Stereoselective Synthesis and Single Crystal X-Ray Structures of Some Sterically Congested Electron-poor *N*-Vinyl Pyrazole Derivatives

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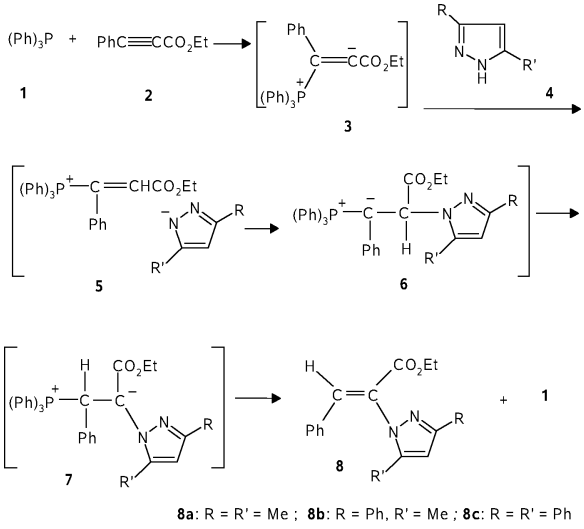
A one-pot synthesis of sterically congested electron-poor *N*-vinyl pyrazoles in fairly good yields by the reaction of ethyl 3-phenyl-2-propynoate, pyrazoles and triphenylphosphine is reported. The structures of these compounds were confirmed by IR, ^{1}H, and ^{13}C NMR spectroscopy, and single crystal X-ray structure determination. The structural analysis of the products indicated that the reaction is completely regio- and stereoselective.

Key words: 3-Phenyl-2-propynoate, Vinyltriphenylphosphonium Salts, Crystal Structure, Phosphorus Ylide, *N*-Vinyl Pyrazoles

Introduction

Pyrazole derivatives are in general well-known nitrogen-containing heterocyclic compounds, and various procedures have been developed for their syntheses [1 – 3]. The chemistry of pyrazole derivatives has been the subject of much interest due to their importance for various applications and their widespread potential and proven biological and pharmacological activities such as anti-inflammatory, antipyretic, analgesic, antimicrobial, antiviral, antitumor, antifungal, pesticidal, anticonvulsant, antihistaminic, antibiotic and anti-depressant properties [1 – 10].



8a: R = R' = Me ; **8b**: R = Ph, R' = Me ; **8c**: R = R' = Ph

Scheme 1.

β-Additions of nucleophiles to the vinyl group of vinylphosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis [11 – 14].

Acetylenic esters are reactive systems and take part in many chemical syntheses as Michael acceptors [15 – 19]. In recent years, we have established a one-pot method for the synthesis of stabilized phosphorus ylides [15 – 24]. In this paper, we wish to describe the preparation of sterically congested electron-poor *N*-vinyl pyrazoles from a 3-phenyl-2-propynoate and pyrazoles in the presence of triphenylphosphine in fairly good yields.

Results and Discussion

The reaction of ethyl 3-phenyl-2-propynoate (**2**) with pyrazole derivatives **4** in the presence of triphenylphosphine (**1**) proceeded spontaneously at r. t. in CH_2Cl_2 and was finished within 72 h. Based on TLC monitoring of the reaction and NMR analyses of the products, in this reaction, *Z* stereoisomers **8a**, **8b** and **8c** were observed only and therefore, the reaction is completely regio- and stereoselective. A reaction mechanism is proposed in Scheme 1. We reduced the amount of triphenylphosphine to 50 % of

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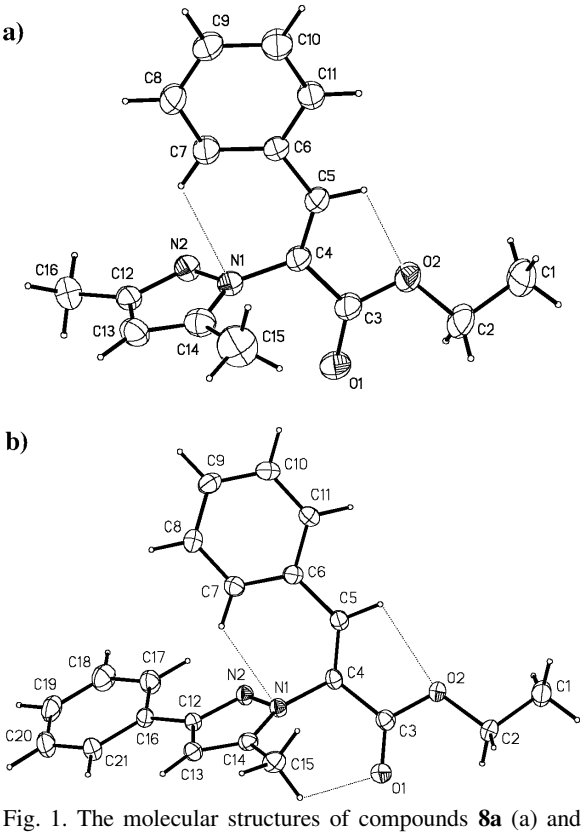

Fig. 1. The molecular structures of compounds **8a** (a) and **8b** (b) showing the atom numbering schemes. The intramolecular C(5)–H(5)···O(2) and C(7)–H(7)···N(1) contacts forming *S*(5) and *S*(6) motifs, respectively, as well as C(15)–H(15A)···O(1) in **8b** are shown with dotted lines. Displacement ellipsoids are drawn at the 30 % (for **8a**) and 50 % (for **8b**) probability level.

mole ratio. In all cases where we used triphenylphosphine as a catalyst in the range of 50 % to 100 % of molar ratio, the reaction time amounted to 72 hours. In all cases where we used triphenylphosphine as a catalyst in the range below 50 % of mole ratio, the reaction time was longer than 72 hours. The reaction proceeded smoothly and cleanly and no side reactions were observed. In the absence of triphenylphosphine no products were observed. The structures of **8a – c** were deduced from their IR, ^{1}H and ^{13}C NMR spectra and single crystal X-ray structure determination.

*Description of the crystal structures of **8a** and **8b***

The crystals of **8a** and **8b** are built up from molecules of structures shown in Fig. 1. The summary of the experimental details are given in Table 1. The overall structures of the presented compounds are similar

Table 1. Crystal data and structure refinement details for **8a** and **8b**.

	8a	**8b**
Crystal data		
Empirical formula	$C_{16}H_{18}N_2O_2$	$C_{21}H_{20}N_2O_2$
Formula weight, g mol^{-1}	270.32	332.39
Crystal system, space group	— monoclinic, $P2_1/n$ —	
a, Å	11.044(3)	7.970(2)
b, Å	7.944(2)	21.427(5)
c, Å	17.605(3)	10.780(3)
β, deg	96.24(3)	108.78(3)
V, Å^3	1535.4(6)	1742.9(8)
Z	4	4
D_{calc}, g cm^{-3}	1.169	1.267
μ, mm^{-1}	0.078	0.082
F(000), e	576	704
Crystal size, mm^3	0.48×0.46×0.26	0.50×0.34×0.17
Crystal color and form	colorless block	colorless plate
Data collection		
Diffractometer	— Kuma KM4CCD —	
Data collection method	— ω scans —	
Monochromator	— graphite —	
Radiation type	— MoK_α (λ = 0.71073 Å) —	
T, K	240(2)	100(2)
θ Range, deg	3.17 – 29.00	3.30 – 28.00
h, k, l Ranges	$-14 \le h \le 15$	$-10 \le h \le 8$
	$-10 \le k \le 9$	$-28 \le k \le 27$
	$-24 \le l \le 24$	$-12 \le l \le 14$
Measured reflections	16548	14709
Independent reflections	3964	4142
Observed refl. [$I \ge 2\sigma(I)$]	2338	3489
Refinement		
Refinement on	F^2	F^2
Data/restraints/parameters	3964/0/184	4142/0/306
$R[F_o^2 \ge 2\sigma(F_o^2)]$[a]	$R1$ = 0.0554	$R1$ = 0.0425
	$wR2$ = 0.1411	$wR2$ = 0.0999
R (all data)[a]	$R1$ = 0.1044	$R1$ = 0.0533
	$wR2$ = 0.1615	$wR2$ = 0.1057
GooF = S	1.063	1.054
Weighting parameter a/b	0.0831/0.0	0.0515/0.5418
$\Delta\rho_{max/min}$, e Å^{-3}	0.17/−0.13	0.27/−0.22

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \sqrt{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]}$; weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

to that observed in their close analogs described by us previously [23, 25]. Like in these compounds, two well defined planes (with the atoms N(1) and C(4) being common) may be distinguished in the molecules of **8a** and **8b**. These are the ethyl (2*Z*)-2-amino-3-phenylacrylate moiety (forming plane 1 with r. m. s. deviation of fitted atoms = 0.155 Å in **8a** and 0.163 Å in **8b**) and the rest of the molecule (plane 2 with r. m. s. = 0.007 Å in **8a** and 0.048 Å in **8b**). The atoms which deviate the most from these planes in **8a** are O(1), being displaced by 0.332(2) Å from plane 1, and C(13) deviating by 0.012(2) Å from plane 2. In **8b** these are

Table 2. Selected interatomic distances (Å), valence angles (deg) and torsion angles (deg) in **8a** and **8b**.

	8a	**8b**		**8a**	**8b**
O(1)–C(3)	1.205(2)	1.212(2)	N(2)–C(12)	1.331(2)	1.340(2)
O(2)–C(2)	1.458(2)	1.462(2)	C(3)–C(4)	1.492(2)	1.492(2)
O(2)–C(3)	1.329(2)	1.340(2)	C(4)–C(5)	1.330(2)	1.343(2)
N(1)–N(2)	1.364(2)	1.369(2)	C(5)–C(6)	1.469(2)	1.468(2)
N(1)–C(4)	1.428(2)	1.429(2)	C(12)–C(13)	1.394(2)	1.413(2)
N(1)–C(14)	1.352(2)	1.369(2)	C(13)–C(14)	1.368(2)	1.372(2)
C(14)–N(1)–N(2)	112.28(13)	112.50(9)	C(12)–N(2)–N(1)	104.56(11)	104.18(9)
N(2)–N(1)–C(4)	120.15(12)	118.08(9)	C(4)–C(5)–C(6)	130.37(14)	129.25(11)
C(14)–N(1)–C(4)	127.57(13)	128.83(10)			
C(4)–N(1)–N(2)–C(12)	−179.3(2)	−172.2(1)	O(2)–C(3)–C(4)–C(5)	−17.2(2)	−10.8(2)
C(3)–O(2)–C(2)–C(1)	179.5(2)	170.6(1)	O(2)–C(3)–C(4)–N(1)	167.0(2)	167.2(1)
C(2)–O(2)–C(3)–C(4)	177.3(2)	179.8(1)	N(1)–C(4)–C(5)–C(6)	−1.2(3)	4.3(2)
N(2)–N(1)–C(4)–C(5)	91.6(2)	61.2(2)	C(4)–C(5)–C(6)–C(7)	−4.1(3)	19.5(2)
N(1)–N(2)–C(12)–C(16)	−179.6(2)	179.5(1)	N(2)–C(12)–C(16)–C(17)	—	−5.2(2)

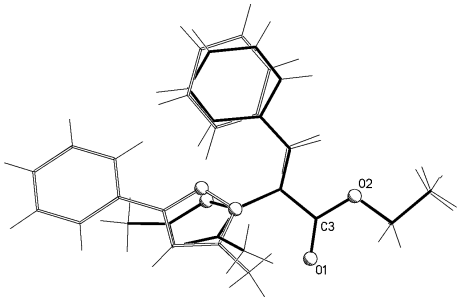

Fig. 2. Comparison of molecular structures of compounds **8a** (solid line) and **8b** (open line). The common reference points are O(1), O(2) and C(3).

N(1) and N(2) deviating by 0.407(1) Å from plane 1 and by 0.093(1) Å from plane 2, respectively.

The dihedral angles between the least-squares planes 1 and 2 are quite different in the presented compounds. They amount to 89.3(1)° in **8a** and 62.2(1)° in **8b** and reveal that the two planes are almost perpendicular to each other in **8a** (like in the tetrahydrophthalimidyl derivative [23]), and not perpendicular in **8b** (like in the 1,3-dioxo-1,3-dihydro-2*H*-isoindolyl derivative [25]). The differences in the molecular structures of compounds **8a** and **8b** are shown in Fig. 2.

As it was observed for close analogs of the described compounds reported by us previously [23, 25], as well as in most of the compounds with related structures, *i. e.* bearing different substituents at atom N(1) and different ester groups (usually –C(O)OMe and –C(O)OEt), deposited at the Cambridge Structural Database [26], the molecules of **8a** and **8b** adopt *Z* geometry with respect to the double bond C(4)–C(5), which is reflected in the value of the torsion angle N(1)–C(4)–C(5)–C(6) of −1.2(3)° in **8a** and 4.3(2)° in **8b** (Table 2). The carbonyl oxygen atom O(1) in the ester group is in *antiperiplanar* conformation in relation to the vinyl carbon atom C(5) in both **8a** and **8b** as also found for most of structurally related compounds [23, 25, 26].

The short C(5)···O(2) and C(7)···N(1) intramolecular contacts in **8a** and **8b**, also observed before [23, 25, 26], may indicate the presence of weak intramolecular hydrogen interactions: C(5)–H(5)···O(2) and C(7)–H(7)···N(1), giving rise to five-membered *S*(5) and six-membered *S*(6) motifs, respectively (see Table 3 for geometrical details). Both of them are formed in plane 1 and stabilize the molecular structures of the compounds. There is another contact, C(15)–H(15A)···O(1), observed in the molecule of **8b**, which results in a seven-membered intramolecular motif. It is to note here that most of the *Z* geometrical isomers of similar structures reported so far [23, 25, 26] also revealed some deviations from the planarity of the fragment defined here as plane 1; they usually showed the phenyl group slightly twisted. That is reflected in the value of the C(4)–C(5)–C(6)–C(7) torsion angle (Table 2), which is significantly larger in compound **8b** than in **8a** and in the tetrahydrophthalimidyl and 1,3-dioxo-1,3-dihydro-2*H*-isoindolyl derivatives [23, 25].

As stated above, the overall conformation of the molecules **8a** and **8b** may be stabilized by the intramolecular interactions C(5)–H(5)···O(2), C(7)–H(7)···N(1) and C(15)–H(15A)···O(1) (for **8b**), resulting in *S*(5), *S*(6) and *S*(7) motifs, respectively. The two former ones are formed in plane 1, but the C(15)–H(15A)···O(1) contact, observed only in the molecule of **8b**, connects the two planes of that molecule and is accompanied by their non-perpendicular mutual orientation, with the dihedral angle between them close to 60° (see Figs. 1 and 2). It is to note that in both **8a** and **8b**, the H(7) atom is in close contact with N(2)

D–H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)	Offset (Å)
compound ***8***[a]					
C(5)–H(5)···O(2)	0.94	2.35	2.736(2)	104	–
C(7)–H(7)···N(1)	0.94	2.38	3.014(2)	124	–
C(9)–H(9)···O(1)^{i}	0.94	2.53	3.445(2)	166	–
C(7)–H(7) ···Cg(1)	0.94	2.51	3.358(2)	150	0.84
C(16)–H(16*A*)· ··Cg(1)^{ii}	0.97	2.96	3.868(2)	156	0.82
compound ***8b***					
C(5)–H(5)···O(2)	0.99(2)	2.38(2)	2.757(2)	102(1)	–
C(7)–H(7)···N(1)	0.98(2)	2.43(2)	2.998(2)	117(1)	–
C(10)–H(10)···O(1)^{iii}	0.96(2)	2.52(2)	3.344(2)	144(2)	–
C(13)–H(13)···N(2)^{iv}	0.95(2)	2.46(2)	3.351(2)	156(2)	–
C(15)–H(15A)···O(1)	1.00(2)	2.64(2)	3.123(2)	109(1)	–
C(19)–H(19) ···O(1)^{v}	0.97(2)	2.46(2)	3.344(2)	152(2)	–
C(7)–H(7)· ··Cg(1)	0.98(2)	2.45(2)	3.209(2)	134(2)	0.62

Table 3. Geometry of proposed hydrogen bonds and C–H···O/N/π close contacts for **8a** and **8b** (Å, deg)[a].

[a] Symmetry codes: [i] $x-1, y, z$; [ii] $-x+2, -y, -z+1$; [iii] $x+1/2, -y+3/2, z-1/2$; [iv] $x+1/2, -y+3/2, z+1/2$; [v] $-x+1/2, y+1/2, -z+3/2$; Cg(1) is the centroid of the pyrazolyl ring [N(1)–N(2)–C(12)–C(13)–C(14)].

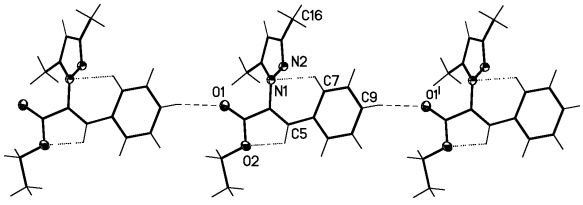

Fig. 3. A fragment of infinite chains formed along the *a* axis in the crystal of **8a** with adjacent molecules joined by C(9)–H(9)· ··O(1)^{i} hydrogen bonds (dashed lines). Intramolecular C–H···O/N close contacts are shown with dotted lines. Symmetry codes are given in Table 3.

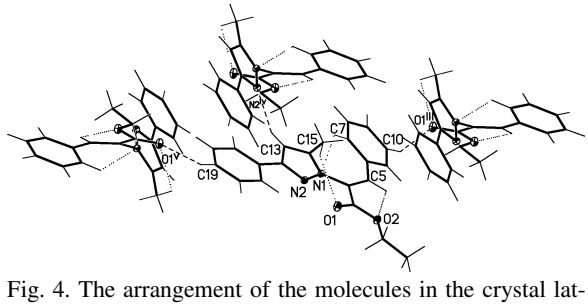

Fig. 4. The arrangement of the molecules in the crystal lattice of **8b**. Intermolecular C–H···O/N bonds are shown with dashed lines, intramolecular with dotted lines. Symmetry codes are given in Table 3.

(with H···N distances of about 2.6 Å). Besides, the same H(7) atom is involved in intramolecular C(7)–H(7)···π[Cg(1)] interaction in the crystals of both compounds (see Table 3 for details).

The molecules in the crystal of compound **8a** are joined to each other by C(9)–H(9)···O(1)^{i} interactions to form infinite chains along the *a* axis (Fig. 3; symmetry codes are given in Table 3). Two adjacent chains are arranged in the crystal lattice by means of C(16)–H(16A)···π[Cg(1)^{ii}] interactions giving rise to ribbons parallel to the *a* axis.

The packing diagram in the crystal of **8b** is of quite different type. The carbonyl oxygen atom O(1) in the ester group, beside the intramolecular C(15)–H(15A)···O(1) contact, is also involved in two additional intermolecular interactions of the C–H···O type. Atom O(1) accepts atoms H(10) and H(19) of the phenyl groups of two different adjacent molecules, which gives rise to trifurcated, four-centered C(15)–H(15A)···O(1), C(10)–H(10)···O(1)^{iii}, C(19)–H(19)···O(1)^{v} contacts. The latter interactions, in combination with C(13)–H(13)···N(2)^{iv}, result in a three-dimensional network of hydrogen bonds, observed in the crystal lattice of compound **8b** (Fig. 4).

Conclusions

In conclusion, we have developed a convenient, one-pot regio- and stereoselective method for preparing sterically congested electron-poor *N*-vinyl pyrazoles (**8a**–**c**) utilizing *in situ* generation of vinyl phosphonium salts. Other aspects of this process are under investigation. The X-ray structures of **8a** and **8b** (in their *Z* isomeric forms) reveal that in the solid state, the overall structure of the compounds is similar, but with some differences in the mutual orientation of the two main planes of the molecules and in the twisting of the phenyl ring in the phenylacrylate moiety. Besides, the connectivity pattern of the molecules *via* hydrogen bonds is different in the two structures.

Experimental Section

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a Mattson-1000 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Spectrospin spectrometer at 250 and 62.5 MHz, respectively.

*Preparation of ethyl (Z)-2-(3,5-dimethyl-1H-pyrazol-1-yl)-3-phenyl-2-propenoate (**8a**)*

General procedure

To a magnetically stirred solution of triphenylphosphine (0.262 g, 1 mmol) and 3,5-dimethyl-1*H*-pyrazole (0.096 g, 1 mmol) in dichloromethane (5 mL) was added dropwise a mixture of ethyl 3-phenyl-2-propynoate (0.17 mL, 1 mmol) in dichloromethane (2 mL) at −10 °C over 15 min. The mixture was allowed to warm up to r. t. and stirred for 72 hrs at r. t. The solvent was removed under reduced pressure and the viscous residue was purified by flash column chromatography (silica gel; petroleum ether/ethyl acetate). The solvent was removed under reduced pressure and the product was obtained as white crystals. Yield: 0.216 g (80 %); m. p. 52.0 – 55.0 °C. – IR (KBr): ν = 3096, 2984, 1715, 1646 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.32 (t, 3 H, ^3J = 7.2 Hz, CH_3 of OEt), 1.96 and 2.32 (2 s, 6 H, 2 CH_3), 4.32 (q, 2 H, ^3J = 7.2 Hz, OCH_2), 5.99 (s, 1 H, pyrazole ring), 6.85 – 7.35 (m, 5 H, arom.), 7.92 (s, 1 H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 10.73, 13.77 and 14.23 (3 CH_3), 61.73 (OCH_2), 106.21, 128.79, 130.45, 130.76 and 140.14 (7 CH); 127.21, 131.91, 140.28 and 149.95 (4 C); 164.25 (C=O of ester). – $C_{16}H_{18}N_2O_2$ (270.33): calcd. C 71.09, H 6.71, N 10.36; found C 71.01, H 6.79, N 10.42.

*Preparation of single crystals of ethyl (Z)-2-(3,5-dimethyl-1H-pyrazol-1-yl)-3-phenyl-2-propenoate (**8a**)*

Colorless single crystals of **8a** were obtained from slow evaporation of its dichloromethane/light petroleum ether (1 : 1) solution (20 – 25 °C). The crystals were filtered off, washed with a cold mixture of dichloromethane/light petroleum ether (1 : 1) and dried at r. t. (m. p. 52.0 – 55.0 °C).

*Selected data for ethyl (Z)-2-(5-methyl-3-phenyl-1H-pyrazol-1-yl)-3-phenyl-2-propenoate (**8b**)*

White crystals. Yield: 0.23 g (68 %); m. p. 77.0 – 80.0 °C. – IR (KBr): ν = 2992, 2923, 1715, 1646 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.38 (t, 3H, ^3J = 7.2 Hz, CH_3 of OEt), 2.12 (3 H, 1 s, CH_3), 4.38 (q, 2 H, ^3J = 7.2 Hz, OCH_2), 6.60 (s, 1 H, pyrazole ring), 6.99 (d, 2 H, ^3J = 7.0 Hz, arom.), 7.91 (d, 2 H, ^3J = 7.5 Hz, arom.), 7.27 – 7.48 (m, 6 H, arom), 8.05 (s, 1 H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 10.97 and 14.28 (2 CH_3), 61.88 (OCH_2), 103.76, 125.87, 127.81, 128.53, 128.92, 130.58, 130.97 and 140.73 (12 CH), 127.21, 131.81, 133.4, 141.05 and 152.56 (5 C), 164.25 (C=O of ester). – $C_{21}H_{20}N_2O_2$ (332.4): calcd. C 75.88, H 6.06, N 8.44; found C 75.95, H 6.00, N 8.50.

*Preparation of single crystals of ethyl (Z)-2-(5-methyl-3-phenyl-1H-pyrazol-1-yl)-3-phenyl-2-propenoate (**8b**)*

Colorless single crystals of **8b** were obtained from slow evaporation of its saturated dichloromethane/light petroleum ether (1 : 4) solution (20 – 25 °C). The crystals were filtered off, washed with a cold mixture of dichloromethane/light petroleum ether (1 : 4) and dried at r. t. (m. p. 77.0 – 80.0 °C).

*Selected data for ethyl (Z)-2-(3,5-diphenyl-1H-pyrazol-1-yl)-3-phenyl-2-propenoate (**8c**)*

Colorless oil. Yield: 0.24 g (60 %). – IR (neat): ν = 3061, 2984, 1723, 1646 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.20 (t, 3H, ^3J = 7.2 Hz, CH_3 of OEt), 4.24 (q, 2 H, ^3J = 7.2 Hz, OCH_2), 6.90 (s, 1 H, pyrazole ring), 7.02 – 7.52 (m, 15 H, arom.), 7.95 (s, 1 H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 14.03 (CH_3), 61.74 (OCH_2), 104.18, 125.97, 127.77, 128.10, 128.40, 128.48, 128.60, 128.74, 130.60, 130.73 and 140.41 (17 CH), 128.30, 130.00, 131.99, 133.10, 145.97 and 152.90 (6 C), 164.25 (C=O of ester). – $C_{26}H_{22}N_2O_2$ (394.47): calcd. C 79.16, H 5.62, N 7.10; found C 79.07, H 5.56, N 7.16.

*Crystal structure determination of **8a** and **8b***

The crystallographic measurements for crystals of **8a** and **8b** were performed on a κ-geometry Kuma KM4CCD automated four-circle diffractometer with graphite-monochromatized MoK_α radiation. The data were collected at 240(2) and 100(2) K for **8a** and **8b**, respectively, using the Oxford Cryosystems cooler. Crystals of **8a** cracked at temperatures below 235 K. A summary of the conditions for the data collection and the structures refinement parameters are given in Table 1. The data were corrected for Lorentz and polarization effects. Data collection, cell refinement, and data reduction and analysis were carried out with the KM4CCD software CrysAlis CCD and CrysAlis RED, respectively [27]. The structures were solved by Direct Methods using SHELXS-97 [28] and refined by a full-matrix least-squares technique using SHELXL-97 [29] with anisotropic displacement parameters for non-H atoms. All H atoms in **8b** were found in difference Fourier maps and were refined isotropically. The H atoms in **8a** were also found in difference Fourier maps, but in the final refinement cycles, they were treated as riding atoms, with C–H distances of 0.94 – 0.98 Å, and with U_{iso} values of 1.5 U_{eq}(C) for CH_3 groups, and 1.2 U_{eq}(C) for CH_2 and CH groups. All figures were made using the XP program [30].

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC-656361 (**8a**) and CCDC-656362 (**8b**). Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

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