Synthesis of 2-Alkenylpyrazol-3(2*H*)-one Derivatives Under Mild Conditions

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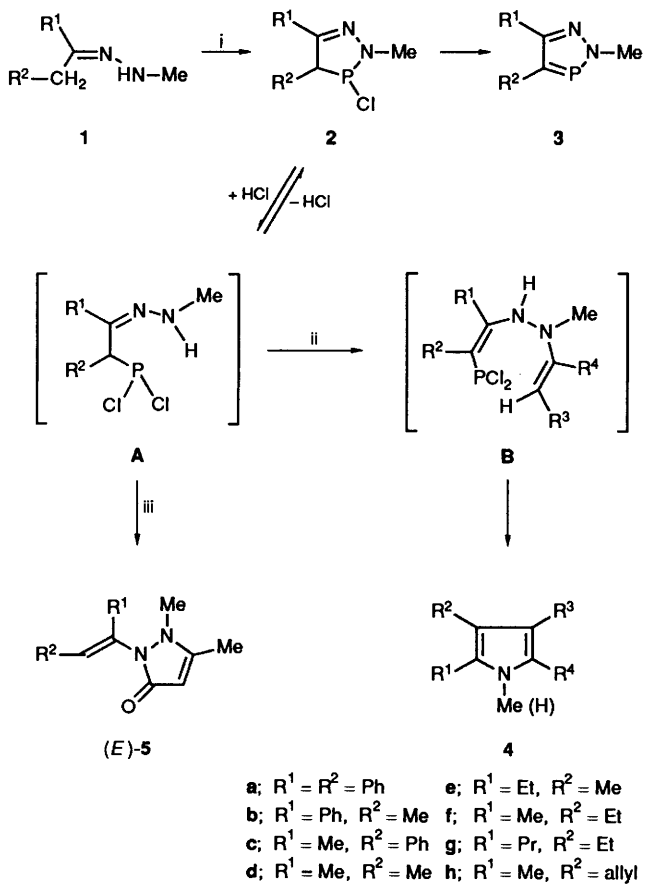
The title compounds have been synthesized by a one-pot two-stage reaction of PCl_3, ketone methylhydrazones and methyl acetoacetate. Both stages were carried out at room temperature and the corresponding 2-alkenyl-1,5-dimethylpyrazol-3(2*H*)-ones **5**, which are an unknown series of pyrazolones, were obtained in good yields. Use of a variety of enolizable ketones has shown that the reaction always occurs with the predominance of the (*E*)-isomer. X-Ray structure determinations of an (*E*)- and a (*Z*)-derivative [(*E*)-**5c**·HCl and (*Z*)-**5b**] permitted the assignment of their structures. The aromaticity of these derivatives is discussed.

Some years ago we discovered[1] that the reaction between an arylhydrazone and PCl_3 gives indoles in very good yields in a few minutes, at room temperature, and that the intermediate of this indolization is an *in situ*-generated chlorodihydrodiazaphosphole such as compound **2** (see Scheme 1). More recently



a; $R^1 = R^2 = Ph$ **e**; $R^1 = Et$, $R^2 = Me$
b; $R^1 = Ph$, $R^2 = Me$ **f**; $R^1 = Me$, $R^2 = Et$
c; $R^1 = Me$, $R^2 = Ph$ **g**; $R^1 = Pr$, $R^2 = Et$
d; $R^1 = Me$, $R^2 = Me$ **h**; $R^1 = Me$, $R^2 = allyl$

Scheme 1 *Reagents and conditions:* i, PCl_3, room temp.; ii, $R^3CH_2COR^4$, PCl_3; iii, $MeCOCH_2CO_2Me$, PCl_3, room temp.

we have found[2] that a related two-stage reaction can be used for the synthesis of substituted pyrroles. The first stage is a well known[3] reaction which consists of the addition of PCl_3 to hydrazones **1** leading to the formation of an intermediate **2** which gives diazaphosphole **3** after heating. Since at present it is not known how compound **2** is formed, the possibility that it might be formed *via* intermediate **A** cannot be excluded. However, it is thought[1] that in the first step PCl_3 undergoes a nucleophilic attack more probably by the nitrogen than by the carbon atom. Presumably intermediate **2** might be in equilibrium with the hypothetical ring-opened product **A** arising from cleavage of P–N bond due to the large excess of HCl present in the reaction mixture. Such a hypothesis was previously suggested in order to explain the proposed mechanism for the related indolization.[1] The second stage, an addition of an enolizable ketone and PCl_3 to the previous reaction mixture, gives the corresponding pyrrole **4** presumably *via* the hypothetical dienehydrazine **B** by a series of steps analogous to the Piloty mechanism.[4] In this instance the phosphorus moiety could have an important role in promoting the loss of the nitrogen atom.[1]

During a study of the possible extension of this reaction to the formation of functionalized pyrroles a surprising result was discovered. When, in the second state methyl acetoacetate was used instead of the corresponding pyrroles bearing a methoxycarbonyl group, the 2-alkenyl-1,5-dimethylpyrazol-3(2*H*)-one derivatives **5**, which are, to date, an unknown series of pyrazolone derivatives, were obtained. In a recent communication[5] the first two results of this new reaction were reported. In this paper full details of this synthesis using several ketones are described and two X-ray structures are reported which permit the assignment of the (*E*,*Z*)-configuration of **5** and the discussion of the aromaticity of the pyrazolone ring.

Results and Discussion

The overall reaction is depicted in Scheme 1 and the pyrazolones **5** obtained in this manner are summarized. The synthesis of 2-alkenyl-1,5-dimethylpyrazol-3(2*H*)-ones is a one-pot two-stage procedure very similar to the pyrrole synthesis[2] with the difference that the two stages are always carried out at room temperature.

The first stage of this synthesis consists of the addition of PCl_3 to a dry dichloromethane solution of a methylhydrazone **1**. The course of the reaction was followed by GC–MS (gas chromatographic–mass spectrometric) analysis observing the gradual disappearance of **1** and the concomitant appearance of diazaphosphole derivative **3**. It should be noted that compound **3** was not present in the reaction mixture and its formation from precursor **2** occurs only after heating in the chromatograph injector. The first stage went to completion after about 10–15 h, the time depending on the nature of the hydrazone used. In the second stage methyl acetoacetate and equimolar amounts of

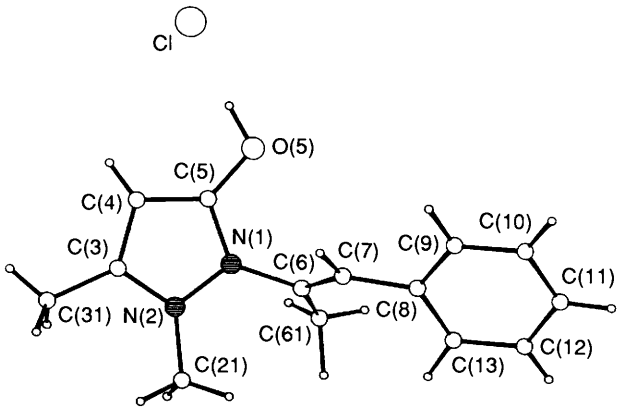


Fig. 1 Perspective view of the structure of compound (*E*)-**5c**·HCl

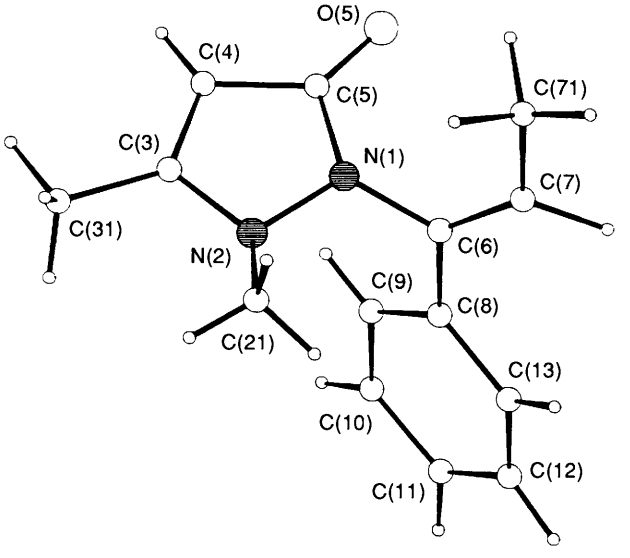


Fig. 2 Perspective view of the structure of compound (*Z*)-**5b**

Table 1 Spectroscopic data for compounds **5**

Compound	Exact mass, found (calc.)	$\delta_H(CDCl_3)$[a]
(*E*)-**5a**	290.141 89	2.35 (br s, 3 H, 5-Me), 3.45 (s, 3 H, 1-Me), 6.45 (br s, 1 H, 4-CH), 7.08 (s, 1 H, PhCH=), 7.15–7.40 (m, 10 H, ArH)
(*E*)-**5b**	228.126 314 (228.126 263)	2.00 (d, *J* 7.4, 3 H, MeCH=), 2.08 (d, *J* 0.8, 3 H, 5-Me), 2.96 (s, 3 H, 1-Me), 5.34 (br q, *J* 0.8, 1 H, 4-CH), 6.12 (q, *J* 7.4, 1 H, MeCH=), 7.10–7.20 (m, 5 H, ArH)
(*Z*)-**5b**	228.126 194 (228.126 263)	1.90 (d, *J* 7.0, 3 H, MeCH=), 2.18 (d, *J* 0.8, 3 H, 5-Me), 3.00 (s, 3 H, 1-Me), 5.38 (br q, *J* 0.8, 1 H, 4-CH), 6.46 (q, *J* 7.0, 1 H, MeCH=), 7.20–7.35 (m, 5 H, ArH)
(*E*)-**5c**	228.126 244 (228.126 263)	2.20 (d, *J* 0.8, 3 H, 5-Me), 2.22 (d, *J* 1.2, 3 H, MeC=), 3.18 (s, 3 H, 1-Me), 5.31 (1, *J* 0.8, 1 H, 4-CH), 6.55 (q, *J* 1.2, 1 H, PhCH=), 7.25–7.40 (m, 5 H, ArH)
(*E*)-**5d**	166.111 40 (166.110 61)	1.73 (dq, J_1 7.2, J_2 1.3, 3 H, MeCH=), 1.77 (dq, J_1 1.2, J_2 1.3, 3 H, MeC=), 2.08 (s, 3 H, 5-Me), 3.02 (s, 3 H, 1-Me), 5.14 (s, 1 H, 4-CH), 5.62 (qq, J_1 7.2, J_2 1.3, 1 H, MeCH=)
(*E*)-**5e**	180.126 211 (180.126 263)	0.90 (t, *J* 7.5, 3 H, $MeCH_2$), 1.82 (br d, *J* 7.0, 3 H, MeCH=), 2.17 (s, 3 H, 5-Me), 2.38 (q, *J* 7.5, 2 H, CH_2Me), 3.10 (s, 3 H, 1-Me), 5.19 (s, 1 H, 4-CH), 5.59 (q, *J* 7, 1 H, MeCH=)
(*E*)-**5f**	180.126 281 (180.126 263)	1.12 (t, *J* 7.6, 3 H, $MeCH_2$), 1.97 (s, 3 H, =CMe), 2.29 (m, *J* 7.6, 2 H, CH_2Me), 2.40 (s, H, 5-Me), 3.61 (s, 3 H, 1-Me), 5.86 (br t, *J* 7.6, 1 H, CH=), 5.90 (s, 1 H, 4-CH)
(*E*)-**5g**	208.157 596 (208.157 563)	0.94 [t, *J* 7.32, 3 H, $Me(CH_2)_2$], 1.12 (t, *J* 7.62, 3 H, $MeCH_2$), 1.30 (quin, *J* 7.32, 2 H, $MeCH_2$), 2.31 [m, 4 H, $Me(CH_2)_2$], 2.41 (s, 3 H, 5-Me), 3.65 (s, 3 H, 1-Me), 5.91 (t, *J* 7.3, 1 H, EtCH=), 6.22 (s, 1 H, 4-H)
(*E*)-**5h**	192.126 221 (192.126 263)	1.99 (s, 3 H, 5-Me), 2.40 (s, 3 H, MeC=), 3.02 (t, *J* 6.6, 2 H, $=CCH_2C=$), 3.66 (s, 3 H, 1-Me), 5.1–5.22 (m, 2 H, $=CH_2$), 5.7–5.9 (m, 1 H, $CH_2=CH$), 5.97 (br t, *J* 7.5, 1 H, $CH_2CH=$), 6.14 (s, 1 H, 4-CH)

[a] *J* Values are given in Hz.

PCl_3 were added, the latter reagent acted as water scavenger to favour the condensation of methyl acetoacetate with the hydrazino group of **A**. At present it is not possible to define the correct pattern of this second stage although it is probable that an intermediate related to **B** is formed which might successively give the product **5**. The course of this stage was followed by TLC and GC–MS analysis and the gradual disappearance of **3** and of the β-keto ester could be observed with concomitant formation of two isomers of **5**, the (*E*)-isomer being predominant. Evaporation under reduced pressure of the reaction mixture was carried out to remove the solvent and the excess of PCl_3. In the reaction mixture the pyrazolones **5** generally existed as their hydrochloride salts which are insoluble in diethyl ether. Therefore, a simple extraction with diethyl ether may be sufficient to eliminate the residual starting material or by-products such as pyrroles and diazaphospholes. The crude product was treated successively with saturated aqueous sodium hydroxide to obtain the free pyrazolones **5** which were isolated as pure compounds by crystallization, distillation or column chromatography. It should be noted that pyrazolones **5** were obtained with longer reaction times using ethyl acetoacetate. Obviously, the presence of PCl_3 is essential in both stages of this synthesis, and no formation of pyrazolone **5** was observed when the reaction between methylhydrazone **1** and methyl acetoacetate was carried out in the absence of PCl_3 even in refluxing benzene in the presence of a large excess of HCl as well as in triethyl phosphate with $POCl_3$ as acid catalyst.

The reaction appears to be quite general since a large variety of enolizable ketones can be used. It is worth noting that γ,δ-unsaturated ketone hydrazone **1h** gave the corresponding diene **5h** without affecting the double bond. The assignment of the configuration of the isomer was obtained by X-ray analysis of two compounds in the two different configurations. In particular, suitable crystals were obtained for (*E*)-**5c** in its hydrochloride form and (*Z*)-**5b**. The X-ray structures are shown in Figs. 1 and 2, respectively.

All the pyrazolones described in this paper are new compounds and were identified essentially by ^1H NMR spectroscopy and mass spectrometry (Table 1). The assignment of their configurations was based on the comparison of their spectroscopic data with those of (*E*)-**5c**·HCl and (*Z*)-**5b**. By the method described in this paper several differently substituted 2-alkenyl-1,5-dimethylpyrazol-3(2*H*)-ones (hitherto rather inaccessible by other methods) can be easily prepared using readily available starting materials and reagents under very mild reaction conditions. Finally our results provide further evidence that diazaphosphole derivatives, generated *in situ*, can be intermediates in the synthesis of several azaheterocycles.

Table 2 Fractional atomic coordinates (× 10^4) for non-H atoms with esds in parentheses for (*E*)-**5c**·HCl

	x	*y*	*z*
Cl	4184(0)	6300(1)	3436(0)
O(5)	2839(1)	5263(2)	2789(1)
N(1)	1563(1)	5721(2)	2816(1)
N(2)	1029(1)	6251(2)	3240(1)
C(3)	1363(1)	6480(3)	3791(1)
C(4)	2122(1)	6140(3)	3725(1)
C(5)	2233(1)	5670(3)	3110(1)
C(6)	1412(1)	5576(3)	2158(1)
C(7)	1510(1)	3927(3)	1918(1)
C(8)	1474(1)	3374(3)	1260(1)
C(9)	1913(1)	1908(3)	1077(1)
C(10)	1936(2)	1349(4)	465(1)
C(11)	1499(1)	2193(4)	26(1)
C(12)	1033(1)	3598(3)	201(1)
C(13)	1017(1)	4202(3)	813(1)
C(21)	233(1)	6236(5)	3092(1)
C(31)	925(2)	6990(5)	4352(1)
C(61)	1226(2)	7319(3)	1842(1)

Molecular Geometry.—Final atomic coordinates are given in Table 2. The arbitrary numbering scheme used in the crystal analysis is shown in Fig. 1, which represents a perspective view of the molecule.

As far as we are aware, this work represents the first example of an X-ray structural study in which a 1,5-dimethylpyrazole, having a hydroxy group in position 3, becomes a pyrazolinium ion with a positive charge hypothetically delocalized on C(3)–C(4)–C(5).

The intramolecular bond lengths and angles, in line with the hybridization expected for the atoms involved, and torsion angles reported in Table 3, show a conformational geometry which is apparently similar to that found in the analogous (*Z*)-**5b** previously studied[5] (Fig. 2). The main differences concern the conformation of the pyrazole moiety; in fact the electron deficiency considerably modifies all of the geometrical parameters of the five-membered ring. Bond distances attenuate their single or double bond character and, in particular, the C(3)–C(4) bond lengthens, while all the other bonds shorten, becoming comparable with C(4)–C(5) and N(1)–N(2). The bond angles on the ring are not greatly altered settling about the theoretical value of 108°; greater variations are observed on the external angles of N(1), N(2) and C(5); however, while this last atom maintains its strict sp^2 character, N(1) and N(2) modify their configuration from pyramidal to planar as can be explained by the out-of-plane distances reported in Table 4 and by the sum of bond angles becoming 359.3° from 352.6 and 347.7°, respectively.

The analysis of the planarity, reported in Table 4, confirms that the pyrazole ring modifies its geometry, the conformational analysis[6] indicates that the five-membered ring changes its conformation from twist with C_2 symmetry into envelope with C_s symmetry very close to the planar geometry.

The perimeter of the pyrazole ring, 6.88 Å, is the shortest of those reported in the literature, in agreement with the conclusions of Barton *et al.*[7] that the perimeter of a potentially aromatic molecule can act as a measure of its aromaticity.

Regarding the geometry of the ethylenic C(6)=C(7) double bond, the distortion about the double bond is given in terms of the *cis*-torsion angle C(61)–C(6)–C(7)–C(8) in *E*-**5c** and of the *trans*-torsion angle C(8)–C(7)–C(6)–C(71) in *Z*-**5b** derivative [1.3(4) and 179.4(3)° respectively]: the puckering value indicates no variation in the ethylenic moiety for the two compounds.

The chlorine ion is involved in a hydrogen bond with the hydroxy group [O(5)···Cl = 2.872(2), H(5)···Cl = 1.94(8) Å; O(5)–H(5)···Cl = 164(9)°]. Other contacts are consistent with van der Waals interactions.

Table 3 Bond distances (Å) and angles (°) and selected torsion angles (°) for compound (*E*)-**5c**·HCl compared with the previously studied compound (*Z*)-**5b**

	(*E*)-**5c**	(*Z*)-**5b**
O(5)–C(5)	1.315(3)	1.234(3)
N(1)–N(2)	1.373(3)	1.406(3)
N(1)–C(5)	1.350(3)	1.394(3)
N(1)–C(6)	1.444(3)	1.425(3)
N(2)–C(3)	1.336(3)	1.368(3)
N(2)–C(21)	1.452(3)	1.455(3)
C(3)–C(4)	1.381(3)	1.344(3)
C(3)–C(31)	1.484(3)	1.493(4)
C(4)–C(5)	1.381(3)	1.435(3)
C(6)–C(7)	1.332(3)	1.329(3)
C(6)–C(8)	—	1.484(3)
C(6)–C(61)	1.491(3)	—
C(7)–C(8)	1.473(3)	—
C(7)–C(71)	—	1.495(4)
C(8)–C(9)	1.391(3)	1.387(3)
C(8)–C(13)	1.399(3)	1.395(3)
C(9)–C(10)	1.379(3)	1.382(4)
C(10)–C(11)	1.372(4)	1.382(4)
C(11)–C(12)	1.379(3)	1.370(5)
C(12)–C(13)	1.389(3)	1.385(4)
N(2)–N(1)–C(5)	108.0(2)	109.2(2)
N(2)–N(1)–C(6)	122.9(2)	119.1(2)
C(5)–N(1)–C(6)	128.4(2)	124.3(2)
N(1)–N(2)–C(3)	108.5(2)	106.3(2)
N(1)–N(2)–C(21)	121.8(2)	116.7(2)
C(3)–N(2)–C(21)	129.0(2)	124.7(2)
N(2)–C(3)–C(4)	108.7(2)	110.5(2)
N(2)–C(3)–C(31)	121.3(2)	120.4(2)
C(4)–C(3)–C(31)	130.0(2)	129.1(2)
C(3)–3(4)–C(5)	106.5(2)	108.6(2)
O(5)–C(5)–N(1)	119.0(2)	123.2(2)
O(5)–C(5)–C(4)	132.6(2)	132.1(2)
N(1)–C(5)–C(4)	108.4(2)	104.7(2)
N(1)–C(6)–C(7)	115.0(2)	118.6(2)
N(1)–C(6)–C(8)	—	116.1(2)
N(1)–C(6)–C(61)	115.1(2)	—
C(7)–C(6)–C(8)	—	125.3(2)
C(7)–C(6)–C(61)	129.8(2)	—
C(6)–C(7)–C(8)	128.2(2)	—
C(6)–C(7)–C(71)	—	125.1(2)
C(6)–C(8)–C(9)	—	120.2(2)
C(6)–C(8)–C(13)	—	121.4(2)
C(7)–C(8)–C(9)	117.5(2)	—
C(7)–C(8)–C(13)	124.3(2)	—
C(9)–C(8)–C(13)	118.1(2)	118.3(2)
C(8)–C(9)–C(10)	121.3(2)	120.9(2)
C(9)–C(10)–C(11)	120.2(2)	120.1(3)
C(10)–C(11)–C(12)	112.6(2)	119.9(3)
C(11)–C(12)–C(13)	120.8(2)	120.4(3)
C(8)–C(13)–C(12)	119.9(2)	120.5(2)
N(2)–N(1)–C(5)–O(5)	−177.4(2)	−171.3(2)
C(6)–N(1)–C(5)–O(5)	−7.5(3)	−21.8(4)
C(5)–N(1)–C(6)–C(7)	71.8(3)	85.3(2)
N(2)–N(1)–C(6)–C(7)	−119.8(2)	−128.0(3)
N(2)–N(1)–C(6)–C(8)	—	55.3(3)
N(2)–N(1)–C(6)–C(61)	64.6(3)	—
N(2)–N(1)–C(5)–C(4)	1.0(2)	7.3(3)
C(5)–N(1)–N(2)–C(3)	−1.5(2)	−9.3(2)
C(6)–N(1)–N(2)–C(21)	16.9(3)	55.4(3)
N(1)–N(2)–C(3)–C(4)	1.4(2)	7.5(3)
C(21)–N(2)–C(3)–C(31)	−7.4(4)	−33.3(4)
N(2)–C(3)–C(4)–C(5)	−0.8(2)	−3.1(3)
C(3)–C(4)–C(5)–N(1)	−0.1(2)	−2.7(3)
N(1)–C(6)–C(7)–C(8)	−173.6(2)	—
N(1)–C(6)–C(7)–C(71)	—	3.2(4)
C(61)–C(6)–C(7)–C(8)	1.3(4)	—
C(8)–C(6)–C(7)–C(71)	—	179.4(3)

Table 4 Analysis of the planarity in (*E*)-**5c**·HCl and (*Z*)-**5b** derivatives (*a*) Distances (Å × 10^3) of relevant atoms from the mean plane with standard deviations in parentheses; and (*b*) planes between angles (°)

	(*E*)-**5c**	(*Z*)-**5b**
(*a*) Plane *A*: N(1), N(2), C(3), C(4), C(5)		
N(1)	−5(2)	45(2)
N(2)	6(2)	−45(2)
C(3)	−9(2)	33(3)
C(4)	2(2)	1(3)
C(5)	6(2)	−34(3)
O(5)[a]	51(2)	−138(3)
C(6)[a]	174(2)	−415(3)
C(21)[a]	−160(4)	588(3)
C(31)[a]	−52(4)	109(4)
Plane *B*: C(8)–C(13)		
C(8)	18(2)	2(2)
C(9)	−18(2)	1(2)
C(10)	8(3)	1(3)
C(11)	15(2)	1(3)
C(12)	−10(2)	−5(3)
C(13)	−5(2)	3(2)
C(7)[a] or C(6)[a]	49(2)	−30(2)
Plane *C*: N(2), C(5), C(6)		
N(1)[a]	−72(2)	−222(2)
Plane *D*: N(1), C(3), C(21)		
N(2)[a]	−67(2)	288(3)
Plane *E*: N(2), C(4), C(31)		
C(3)[a]	−7(2)	−10(3)
Plane *F*: O(5), N(1), C(4)		
C(5)[a]	13(2)	11(3)
(*b*) *A*–*B*	38.7(1)	77.7(1)

[a] Atom not used to define the plane.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 200.00 and 50.30 MHz respectively using a Gemini 200 instrument. Chemical shifts are given in ppm from Me_4Si. *J* Values are given in Hz. Mass spectra were recorded with a VG 7070 spectrometer and GC–MS with an HP-5890 gas chromatograph equipped with a methyl silicone capillary column and an HP-5970 mass detector. M.p.s are uncorrected and were determined with a Büchi apparatus. Analytical samples of oily pyrazolones were obtained by bulb-to-bulb distillation and b.p.s given are the oven temperature. Commercial PCl_3 was used without further purification. Yields are based on starting quantities of methyl acetoacetate. The microanalyses were performed on pure isomers and the results were practically identical.

Methylhydrazones.—These were obtained by heating the respective methylhydrazine and ketone together in equivalent amounts in benzene solution at reflux for *ca.* 3 h under Dean–Stark conditions. After removal of the solvent the crude products were used immediately.

General Procedure for **5a–h**.—Phosphorus trichloride (11 mmol) was added, at room temperature, to a stirred dichloromethane solution (50 cm^3) of a hydrazone **1** (10 mmol). The mixture was allowed to react at room temperature, with further addition (if necessary) of dichloromethane to ensure homogeneity.

After about 10 h, methyl acetoacetate (7 mmol) and further PCl_3 (7 mmol) were added to the mixture which was maintained at room temperature for about 12 h. The course of the reaction was followed by GC–MS and TLC analyses. Evaporation under reduced pressure at 60–70 °C using a Rotavapor was carried out to remove the solvent and the excess of PCl_3. The residue containing pyrazolone **5** hydrochloride was extracted with small portions of diethyl ether to remove the residual starting material and by-products. The crude oil or solid, insoluble in ether, was dissolved in dichloromethane and washed with saturated aqueous sodium hydroxide until it became neutral, and then dried (Na_2SO_3). The solvent was evaporated under reduced pressure to give crude product **5** as a mixture of stereoisomers in which the (*E*)-isomer was always predominant. The ratio of stereoisomers was determined from the ^{1}H NMR spectra and the products were purified by silica gel column chromatography or for solid (*E*)-isomers by recrystallization. To obtain pure hydrochloride forms of **5**, gaseous hydrogen chloride was passed over a diethyl ether solution of **5** and the resultant precipitate was removed by filtration. Pyrazolones **5** were characterized by ^{1}H NMR spectroscopy and mass spectroscopy (see Table 1) and microanalysis and for the structures of (*Z*)-**5b** and (*E*)-**5c**·HCl were assigned by X-ray analysis (see Molecular geometry).

1,5-*Dimethyl*-2-(1,2-*diphenylvinyl*)*pyrazol*-3(2H)-*one* **5a**. The first stage of the reaction went to completion in 12 h at room temperature and the second stage in 13 h to give pyrazolones **5a** in 55% yield with an *E*:*Z* ratio of about 5:1. Pure compound (*E*)-**5a** was obtained by chromatographic separation on a silica gel column (diethyl ether–methanol–dichloromethane, 4:1:1) as white crystals (from methanol and diethyl ether) m.p. 223–224 °C (R_F 0.6) (Found: C, 78.5; H, 6.2; N, 9.5. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%).

1,5-*Dimethyl*-2-(1-*phenylprop*-1-*enyl*)*pyrazol*-3(2H)-*one* **5b**.—The first stage went to completion in 12 h and the second stage in 12 h to give pyrazolones **5b** in 75% yield in an *E*:*Z* ratio of about 3:1. Chromatographic separation on a silica gel column in the same eluent as above gave pure compound (*E*)-**5b** as a glassy oil, b.p. 175 °C at 0.5 mmHg (R_F 0.5), selected δ_C 12.4 (5-Me), 14.3 (*Me*CH=), 33.7 (NMe), 95.5 (MeCH=), 152.7 (C-5) and 166.7 (C=O); and pure isomer (*Z*)-**5b** (R_F 0.55) as white crystals (from CCl_4) m.p. 123–125 °C; selected δ_C 12.4 (5-Me), 13.9 (*Me*CH=), 33.3 (NMe), 95.1 (MeCH=), 152.6 (C-5) and 165.3 (C=O) (Found: C, 73.45; H, 6.9; N, 12.2. $C_{14}H_{16}N_2O$ requires C, 73.6; H, 7.0; N, 12.3%).

1,5-*Dimethyl*-2-(1-*methyl*-2-*phenylvinyl*)*pyrazol*-3(2H)-*one* **5c**. In the same manner pyrazolones **5c** were obtained in 70% yield in an *E*:*Z* ratio of 5:1. Pure isomer (*E*)-**5c** (R_F 0.4) was obtained as white crystals (from diethyl ether), m.p. 168–169 °C. The hydrochloride form had m.p. 187–188 °C (Found: C, 73.5; H, 6.95; N, 12.2. $C_{14}H_{16}N_2O$ requires C, 73.6; H, 7.0; N, 12.3%).

1,5-*Dimethyl*-2-(1-*methylprop*-1-*enyl*)*pyrazol*-3(2H)-*one* **5d**. In a similar manner pyrazolones **5d** in an *E*:*Z* ratio of 5:1 were obtained in 63% yield. Pure isomer (*E*)-**5d** was isolated as a yellow glassy oil (b.p. 165–170 °C, 0.05 mmHg) or a greasy white solid (Found: C, 64.85; H, 8.4; N, 16.8. $C_9H_{14}N_2O$ requires C, 65.0; H, 8.5; N, 16.85%).

2-(1-*Ethylprop*-1-*enyl*)-1,5-*dimethylpyrazol*-3(2H)-*one* **5e**. In a similar manner pyrazolones **5e** were obtained in 63% yield (*E*:*Z*, 6:1). Pure isomer (*E*)-**5e** (R_F 0.4) was obtained as a white solid m.p. 40–41 °C (Found: C, 66.5; H, 8.8; N, 15.45. $C_{10}H_{16}N_2O$ requires C, 66.6; H, 8.95; N, 15.55%).

1,5-*Dimethyl*-2-(1-*methylbut*-1-*enyl*)pyrazol-3(2H)-*one* **5f**. In the same manner pyrazolones **5f** were obtained in 60% yield (*E*:*Z*, 4:1). Pure isomer (*E*)-**5f** (R_F 0.4) was isolated as oil (b.p. 135–138 °C, 0.03 mmHg) (Found: C, 66.4; H, 8.8; N, 15.5. $C_{10}H_{16}N_2O$ requires C, 66.6; H, 8.95; N, 15.55%).

1,5-*Dimethyl*-2-(1-*propylbut*-1-*enyl*)*pyrazol*-3(2H)-*one* **5g**. The second stage went to completion in 16 h and the pyrazolones **5g** (*E*:*Z*, 9:1) were obtained in 60% yield. Pure isomer (*E*)-**5g** (R_F 0.6) was isolated as a pale greasy solid (Found: C, 69.0; H, 9.6; N, 13.3. $C_{12}H_{20}N_{20}$ requires C, 69.2; H, 9.7; N, 13.45%).

1,5-Dimethyl-2-(1-methylpenta-1,4-dienyl)pyrazol-3(2H)-one **5h**. The first stage, went to completion in 12 h, the second in 15 h, and pyrazolones **5h** were obtained in 55% yield (*E*:*Z*, 2:1). Pure isomer (*E*)-**5h** was purified by silica gel column chromatography (diethyl ether–methanol–dichloromethane, 3:1:1) as white crystals m.p. 70–71 °C (Found: C, 68.6; H, 8.3; N, 14.5. $C_{11}H_{16}N_2O$ requires C, 68.7; H, 8.4; N, 14.6%).

Reaction of **1a** *with Methyl Acetoacetate Without* PCl_3.—Equimolar amounts of **1a** and methyl acetoacetate were allowed to reflux in benzene solution saturated with HCl for about 5 h. No formation of pyrazolone **5a** was observed even after prolonged reaction times. Furthermore no formation of **5a** was observed when the same starting materials were allowed to react at room temperature for some days in triethyl phosphate with $POCl_3$ as acid catalyst.

Crystal Structure of 3-Hydroxy-1,5-dimethyl-2[(1-E)-1-methyl-2-phenylvinyl]pyrazolium Chloride E-**5c**·HCl.—Crystals, obtained from a methanol solution, were colourless prisms. Lattice constants were determined using a program[8] on the diffractometer which repeatedly rectifies the values of (θ,χ,φ) angles of thirty reflections to obtain the maximum of the peak when the angles are not moving more than 0.01°.

Crystal data. $C_{14}H_{17}ClN_2O$, $M = 264.7$. Orthorhombic, $a = 17.794(3)$, $b = 7.374(2)$, $c = 21.495(3)$ Å; $V = 2820.4(9)$ Å^3, $Z = 8$, $D_c = 1.25$ g cm^{-3}, Cu-Kα radiation, $\lambda = 1.5418$ Å; μ(Cu-Kα) 23.4 cm^{-1}. Space group *Pbca* (D_{2h}^{15} No. 61) from systematic absences.

X-Ray measurements were performed at $T = 294$ K on a Siemens AED single-crystal diffractometer on line to an IBM PS/2 M30 computer, in the range $3 < \theta < 70°$ using Ni-filtered Cu-Kα radiation. The diffraction angle θ for every reflection was determined on the basis of the orientation matrix and the outline of the diffraction peak was collected in the θ–2θ step scanning mode using a scan width in the range $(\theta - 60)$–$(\theta + 0.60 + \Delta\lambda/\lambda \text{ tg}\theta)°$. The intensities I_{hkl} were determined by analysing the reflection profiles with the Lehmann and Larsen procedure.[9] 5959 Reflections ($-21 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 8$, $0 \leqslant l \leqslant 26$) were measured, of which 2071 (internal R merging factor 0.014) having $I_{hkl} > 2\sigma(I_{hkl})$ [$\sigma(I)$ based on statistic counting] were retained as 'observed' and used in the refinement. One standard reflection, measured for every 50 reflections collected to monitor crystal decomposition and instrumental linearity, showed no significant variation. The dimensions of the specimen were 0.19 × 0.24 × 0.62 mm. Corrections for Lorentz and polarization effects were performed, no corrections were made for absorption effects.

Structure analysis and refinement. The structure was solved by direct methods by use of SHELXS86[10] and refined by SHELX76[11] with cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.036$, $R_w = 0.044$. The weighting function was of the form $w^{-1} = \sigma^2(F_o) + 0.05 F_o^2$. All the hydrogen atoms were located in the ΔF map. Maximum shift of parameters was 0.6σ, $\Delta\rho_{max} = 0.48$, $\Delta\rho_{min} = -0.38$ eÅ^{-3}. Atomic scattering factors were taken from ref. 12 for non-hydrogen atoms and from ref. 13 for hydrogen. Anisotropic thermal parameters and H-atom positional parameters have been deposited at the Cambridge Crystallographic Data Centre.*

The calculations were carried out on the GOULD 6040 POWERNODE computer at the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. of Parma. Bibliographic searches were carried out using the Cambridge Crystallographic Data Files through the Servizio Italiano di Diffusione dei Dati Cristallografici, Parma.

* For details of the CCDC deposition scheme see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1992, issue 1.

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Paper 1/06252B
Received 12*th December* 1991
Accepted 23*rd March* 1992