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NEW SYNTHESES OF 5-ACYLHYDANTOINS AND OF 5-ACYL-4-HYDROXYOXAZOLES

PRECURSORS OF β-KETO-α-AMINO ACIDS AND OF β-KETO-α-HYDROXY ACID AMIDES

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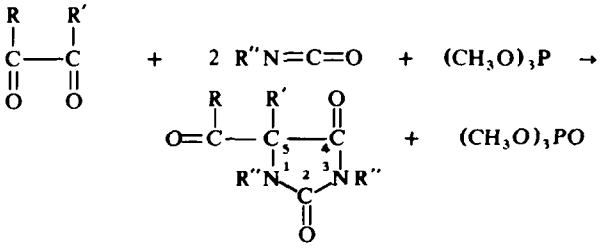
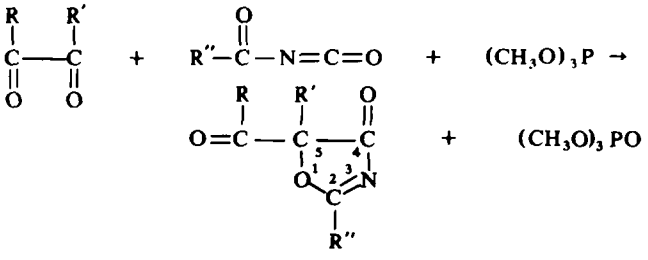
Abstract—The 2,2,2-trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene made from biacetyl and trimethyl phosphite reacted with one mole equiv. of *para*-substituted phenylisocyanates to give 2,2,2-trimethoxy-4-(*p*-substituted)phenylimino-5-acetyl-5-methyl-2,2-dihydro-1,3,2-dioxaphospholanes. The latter reacted with another mole of isocyanate and gave 1,3-diaryl-5-acetyl-5-methyl-hydantoins, precursors of β-keto-α-amino acids. The phenylglyoxal-trimethyl phosphite adduct gave a tautomeric form of the 5-benzoyl-hydantoin. The phenylglyoxal-trimethyl phosphite adduct reacted with one mole equiv of aroyl- and acyl-isocyanates and yielded 2-aryl- or 2-alkyl-5-benzoyl-4-hydroxyoxazoles, the tautomers of 4-oxazolones and the precursors of β-keto-α-hydroxyacid amides. The 4-methoxyoxazoles were made from the 4-hydroxyoxazoles and diazomethane.

THIS paper describes some applications of two[1,2] recently discovered reactions which lead to 5-acylhydantoins and 5-acyl-4-oxazolones, respectively, Eq. 1 and 2.

Eq 1



Eq 2



The hydantoins[3] are precursors of the α-amino acids, while the 4-oxazolones[4] can be readily hydrolyzed to α-hydroxy-acid amides. These heterocycles display valuable pharmacological activity.[3,4] For these reasons, we have investigated the scope of these new reactions.[1,2]

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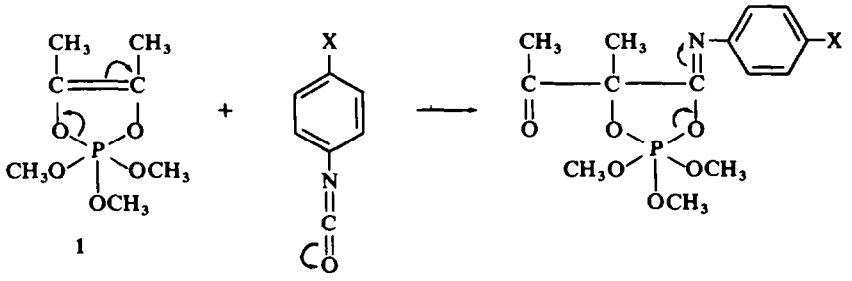
RESULTS

Reaction of 2,2,2-trialkoxy-2,2-dihydro-1,3,2-dioxaphospholenes with arylisocyanates. The phospholene **1** made from biacetyl and trimethyl phosphite[5] reacted with one mole equivalent of the arylisocyanates, **2–6**, having electron-withdrawing and electron-releasing substituents, and yielded the corresponding 4-aryliminodioxaphospholanes, **7–11**.

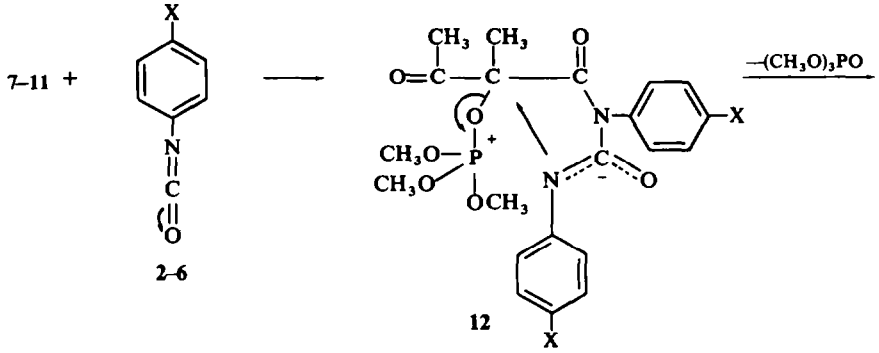


1

2: X = F
3: X = Cl
4: X = Br
5: X = NO_2
6: X = CH_3

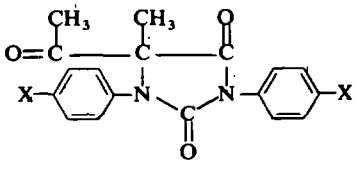
7: X = F
8: X = Cl
9: X = Br
10: X = NO_2
11: X = CH_3

The iminophospholanes, **7–11**, reacted with a second mole of the isocyanates and gave the corresponding hydantoins **13–17**, whose properties are listed in Table 1. It is assumed that the hydantoins were formed *via* the ambident dipolar adduct **12**.



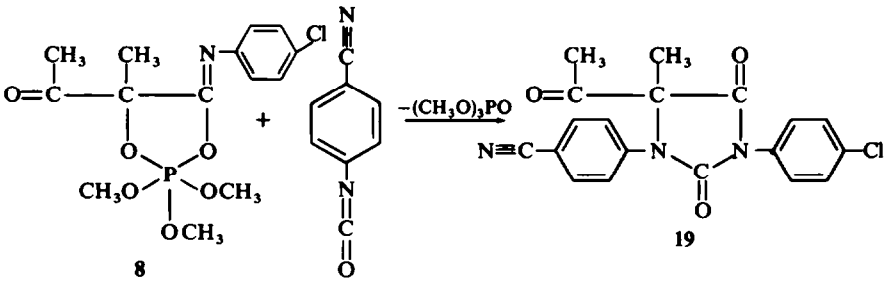
2–6

12



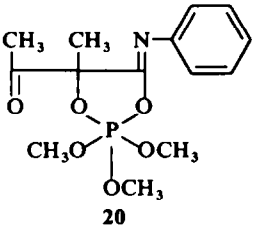
13: X = F
14: X = Cl
15: X = Br
16: X = NO_2
17: X = CH_3

The hydantoins can be made from the phospholene **1** and two mole equivalents of the isocyanate without isolation of the phospholane, **7–11**. However, the latter can be isolated and then combined with a different isocyanate to give a mixed diarylhydantoin, for example the cyano-chloro derivative **8** + **18** → **19**.



8 18 19

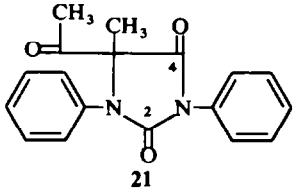
The structure of the phospholanes was based on the data given in the Experimental Section together with the data of the parent compound **20** already discussed.[1]



20

δ^{31} P = +57·8 ppm *vs* H_3PO_4 = O
τ CH_3CO = 7·71 ppm *vs* TMS = 10
τ CH_3 = 8·36 ppm
τ CH_3O = 6·40; J_{HP} = 13 cps
$\bar{\nu}$ C=N = 1672 cm^{-1}
$\bar{\nu}$ C=O = 1730 cm^{-1}

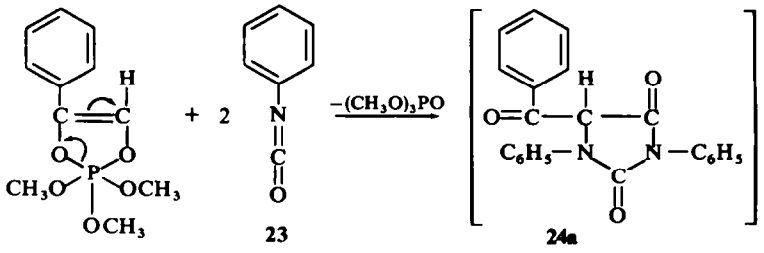
The structure of the hydantoins followed from the data of Table 1 and those of the parent compound[1] **21**.



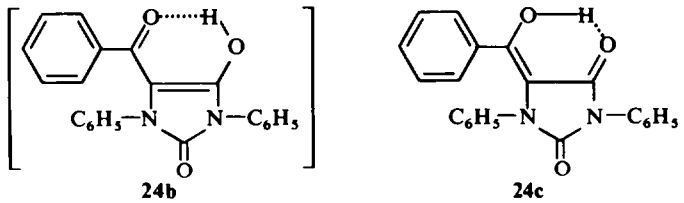
21

τ CH_3CO = 7·68 ppm
τ CH_3 = 8·18 ppm
$\bar{\nu}$ ^{4}C=O = 1779 cm^{-1}
$\bar{\nu}$ ^{2}C=O = 1715 cm^{-1}
$\bar{\nu}$ CH_3CO = 1730 cm^{-1}

The phospholene **22** made from phenylglyoxal,[6] $C_6H_5.CO.COH$, and trimethyl phosphite, reacted with two mole equivalents of phenylisocyanate **23** to give a hydantoin which can exist in three tautomeric forms **24a**, **24b** and **24c**. The data of Table 1 favor the 5-enol-4-keto structure **24c** for this material in the crystalline state and in solution. Note the band at 3274 cm^{-1} for the hydrogen-bonded hydroxyl, and the bands at 1754, 1715 and 1667 cm^{-1} for the 4-keto, 2-keto, and 5-enol functions, respectively, in a KBr pellet and in a Nujol mull.

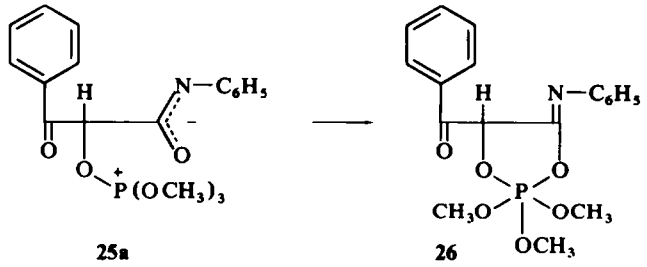


22 23 24a



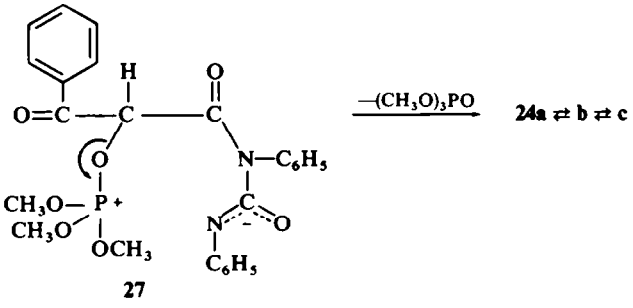
24b 24c

Phenylglyoxal, the phosphite, and the isocyanate, can form an ambient dipolar 1:1 adduct **25a**, which can close to an iminophospholane **26**. (Two other tautomeric forms can be written for **26**. with the hydrogen on oxygen and on nitrogen, respectively).



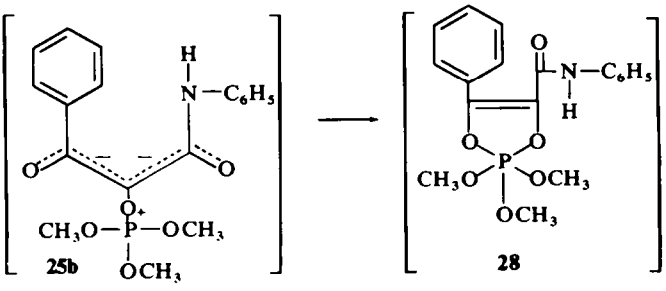
25a 26

A nucleophilic attack by the nitrogen of **26** on another isocyanate molecule gives **27**, the precursor of the hydantoin, **24**.

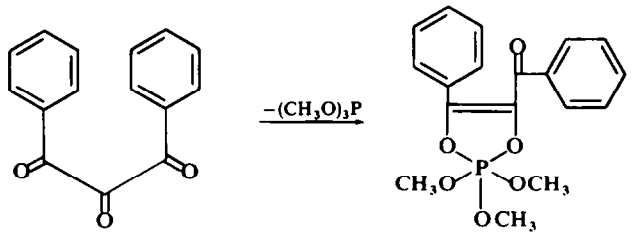


27

It should be noted that a transfer of the "active hydrogen" from carbon to nitrogen in the 1:1 adduct **25a** would give the new adduct **25b**. This can cyclize to the oxyphosphorane **28** or to one of the tautomers of **26** (with hydrogen on nitrogen). The phosphorane **28** is simply the product of the addition of phosphite to an α,β-diketoamide, $C_6H_5.CO.CO.CONHC_6H_5$. The corresponding phosphorane **30** made from a vicinal triketone **29** has been isolated.[6] Dipolar 1:1 adducts analogous to **25b** have been postulated in the reactions of phosphites with alloxan[7] and with oxomalonic[8] and pyruvic esters.[9]



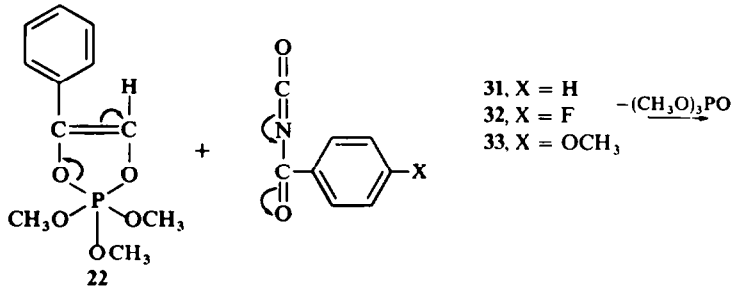
25b 28



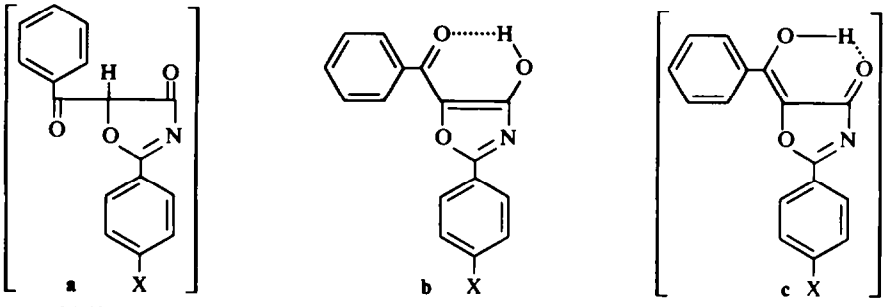
29 30, $\delta^{31}P = +49{\cdot}3$ ppm

The formation of the hydantoin **24c** suggests that these proton transfers do not interfere with the new synthesis; they may not occur under certain conditions or, if they do, the resulting intermediates must lead to the hydantoin as final product.

Reaction of dioxaphospholenes with aroyl- and acyl-isocyanates. The reaction of the phenylglyoxal-phosphite adduct **22** with benzoylisocyanate **31** was highly exothermic at 20°, and was best carried out at −20° to 0° in methylene chloride solution. The products were trimethyl phosphate and 2-phenyl-5-benzoyl-4-hydroxy-oxazole, **34b**, one of the tautomers of the 4-oxazolones **34a** and **34c**.



22

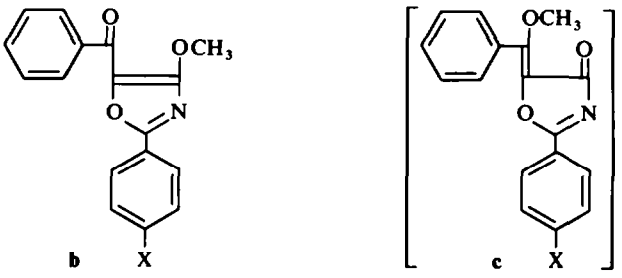


a X
34, X = H;

b X
35, X = F;

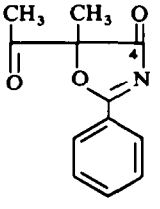
c X
36, X = OCH_3

The properties of the hydroxyoxazole **34b** are given in Table 2. Note the position of the proton signal in the NMR spectrum, and the typical IR spectrum[10] of a benzoyl group engaged in hydrogen-bonding ("conjugate chelation"). Structure **34b** is supported also by the properties of the methyl ether prepared by reaction of **34b** with diazomethane. The ether was formulated as 2-phenyl-5-benzoyl-4-methoxy-oxazole (**37b**) from the properties given in Table 3.



37, X = H; **38**, X = F; **39**, X = OCH_3

The spectral properties of the hydroxy- and methoxyoxazoles **34b** and **37b** should be compared with those of the related 4-oxazolone, **40**, already discussed.[1]

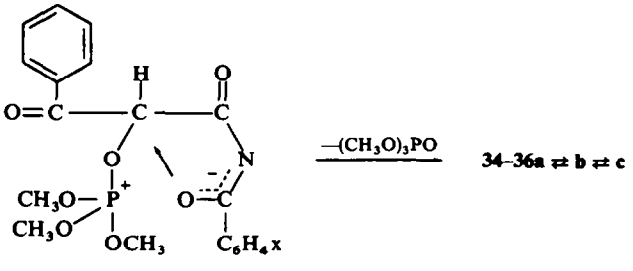


40

τ CH_3CO = 7·75 ppm
τ CH_3 = 8·22 ppm
$\bar{\nu}$ $^4C{=}O$ = 1764 cm^{-1}
$\bar{\nu}$ CH_3CO = 1730 cm^{-1}

An examination of the IR spectra of the original reaction-mixture and of all fractions resulting from the synthesis of the oxazole **34b**, revealed the presence of another structure(s) with bands at 1754, 1715 and 1695 cm^{-1}. This material could not be isolated in pure form but the evidence points to the other tautomer(s), **34c** and **34a**.

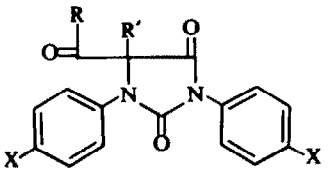
The formation of the oxazole **34b** can be viewed as an intramolecular displacement of phosphate from the ambident dipolar 1 : 1 adduct **41** resulting from the phospholene **22** and the aroylisocyanate. The same comments can be made concerning the possible transfer of the "active hydrogen" from carbon to nitrogen in adduct **41**, as were made in connection with adduct **25a** → **25b**.



41

TABLE 1.

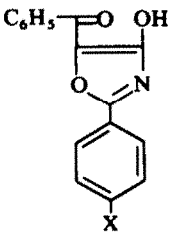
5-ACYLHYDANTOINS FROM α-DICARBONYL COMPOUNDS, ARYLISOCYANATES AND TRIMETHYL PHOSPHITE



X	No	M.p.°	Molecular formula	Calcd, %			Found, %			Yield, %	^{1}H NMR[a]		Ir,[b] $\bar{\nu}$ cm^{-1}
				C	H	N	C	H	N		τR	τR′	
R = R′ = CH$_3$													
F	13	133–134[c]	$C_{18}H_{14}O_3N_2F_2$	62·8	4·1	8·1	62·9	4·1	7·9[d]	66[e]	7·66[f]	8·26	1779; 1730; 1724
Cl	14	161–162[g]	$C_{18}H_{14}O_3N_2Cl_2$	57·4	3·7	7·4	57·3	3·7	7·4[h]	66[e]	7·67[f]	8·25	1779; 1730; 1724
Br	15	173–174[c]	$C_{18}H_{14}O_3N_2Br_2$	46·3	3·0	6·0	45·8	3·3	6·4	65[i]	7·58[j]	8·24	1779; 1730; 1721
NO_2	16	204–205[g]	$C_{18}H_{14}O_7N_4$	54·3	3·5	14·1	54·8	3·6	14·5	65[k]	7·52[l]	8·04	1779; 1730; 1721
CH_3	17	128–130[c]	$C_{20}H_{20}O_3N_2$	71·4	6·0	8·3	71·5	6·0	8·5	40[l]	7·68[f,m]	8·30	1783; 1730; 1721
R = C$_6$H$_5$; R′ = H													
H	24c	241–242[g]	$C_{22}H_{16}O_3N_2$	74·1	4·5	7·9	73·6	4·5	8·4	45	*ca.* 2·6[j]	0·99[n]	1754; 1715[o] 1677; 1039

[a] ^{1}H NMR at 50 Mc/s in ppm *vs.* TMS = 10 (τ values). [b] In CH_2Cl_2. The band at 1780 cm^{-1} was weaker than that at 1724 cm^{-1} the band at 1730 cm^{-1} appeared as a shoulder. [c] From benzene–hexane. [d] F, Calc. 11·0%; Found, 10·5%. [e] 18 hours at reflux in 3·0–3·5 M CH_2Cl_2 solution. [f] In $CDCl_3$. [g] From $C_2H_4Cl_2$. [h] Cl, Calc. 18·6%; Found, 18·5%. [i] 18 hours at reflux in 0·5–1 M $C_2H_4Cl_2$ solution. [j] In $(CD_3)_2SO$. [k] At 20°, external cooling (exothermic reaction), in 3 M CH_2Cl_2. [l] In $AsCl_3$. [m] In $CDCl_3$, the two CH_3-groups on phenyl appeared under this signal. Addition of benzene to $CDCl_3$ gave 3 distinct signals. [n] Enol–OH. [o] In Nujol mull. In KBr pellet: 3279, 1754, 1709, 1667 and 1654 cm^{-1} (the last four bands of about equal intensities. In dilute $C_2H_4Cl_2$: 1770, 1718 and 1680 cm^{-1}; weak 3571 and 3333 cm^{-1}.

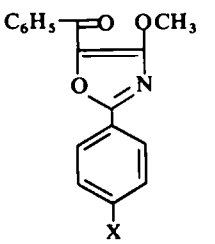
TABLE 2. 4-HYDROXYOXAZOLES FROM PHENYLGLYOXAL, AROYLISOCYANATES AND TRIMETHYL PHOSPHITE



X	No	M.p.°	Molecular Formula	Calc, %			Found, %			Yield,[a] %	τ_{OH}[b]	Ir,[c] $\bar{\nu}$ cm^{-1}
				C	H	N	C	H	N			
H	**34b**	140–142[d]	$C_{16}H_{11}O_3N$	72·4	4·2	5·3	72·5	4·4	5·7	65	−1·75	3322; 1626[e]
F	**35b**	160–161[d]	$C_{16}H_{10}O_3NF$	67·8	3·5	4·9	67·7	3·5	4·7[f]	71	−1·66	3322; 1626; 1613
CH_3O	**36b**	173–175[d]	$C_{17}H_{13}O_4N$	69·1	4·4	4·7	69·1	4·6	5·0	70	−2·20[g]	3322; 1613[h]

[a] Once recrystallized. [b] ppm *vs.* TMS = 10, in $AsCl_3$ solution. [c] Main bands in CH_2Cl_2 solution. Some of the solutions of the 5-benzoyl-4-hydroxyoxazoles may show bands of variable intensities at 1770–1754, 1724–1715 and 1695–1681 cm^{-1} which are probably due to one or more tautomers. [d] From benzene alone or with hexane. [e] This strong band was flanked by shoulders at 1653, 1605 and 1582 cm^{-1}. [f] F, Calcd, 6·7%; Found, 6·7%. [g] τ_{CH_3O} = 6·08. [h] Flanked by shoulders at 1645, 1587 and 1558 cm^{-1}; also strong bands at 1495 and 1176 cm^{-1}.

TABLE 3. 4-METHOXYOXAZOLES FROM 4-HYDROXYOXAZOLES AND DIAZOMETHANE

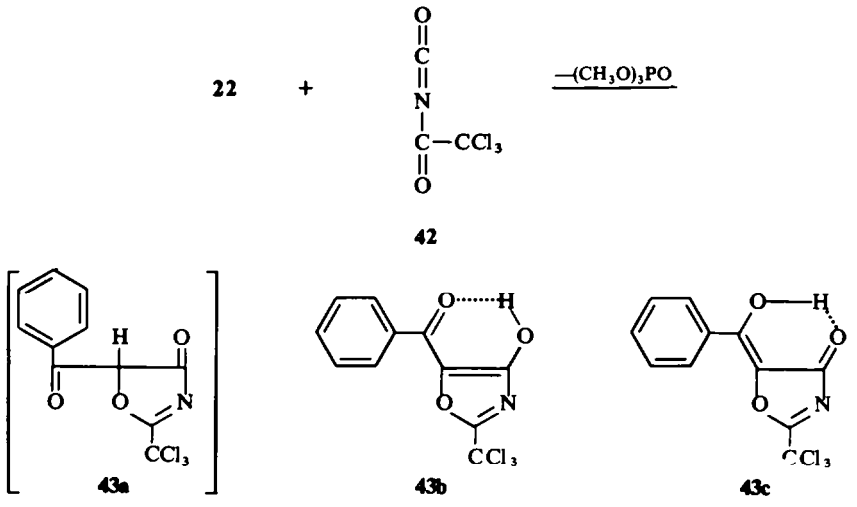


X	No	M.p.°	Molecular Formula	Calcd., %			Found, %			τ_{CH_3O}[a]	IR,[b] $\bar{\nu}$ cm^{-1}
				C	H	N	C	H	N		
H	**37b**	123–124[c]	$C_{17}H_{13}O_3N$	73·1	4·6	5·0	73·2	4·8	5·5	5·90	1639; 1582; 1567; 1449; 1399
F	**38b**	114–115[c]	$C_{17}H_{12}O_4NF$	68·7	4·1	4·7	68·9	4·3	5·1[d]	5·90	1639; 1605; 1582; 1493; 1449; 1389
CH_3O	**39b**	136–137[e]	$C_{18}H_{15}O_4N$	69·9	4·8	4·5	69·3	4·9	4·6	5·88[f]	1639; 1613; 1587; 1497; 1449; 1389

[a] ppm *vs.* TMS = 10 in $CDCl_3$ solution. [b] All sharp and strong bands in CH_2Cl_2 solution. [c] From benzene–hexane. [d] F, Calcd., 6·4%; Found: 7·0%. [e] From benzene or 95% C_2H_5OH. [f] $\tau_{CH_3O,C_6H_4} = 6·16$.

Other 4-hydroxyoxazoles **35b**, **36b**, and their corresponding methyl ethers **38b**, **39b**, were prepared and are described in Tables 2 and 3, respectively.

The reaction of phospholene **22**, with trichloroacetylisocyanate **42** was carried out at −40°. The data given in the Experimental Section support the 4-hydroxyoxazole structure **43b** for the substance initially obtained from the reaction mixture. However, as this material was recrystallized from benzene and then from chloroform it changed to a sparingly soluble crystalline form which probably had the 5-enol-4-oxazolone structure **43c** because the IR spectrum of a KBr pellet showed relatively strong bands at 3226 and at 1739–1681 cm^{-1}.



EXPERIMENTAL

Analyses were performed by the Schwarzkopf Microanalytical Laboratories.

The *trimethyl phosphite* was dried over Na ribbon, decanted, and freshly distilled. The *biacetyl* and *phenylglyoxal* were freshly distilled. The *aroylisocyanates* were prepared from oxalyl chloride Cl.CO.CO.Cl and the amide, $Ar.CO.NH_2$, by the procedure of Speziale and Smith,[11] but using CH_2Cl_2 as solvent. The *arylisocyanates* were commercial samples used after distillation or as received. Moisture must be excluded in all operations which involve the phospholenes, phospholanes and isocyanates, *in particular the aroylisocyanates.*

Synthesis of hydantoins from biacetyl, arylisocyanates and trimethyl phosphite

Compound **1**, was prepared from biacetyl and trimethyl phosphite[5] and allowed to react with two mole equiv of the arylisocyanate in CH_2Cl_2 or $C_2H_4Cl_2$ as specified in Table 1. The solvent was evaporated in vacuum (20 mm, 30°), the residue was treated with cold ether or EtOH to remove trimethyl phosphate, and the sparingly soluble hydantoin was purified by recrystallization from the solvent indicated. The properties of the hydantoins are given in Table 1.

2,2,2-Trimethoxy-4-p-chlorophenylimino-5-acetyl-5-methyl-2,2-dihydro-1,3,2-dioxaphospholane **8**. The adduct **1** (2 moles) and *p*-chlorophenylisocyanate (1 mole) were mixed in 3·5M CH_2Cl_2 at 20°. After 30 min at 20° and 2 hr under reflux, the solvent was evaporated at 30° (20 mm). The solid residue was recrystallized from benzene and gave **8**, m.p. 120–121° in 70% yield. The analytical sample was recrystallized also from $CHCl_3$-hexane. (Found: C, 46·3; H, 5·2; N, 3·6. $C_{14}H_{19}O_6NClP$ requires: C, 46·3; H, 5·2; N, 3·8%); $\partial^{31}P = +58·2$ ppm *vs.* H_3PO_4 (in $H.CO.N(CH_3)_2$). The ^1H NMR spectrum ($CDCl_3$) had a doublet at τ 6·36, $J_{HP} = 13$ c/s (CH_3O); a singlet at τ 7·68 (CH_3CO); and a singlet at τ 8·31 (CH_3C). The IR spectrum (CH_2Cl_2) had bands at 1724 (C = O) and 1672 cm^{-1} (C = N) μ.

Reaction of the p-*chlorophenylimino-dioxaphospholane,* **8**, *with* p-*cyanophenylisocyanate* **18**. The imino-phospholane **8** (5·18 g) was added to **18** (2·25 g, one mole equiv) in THF (35 ml) at 30°. The soln was stirred 24 hr at 30° and evaporated at 30° and 20 mm. The residue was kept 24 hr at −20° in ether (25 ml) and the resulting **19** (4 g, 72%, m.p. 125–130°) was filtered and recrystallized from benzene to give **19**, m.p. 139–141°. (Found: C, 62·2; H, 3·9; N, 11·5; Cl, 9·2. $C_{19}H_{14}O_3N_3Cl$ requires: C, 62·1; H, 3·8; N. 11·4; Cl, 9·5%); the ^{1}H NMR spectrum ($CDCl_3$) had singlets at τ 7·60 (CH_3CO) and τ 8·12 (CH_3C). The IR spectrum (CH_2Cl_2) had bands at 2222 (C≡N), 1779 (C=O), 1739 (C=O) and 1721 cm^{-1}.

2,2,2-*Trimethoxy*-4-p-*tolylimino*-5-*acetyl*-5-*methyl*-2,2-*dihydro*-1,3,2-*dioxaphospholane* **11**. *p*-Tolylisocyanate (8·9 g) was added to the adduct, **1**, (70·6 g; 5 mole equiv), at 20°, with stirring. After 24 hr at 20°, the mixture was dissolved in CH_2Cl_2 and kept at 20° a few hr longer without much change. The soln was evaporated (30°, 20 mm) and the residue was kept at −20° in ether. The crude phospholane (19 g) had small amounts of hydantoin, which were removed by crystallization from benzene-hexane; **11** had m.p. 110–111° (60% yield). (Found: C, 52·7; H, 6·7; N, 4·3; P, 9·2. $C_{15}H_{22}O_6NP$ requires: C, 52·5; H, 6·5; N, 4·1; P, 9·0%); ∂^{31} P = +57·3 ppm ($CDCl_3$). The ^{1}H NMR spectrum ($CDCl_3$) had a doublet at τ 6·45, J_{HP} = 13 c/s (CH_3OP); a singlet at τ 7·70 (CH_3CO) covering another singlet due to the $CH_3 \cdot C_6H_4$-group; and a singlet at τ 8·32 (CH_3C). The IR spectrum (CH_2Cl_2) had bands at 1730 (C=O) and 1678 (C=N).

Synthesis of hydantoin **24c** *from phenylglyoxal, phenylisocyanate and trimethyl phosphite*

(a) Compound **22**, was prepared from phenylglyoxal and trimethyl phosphite.[6] The phospholene **22** (6·17 g) in CH_2Cl_2 (25 ml) was added to phenylisocyanate (5·7 g, 2 mole equiv) in CH_2Cl_2 (25 ml) at 0° over 1 hr-period. After 24 hr at 20°, the solid hydantoin had precipitated. (There was some unreacted phenylisocyanate which persisted even after 48 hr at 40°). The solvent was evaporated at 30° (20 mm) and the residue was stirred with cold ether (50 ml) and filtered, giving **24c**, m.p. 230–235°, in 45% yield; see Table 1.

(b) *Without isolation of phospholene.* Phenylglyoxal (4·99 g, 0·372 mole) in CH_2Cl_2 (25 ml) was added over a 1·5 hr period to a mixture of trimethyl phosphite (4·6 g, 0·372 mole) and phenylisocyanate (8·85 g, 0·743 mole) at 0°. The soln was kept 1 hr at 0°, 2 hr at 20° and 1 hr at 40°. The hydantoin (3·6 g, ca. 30%, m.p. 225–235°) separated on cooling and was recrystallized from $C_2H_4Cl_2$ as before (m.p. 241–242°; 25% yield).

Synthesis of 4-*oxazolones* (4-*hydroxyoxazoles*) *from phenylglyoxal, aroylisocyanates and trimethyl phosphite.* The adduct[6] **22** (1 mole equiv) was added, dropwise, as a neat liquid or as a 3 M CH_2Cl_2 soln, to a 1–2 M CH_2Cl_2 soln of the aroylisocyanate (1 mole equiv.) kept at −20° to 0°. The reaction was exothermic. The soln was stirred 1 hr at 0° and 3–6 hr at 20°. The solvent was evaporated at 30° and 20 mm and the residue was stirred with cold ether and filtered. The 4-hydroxyoxazoles (tautomers of 4-oxazolones) were purified as indicated in Table 2).

Reaction of 4-*hydroxyoxazoles* **34–36** *with diazomethane.* Ethereal diazomethane was added to the suspension of the 4-hydroxyoxazole (**34–36**) in MeOH (12 ml of CH_3OH per g). Evolution of N_2 was noted. The soln was kept 10 hr at 0° and was evaporated at 30° and 20 mm. The IR spectrum of the crude residue was nearly identical to that of the pure 4-methoxyoxazole (**37–39**). The latter was purified as indicated in Table 3.

Reaction of the phenylglyoxal-trimethyl phosphite adduct with trichloroacetylisocyanate. The phospholene **22** (7·45 g) was added, dropwise, over a 1 hr-period, to a soln of $Cl_3CO.NCO$[2,11] (5·45 g; one mole equiv) in CH_2Cl_2 (25 ml) at −40°. The soln was kept 1 hr at −40° and 2 hr at +20°; the IR spectrum of an aliquot showed complete reaction of the isocyanate. The solvent was evaporated (30°, 20 mm), the residue was kept 24 hr at −20° under ether (30 ml), and the mixture was filtered. (a) *The ether-insoluble colorless crystals* (**43b**; 3·8 g; 43%; m.p. 135–145°) had the following partial IR spectrum in CH_2Cl_2: 6·10 (strong), 6·23, 6·30 and 6·38 μ (set of weaker bands). The ^{1}H NMR spectrum in $CDCl_3$ had a one ^{1}H signal at τ 0·27 in addition to the five aromatic protons. One crystallization from benzene–hexane *lowered* the m.p. to 120–137°. The IR spectrum in CH_2Cl_2 was as before but a new set of three much weaker bands appeared at 1786 (very weak), 1754 (strongest) and 1681 (medium) cm^{-1}. The ^{1}H NMR in $CDCl_3$ had a signal at τ 0·54. (Found: C, 44·1; H, 2·2; N, 5·0. $C_{11}H_6NO_3Cl_3$ requires: C, 43·4; H, 2·0; N, 4·6%). Recrystallization from $CHCl_3$-hexane gave crystals with m.p. 130–140°. These were no longer sufficiently soluble in the usual solvents for ^{1}H NMR analysis. However, the IR spectrum of a saturated CH_2Cl_2 soln had changed to the following: 1786 (w), 1754 (s), 1681 (m) cm^{-1}, there was a band at 3333 cm^{-1}. Another crystallization from $CHCl_3$ gave a solid m.p. 136–140°, whose KBr pellet had strong bands at 3226 cm^{-1} and 1739–1681 cm^{-1} probable structure **43c**.

(b) *The ether-soluble portion* was evaporated. The residue, in CH_2Cl_2 solution, had the IR bands of $(CH_3O)_3PO$ and bands at 3333, 1786, 1754 and 1689 cm^{-1} as before. The ^1H NMR in $CDCl_3$ had the doublet of the phosphate and a signal at τ 0·37.

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