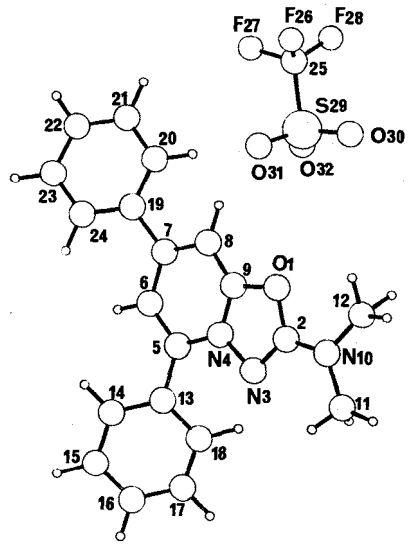


Figure 1. The molecular structure of the title compound **4** with the atomic numbers used in the crystallography work[5]

Table 1. Final atomic coordinates of **4**

Atom	x/a	y/b	z/c
O1	0.4042(4)	0.2645(9)	0.3866(2)
C2	0.3054(7)	0.2477(14)	0.3898(4)
N3	0.2398(5)	0.2238(10)	0.3391(3)
N4	0.3054(4)	0.2210(10)	0.2994(3)
C5	0.2770(5)	0.2026(10)	0.2395(3)
C6	0.3563(5)	0.2072(10)	0.2098(3)
C7	0.4586(4)	0.2329(11)	0.2394(3)
C8	0.4821(6)	0.2555(12)	0.3003(3)
C9	0.4020(5)	0.2462(13)	0.3273(3)
N10	0.2839(6)	0.2589(14)	0.4425(3)
C11	0.1786(16)	0.2196(32)	0.4477(8)
C12	0.3673(13)	0.2727(28)	0.4964(5)
C13	0.1695(5)	0.1800(10)	0.2093(4)
C14	0.1363(6)	0.2728(16)	0.1566(4)
C15	0.0345(7)	0.2453(20)	0.1257(4)
C16	-0.0299(7)	0.1321(19)	0.1484(7)
C17	0.0025(7)	0.0409(16)	0.2014(6)
C18	0.1026(6)	0.0647(13)	0.2336(5)
C19	0.5405(5)	0.2411(11)	0.2046(3)
C20	0.6413(5)	0.1989(11)	0.2336(4)
C21	0.7168(7)	0.1985(13)	0.2016(6)
C22	0.6927(7)	0.2378(16)	0.1423(6)
C23	0.5959(7)	0.2850(15)	0.1130(5)
C24	0.5186(6)	0.2836(12)	0.1449(3)
S29	0.7202(2)	0.2359(4)	0.4350(1)
O30	0.7192(6)	0.2313(14)	0.4966(3)
O31	0.6775(6)	0.4045(10)	0.4043(3)
O32	0.6947(5)	0.0613(10)	0.4030(4)
C25	0.8536(8)	0.2605(19)	0.4362(5)
F26	0.9079(5)	0.1141(12)	0.4634(3)
F27	0.8718(5)	0.2631(12)	0.3822(3)
F28	0.8926(6)	0.4171(12)	0.4626(4)

The distribution of the bond lengths and bond angles together with the conformation adopted present the cation with a quite planar fused ring system as a basic moiety, that supports the positive charge at N4, and the adjacent phenyl rings with twists of −5.1(14) and −39.9(11)° (see Table 2). The anion shows a geometry that falls within the range of values found in the Cambridge Data File CPS[5] from which the mean values are given in Table 2. This group links the cation moieties through van der Waals contacts, some of which may be remarked as those of the oxygen atoms of the SO_3[6] (see Table 2).

Table 2. Selected geometrical characteristics of **4** (Å, °)

O1-C2	1.353(11)	O1-C9	1.371(8)
C2-N3	1.314(10)	C2-N10	1.317(13)
N3-N4	1.405(9)	N4-C5	1.361(9)
N4-C9	1.329(8)	N10-C11	1.474(24)
N10-C12	1.484(14)	S29-O30	1.429(7)
S29-O31	1.432(7)	S29-O32	1.431(8)
S29-C25	1.797(11)	C25-F26	1.333(14)
C25-F27	1.325(14)	C25-F28	1.308(15)
C2-O1-C9	104.0(6)	O1-C2-N10	1.177(8)
O1-C2-N3	115.8(8)	N3-C2-N10	126.5(9)
C2-N3-N4	101.0(6)	N3-N4-C9	111.6(6)
N3-N4-C5	126.2(6)	C5-N4-C9	122.1(6)
N4-C9-C8	124.9(6)	O1-C9-C8	127.5(6)
O1-C9-N4	107.5(6)	C2-N10-C12	120.2(10)
C2-N10-C11	118.4(10)	C11-N10-C12	120.4(10)
O32-S29-O31	115.0(5)	O30-S29-O32	116.3(5)
O30-S29-O31	115.1(5)	C25-S29-O30	102.5(5)
C25-S29-O31	102.6(5)	C25-S29-O32	102.4(5)
S29-C25-F26	112.0(8)	S29-C25-F27	112.3(7)
S29-C25-F28	112.5(8)	F26-C25-F27	105.1(9)
F26-C25-F28	107.6(10)	F27-C25-F28	107.0(9)
O1-C2-N10-C12	-5.1(14)	N4-C5-C13-C18	39.9(11)
C6-C7-C19-C24	120.5(10)		
O31...H8(x,y,z)		2.49(5)	
O30...H11A(1-x,-y,1-z)		2.68(18)	
O31...H6(1-x,1/2+y,1/2-z)		2.47(8)	
O31...H12C(1-x,1-y,1-z)		2.44(16)	
O32...H12B(1-x,-y,1-z)		2.68(13)	
O32...H14(1-x,y-1/2,1/2-z)		2.48(9)	
O32...H24(1-x,y-1/2,1/2-z)		2.55(9)	
CPS mean values:			
S-O 1.427(20)	S-C 1.795(53)	C-F 1.320(20)	
O-S-O 114.6(20)	O-S-C 103.7(23)	F-C-S 111.5(30)	
F-C-F 107.3(25)			

The compound packs in centrosymmetric layers, at 1/4 and 3/4 along the *b* axis, formed by pairs of anion-cation groups (see Figure 2). Within each layer the groups are related by the *c*-glide plane, giving rise to a superposition of the fused system with a phenyl ring, the one less twisted.

Similarly, compound **3** is transformed by the action of hydrogen chloride into the salt **5**, which is converted into the mesoionic compound **3** by the action of aqueous sodium hydroxide[7].

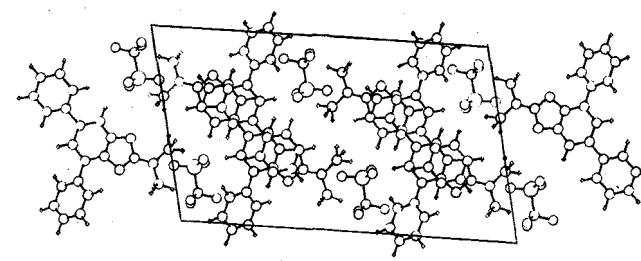
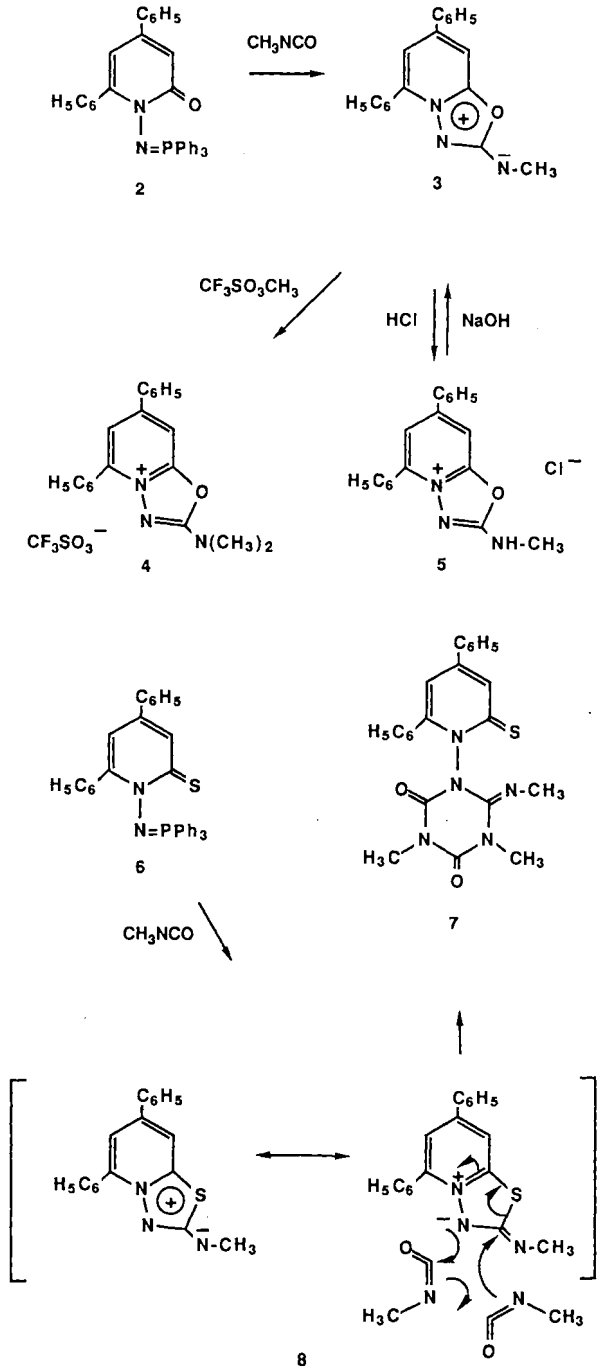


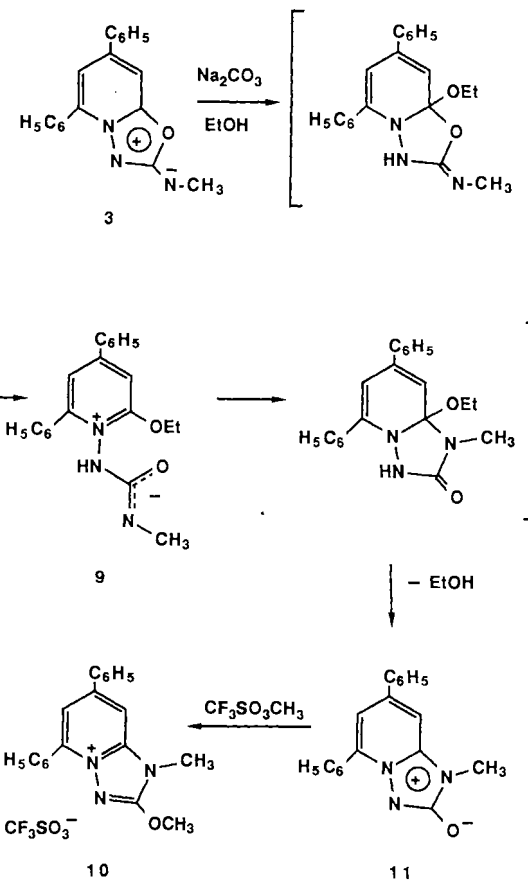
Figure 2. The packing of compound **4** shown in a projection along the *b* axis as to remark the superposition of the fused and the phenyl rings

On the other hand, attempts to prepare the mesoionic thioanalog compound **8** were unsuccessful. Thus, iminophosphorane **6** derived from 1-amino-4,6-diphenyl-2(1*H*)-pyridinethione reacts with methyl isocyanate in dry benzene



at room temperature to give a complex mixture from which only the *N,N'*-linked biheterocycle **7** could be isolated in low yield (27%). Support for the formulation **7** is provided by the spectral data. The IR spectrum shows absorption bands at 1738 and 1687 cm^{-1} due to the carbonyl and C=N bonds. The ^{1}H-NMR spectrum shows, among others, two singlets at δ = 8.15 and 7.10 characteristic of the ring protons 3-H and 5-H of the 2-pyridinethione ring and a broad singlet at δ = 3.30 due to the three *N*-methyl groups. The mass spectrum shows the expected molecular ion peak, characteristic fragments also are [M^+ − 32], [M^+ − 2 CH_3-NCO], [CH_3NCO], and [CH_3NCNCH_3]. Presumably, the conversion **6** → **7** involves initial formation of the mesoionic 1,3,4-oxadiazolo[3,2-*a*]pyridinylium-2-methylaminide **8** which reacts with two molecules of methyl isocyanate to give **7**.

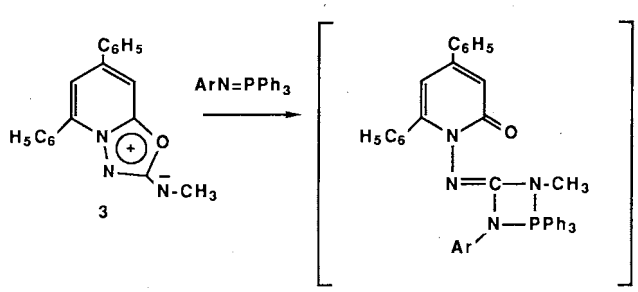
Several methods and reagents have been used to effect the interconversion between mesoionic isomers: i) heating in protic solvents, ii) treatment with hot ethanolic sodium ethoxide, iii) heating, and iv) heating with aryl isocyanates or isothiocyanates. In this context, isomerization of 1,3,4-thiadiazolium-2-aminides to 1,3,4-triazolium-2-thiolates has been reported[8]; however, no method of interconverting mesoionic 1,3,4-oxadiazolium-2-aminides to 1,3,4-triazolium-2-olates has been described[3]. We have now found that the mesoionic compound **3** undergoes rearrangement to the isomeric 1,3,4-triazolo[3,2-*a*]pyridinylium-2-olate **11**. When an ethanolic solution of **3** is heated in the presence of sodium carbonate the isomeric mesoionic compound **11** is isolated in 55% yield. The IR spectrum of **11** shows a strong absorption band at 1699 cm^{-1} due to the exocyclic carbonyl group. In the ^{1}H-NMR spectrum the chemical shift of the *N*-methyl group is characteristic at δ = 3.60. In the ^{13}C-NMR spectrum the *N*-methyl group carbon appears at δ = 26.75. The mass spectrum shows the expected molecular ion peak in high intensity, and peaks [M^+ − NCO] and [M^+

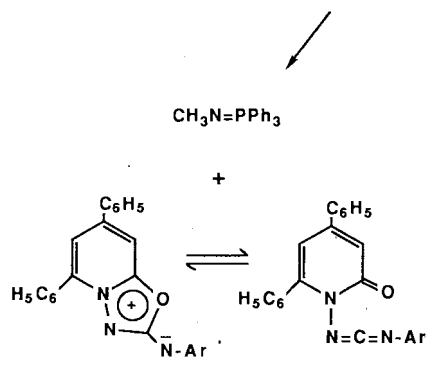


– CH_3NCO] are also found. Compound **11** undergoes *O*-methylation by the action of methyl trifluoromethanesulfonate to give the 1,3,4-triazolo[3,2-*a*]pyridinium salt **10** in almost quantitative yield. The ^{1}H-NMR spectrum of **10** shows two singlets at $\delta = 4.00$ and 4.35 attributable to the *N*- and *O*-methyl groups, respectively.

Presumably the isomerization **3** → **11** involves nucleophilic attack at the 5-position of the five-membered ring to give the betaine **9** which undergoes cycloelimination.

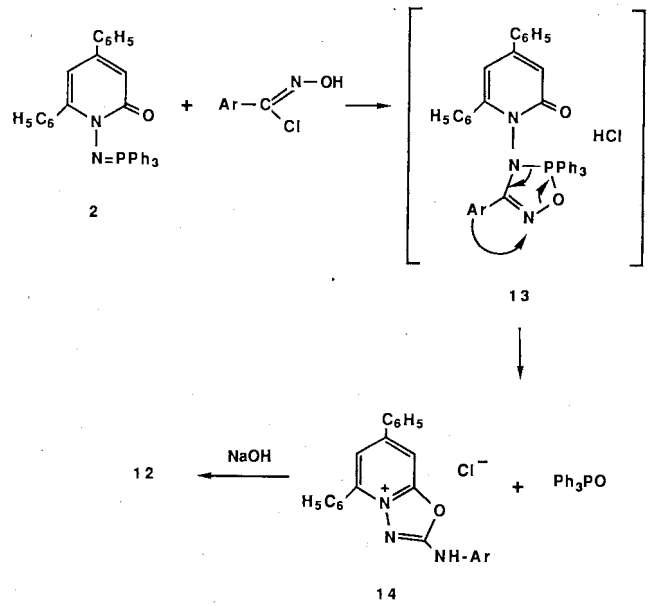
While there have been reported a number of methods for the preparation of mesoionic compounds **1**, only a limited number of reactions have so far been developed for the substitution reaction of the exocyclic heteroatom. Such processes include replacement of oxygen by a carbanionoid[9] or arylamino[10] group. We have found a general method for the substitution of the methyl group in **3** by an aryl group by the reaction of **3** with (arylimino)phosphoranes in dry toluene at reflux temperature. It is conceivable that the conversion **3** → **12** involves an initial [2 + 2] cyclocondensation of the iminophosphorane with the valence tautomer heteroaryl methyl carbodiimide to give the heteroaryl aryl carbodiimide, which cyclizes spontaneously to the 2-arylaminide **12**.





12	a	b	c	d
Ar	C_6H_5	4-ClC_6H_4	4-BrC_6H_4	4-$CH_3OC_6H_4$

Furthermore, an alternative route for the preparation of compound **12** involves the reaction of iminophosphorane **2** with hydroximoyl chlorides. Thus, **2** reacts with several hydroximoyl chlorides in dry benzene at reflux temperature to give the corresponding 2-(arylamino)-5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridinium chlorides **14** in good yields. When ethanolic solutions of **14** are treated with sodium hydroxide at room temperature the mesoionic 1,3,4-oxadiazolo[3,2-*a*]pyridinylium-2-arylaminides **12** are isolated in nearly quantitative yields. Attempts to prepare **12** from **2** and hydroximoyl chlorides in the presence of triethylamine were unsuccessful. Presumably, the conversion **2** → **14** involves initial acylation of **2** followed by cyclization to give **13** as intermediate which undergoes elimination of triphenylphosphane oxide and migration of the aryl group to give a carbodiimide which cyclizes to **14**.



14	a	b	c	d
Ar	C_6H_5	4-ClC_6H_4	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$

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Experimental

Microanalyses: Perkin-Elmer 240C instrument. – ^{1}H- and ^{13}C-NMR spectra: Varian FT-80 instrument. – IR spectra: Nicolet 5DX, Nujol used in all cases. – Mass spectra: Hewlett-Packard 5993-C. – Melting points (uncorrected): Kofler hot-stage apparatus.

4,6-Diphenyl-1-(triphenylphosphoranylidenamino)-2(1*H*)-pyridinone (**2**)[4a], 4,6-diphenyl-1-(triphenylphosphoranylidenamino)-2(1*H*)-pyridinethione (**6**)[4a], (arylimino)triphenylphosphoranes[11], and hydroximoyl chlorides[12] were prepared following the methods described in the literature.

X-ray Crystallography of **4**: $(C_{20}H_{18}N_3O)^+(CF_3SO_3)^-$, M = 465.45, monoclinic, space group $P2_1/c$, a = 13.4472(6), b = 7.0011(2), c = 23.1390(13) Å, β = 102.720(4)°, D_c = 1.455 g · cm^{-3}, Z = 4. Cell constants obtained from a least-squares fit using 70 reflexions up to Θ = 45° and Cu-K_α radiation. A transparent plate sample (0.33 × 0.13 × 0.05 mm) was used for the analysis on a Philips PW1100 diffractometer, with Cu-K_α radiation, graphite monochromator, $\omega/2\Theta$ scans, bisecting geometry, 1 × 1° detector apertures, 1.5° scan width and using 1 min per reflexion. Good stability for the sample checked every 90 min.

A $\sigma 3(I)$ criterion gave 1652 observed reflexions, up to 62° in Θ. The structure was solved by Direct methods[13,14] and refined by one-block matrix least-squares procedures[15] for 361 parameters. Empirical absorption correction[16] (μ = 18.61 cm^{-1}) resulted with a range of transmision factors between 0.851 and 1.227.

All hydrogen atoms were located with a difference Fourier synthesis. An empirical weigthing scheme, so as to give no trends in $\langle w\Delta^2 F\rangle$ vs. $\langle|F_o|\rangle$ and $\langle\sin(\Theta)/\lambda\rangle$ was introduced. The final shift/error was 0.14 with maximum peak in the final ΔF of 0.28 e Å^{-3}.

The maximum thermal factor was U_{11}(C12) = 0.19(1) Å^2. The final R and R_w values were 0.076 and 0.070, respectively. All the calculations were performed on a VAX 11/750 computer. The atomic scattering factors were taken from the International Tables[17].

5,7-Diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinylium-2-methylaminide (**3**): To a solution of iminophosphorane **2** (0.50 g, 1.0 mmol) in dry benzene (20 ml), methyl isocyanate was added. The reaction mixture was stirred at room temp. for 1 h, and the precipitated solid was collected by filtration, dried, and crystallized from benzene to give **3** as yellow needles: 0.18 g (64%), m.p. 210–212°C. – IR: 1687 cm^{-1}, 1410, 900, 759. – ^{1}H NMR ($CDCl_3$): δ = 3.20 (s, 3H), 7.4–8.5 (m, 12H). – ^{13}C NMR ($CDCl_3$): δ = 12.0 (CH_3), 126.6, 127.8, 128.0, 128.4, 128.6, 128.8, 129.0, 129.1, 129.3, 129.5, 129.7, 130.6, 131.7, 132.2. – MS (70 eV): *m/z* (%) = 301 [M$^+$] (100), 247 (44), 219 (30), 102 (55).

$C_{19}H_{15}N_3O$ (301.3) Calcd. C 75.73 H 5.02 N 13.94
Found C 75.78 H 5.05 N 13.90

2-(Dimethylamino)-5,7-diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinium Trifluoromethanesulfonate (**4**): To a solution of **3** (0.50 g, 1.6 mmol) in dry dichloromethane (30 ml), methyl trifluoromethanesulfonate (0.33 g, 1.9 mmol) was added. The reaction mixture was stirred at room temp. for 1 h. The precipitated solid was collected by filtration, dried, and crystallized from dichloromethane to give **4** as colourless prisms: 0.37 g (50%), m.p. 199–200°C. – IR: 1704 cm^{-1}, 1642, 1274, 1257, 1166, 1030, 640. – ^{1}H NMR ([D$_6$]-DMSO): δ = 3.30 (s, 6H), 7.6–8.4 (m, 10H), 8.55 (d, 1H; *J* = 2 Hz), 8.90 (d, 1H; *J* = 2 Hz). – MS (70 eV): *m/z* (%) = 330 (50), 300 (10), 247 (42), 115 (52).

$C_{21}H_{18}F_3N_3O_4S$ (465.4) Calcd. C 54.19 H 3.90 N 9.03
Found C 54.15 H 3.87 N 9.01

2-(Methylamino)-5,7-diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinium Chloride (**5**): A stream of dry hydrogen chloride was passed through a solution of **3** (0.50 g, 1.6 mmol) in dry dichloromethane (20 ml) at room temp. for 1 h. Then the solution was concentrated under reduced pressure, and the precipitated solid was filtered off, dried, and crystallized from dichloromethane to give **5** as colourless prisms: 0.50 g (90%), m.p. 243–245°C. – IR: 3453 cm^{-1}, 1690, 1643, 767. – ^{1}H NMR ($CDCl_3$): δ = 3.15 (d, 3H), 7.4–8.4 (m, 12H), 9.35 (s, broad, 1H). – MS (70 eV): *m/z* (%) = 301 [M$^+$ – HCl] (49), 300 (53), 247 (49), 219 (100), 202 (69).

$C_{19}H_{16}ClN_3O$ (337.8) Calcd. C 67.56 H 4.77 N 12.44
Found C 67.53 H 4.79 N 12.45

Basic Treatment of **5**: To a well stirred solution of **5** (0.20 g, 0.60 mmol) in water (10 ml) 1 N NaOH (3 ml) was added dropwise until no further precipitation was observed. The precipitated solid was collected by filtration, dried, and crystallized from benzene to give aminide **3**: 0.17 g (95%).

1-(1,2-Dihydro-4,6-diphenyl-2-thioxo-1-pyridinyl)-3,5-dimethyl-6-(methylimino)-5,6-dihydro-1,3,5-triazine-2,4(1H,3H)-dione (**7**): To a solution of iminophosphorane **6** (1.0 g, 1.8 mmol) in dry benzene (50 ml) methyl isocyanate (0.12 g, 1.8 mmol) was added. The reaction mixture was stirred at room temp. for 1 h. The solution was concentrated to dryness, and the residual material was purified by column chromatography (silica gel and dichloromethane/hexane/methanol 8:4:1 as eluent) followed by crystallization from dichloromethane/cyclohexane to give **7** as yellow prisms: 0.20 g (27%), m.p. 235–237°C. – IR: 1738 cm^{-1}, 1687, 1619, 1580, 1528. – ^{1}H NMR ($CDCl_3$): δ = 3.30 (s, 9H), 7.10 (d, 1H; *J* = 2 Hz), 7.4–8.0 (m, 10H), 8.25 (d, 1H; *J* = 2 Hz). – MS (70 eV): *m/z* (%) = 431 [M$^+$] (19), 399 (14), 317 (8), 263 (55), 230 (40), 115 (74), 70 (49), 57 (92), 56 (100).

$C_{23}H_{21}N_5O_2S$ (431.5) Calcd. C 64.02 H 4.91 N 16.23
Found C 64.03 H 4.93 N 16.22

1-Methyl-5,7-diphenyl-1,3,4-triazolo[3,2-a]pyridinylium-2-olate (**11**): To a solution of **3** (0.50 g, 1.6 mmol) in ethanol (25 ml) anhydrous sodium carbonate (0.35 g, 3.3 mmol) was added. The resulting suspension was stirred at reflux temperature for 20 h and filtered. After cooling the precipitated solid was collected by filtration, dried, and crystallized from ethanol to give **11** as colourless needles: 0.27 g (55%), m.p. 240–242°C. – IR: 1699 cm^{-1}, 1670, 1182. – ^{1}H NMR ($CDCl_3$): δ = 3.60 (s, 3H), 7.3–8.2 (m, 12H). – ^{13}C NMR ($CDCl_3$): δ = 26.75 (CH_3), 100.8, 114.4, 126.75, 128.3, 129.1, 129.3, 129.4, 130.2, 130.9, 136.8, 140.0, 142.1, 143.7, 160.6. – MS (70 eV): *m/z* (%) = 301 [M$^+$] (71), 300 (100), 259 (20), 244 (5).

$C_{19}H_{15}N_3O$ (301.3) Calcd. C 75.73 H 5.02 N 13.94
Found C 75.73 H 5.00 N 13.97

2-Methoxy-1-methyl-5,7-diphenyl-1,3,4-triazolo[3,2-a]pyridinium Trifluoromethanesulfonate (**10**): To a solution of **11** (0.50 g, 1.6 mmol) in dry dichloromethane (25 ml) methyl trifluoromethanesulfonate (0.33 g, 2.0 mmol) was added. The reaction mixture was stirred at room temp. for 30 min. The precipitated solid was collected by filtration, dried, and crystallized from ethanol to give **10** as colourless needles: 0.35 g (45%), m.p. 219–221°C. – IR: 1655 cm^{-1}, 1608, 1274, 1256, 1028, 641. – ^{1}H NMR ([D$_6$]DMSO): δ = 4.00 (s, 3H), 4.35 (s, 3H), 7.6–8.5 (m, 11H), 8.70 (d, 1H; *J* = 2 Hz). – MS (70 eV): *m/z* (%) = 326 (21), 301 (75), 300 (100), 235 (30), 217 (51), 203 (45), 202 (67).

$C_{21}H_{18}F_3N_3O_4S$ (465.4) Calcd. C 54.19 H 3.90 N 9.03
Found C 54.20 H 3.87 N 8.98

5,7-Diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinylium-2-arylaminides **12**. – *General Procedure*: To a solution of **3** (0.50 g, 1.6 mmol) in dry toluene (20 ml) the appropriate (arylimino)triphenylphosphorane (1.6 mmol) was added. The solution was stirred at reflux temp. for 15 h. After cooling the solvent was removed under reduced pressure, and the residual material was treated with cold ethanol (20 ml), the separated solid was collected by filtration, dried, and crystallized from ethanol.

5,7-Diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinylium-2-phenylaminide (**12a**): Yield 62%, m.p. 204–206°C (ref.[4a] 206–207°C).

5,7-Diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinylium-2-(4-chlorophenyl)aminide (**12b**): Yield 56%, m.p. 237–239°C (ref.[4a] 236–238°C).

5,7-Diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinylium-2-(4-bromophenyl)aminide (**12c**): Yield 51%, m.p. 254–256°C (ref.[4a], 255–256°C.).

5,7-Diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinylium-2-(4-methoxyphenyl)aminide (**12d**): Yield 65%, m.p. 213–215°C (ref.[4a], 214–215°C).

2-(Arylamino)-5,7-diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinium Chlorides **14**. – *General Procedure*: To a solution of iminophosphorane **2** (0.50 g, 0.95 mmol) in dry benzene (25 ml) the appropriate

hydroximoyl chloride (0.95 mmol) was added. The reaction mixture was stirred at reflux temp. for 24 h. After cooling the precipitated solid was collected by filtration, dried, and crystallized from the appropriate solvent to give **14**.

5,7-Diphenyl-2-(phenylamino)-1,3,4-oxadiazolo[3,2-a]pyridinium Chloride (**14a**): Yield 60%, m.p. 280–282°C, colourless prisms from ethanol/ether. – IR: 3290 cm^{-1}, 1659, 1636, 1592, 1223. – ^1H NMR ([D_6]DMSO): δ = 7.3–8.4 (m, 16H), 9.05 (d, 1H; *J* = 2 Hz), 8.50 (d, 1H; *J* = 2 Hz).

$C_{24}H_{18}ClN_3O$ (399.9) Calcd. C 72.09 H 4.54 N 10.51
Found C 72.06 H 4.54 N 10.53

2-[(4-Chlorophenyl)amino]-5,7-diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinium Chloride (**14b**): Yield 52%, m.p. 281–283°C, colourless needles from ethanol. – IR: 3325 cm^{-1}, 1665, 1636, 1591, 1495. – ^1H NMR ([D_6]DMSO): δ = 7.5–8.4 (m, 15H), 8.55 (d, 1H; *J* = 2 Hz), 9.00 (d, 1H; *J* = 2 Hz).

$C_{24}H_{17}Cl_2N_3O$ (434.3) Calcd. C 66.37 H 3.94 N 9.67
Found C 66.39 H 3.93 N 9.65

5,7-Diphenyl-2-(4-tolylamino)-1,3,4-oxadiazolo[3,2-a]pyridinium Chloride (**14c**): Yield 56%, m.p. 286–287°C, colourless needles from ethanol/ether. – IR: 3302 cm^{-1}, 1676, 1638, 1562, 1512. – ^1H NMR ([D_6]DMSO): δ = 2.40 (s, 3H), 7.2–8.5 (m, 15H), 8.55 (d, 1H; *J* = 2 Hz), 9.00 (d, 1H; *J* = 2 Hz).

$C_{25}H_{20}ClN_3O$ (413.9) Calcd. C 72.55 H 4.87 N 10.15
Found C 72.56 H 4.89 N 10.13

2-[(4-Methoxyphenyl)amino]-5,7-diphenyl-1,3,4-oxadiazolo[3,2-a]pyridinium Chloride (**14d**): Yield 64%, m.p. 248–250°C, colourless needles from ethanol. – IR: 3315 cm^{-1}, 1670, 1642, 1512. – ^1H NMR ([D_6]DMSO): δ = 3.80 (s, 3H), 6.9–8.4 (m, 15H), 8.50 (d, 1H; *J* = 2 Hz), 8.95 (d, 1H; *J* = 2 Hz).

$C_{25}H_{20}ClN_3O_2$ (429.9) Calcd. C 69.85 H 4.69 N 9.77
Found C 69.82 H 4.66 N 9.75

Basic Treatment of **14**: To a well stirred solution of **14** (0.60 mmol) in water (10 ml), 1 N NaOH (3 ml) was added dropwise until no further precipitation was observed. The precipitated solid was collected by filtration, dried, and crystallized from ethanol to give the corresponding **12**.

[1] W. D. Ollis, C. A. Ramsden, *Adv. Heterocycl. Chem.* **19** (1976) 1; C. G. Newton, C. A. Ramsden, *Tetrahedron* **38** (1982) 2965.
[2] P. Molina, A. Arques, I. Cartagena, M. A. Alias, M. C. Foces-Foces, F. H. Cano, *Liebigs Ann. Chem.* **1988**, 133.
[3] W. D. Ollis, C. A. Ramsden, *J. Chem. Soc., Chem. Commun.* **1974**, 1223; *J. Chem. Soc., Perkin Trans. 1*, **1974**, 642.
[4] [4a] P. Molina, M. Alajarín, A. Arques, R. Benzal, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 351. – [4b] P. Molina, M. Alajarín, J. R. Sáez, M. C. Foces-Foces, F. H. Cano, R. M. Claramunt, J. Elguero, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 2037.
[5] F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Northerwell, J. R. Rogers, D. G. Watson, *Acta Cryst., Sect. B*, **35** (1979) 2331.
[6] B. K. Vainshtein, V. M. Fridkin, V. L. Indenbom, *Modern Crystallography II*. p. 87, Springer-Verlag, Berlin 1982.
[7] Further details of the crystal structure investigation are available on request from Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53032, the names of the authors, and the journal citation.
[8] W. D. Ollis, C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 633.
[9] S. Araki, J. Mizuya, Y. Butsugan, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 2439.
[10] P. Molina, M. Alajarín, A. Arques, R. Benzal, H. Hernández, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 1891.
[11] G. M. Brown, E. M. Briggs, J. Jiricny, M. E. Meidine, *Synthesis* **1980**, 295.
[12] K.-Ch. Liu, B. R. Shelton, R. K. Howe, *J. Org. Chem.* **40** (1980) 3916.
[13] C. J. Gilmore, *A Computer program for the automatic solution of crystal structures from X-ray data* (1983), Department of Chemistry, University of Glasgow, Scotland.
[14] P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. Van den Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, V. Parthasarathy, H. J. Bruins Slot, R. C. Haltiwanger, J. M. M. Smits, *Dirdif System* (1984), Crystallography Laboratory, Toernooivel, Nijmegen, The Netherlands.
[15] J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck, H. Flack, *The X-Ray System* (1976), Technical report TR-446, Computer Science Center, Univ. of Maryland, USA.
[16] N. Walker, D. Stuart, "Difabs." *Acta Cryst., Sect. A*, **39** (1983) 158.
[17] *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, England, 1974.

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