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4-Nitrobenzyl 3-oxo-2-(triphenylphosphoranylidene)butanoate

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Key indicators

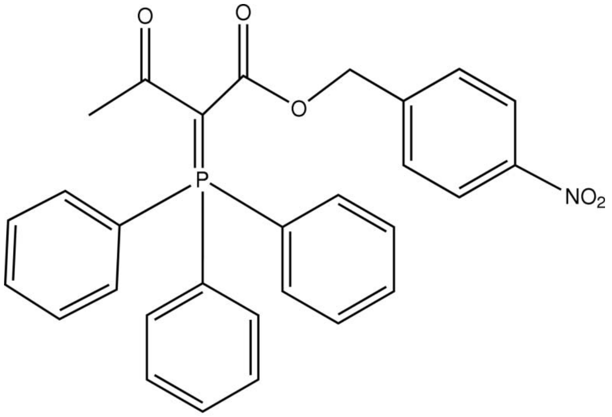
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.054
wR factor = 0.106
Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Colorless crystals of the title compound, $C_{29}H_{24}NO_5P$, were synthesized by the reaction of triphenylphosphine, an iron porphyrin complex and 4-nitrobenzyl 2-diazo-3-oxobutanoate at 353 K. All bond distances and angles are within normal ranges and there are no notable interactions between neighboring molecules.

Comment

Ylides are useful for the extension of carbon chains by incorporating double bonds into molecules (Meshram *et al.*, 1998; Castaneda *et al.*, 2003). Ylides can also be converted into many other functional groups, such as ketones, carboxylic esters and aldehydes. In particular, triphenylphosphonium ylides are popular because of their easy preparation and stability. A new and efficient method for the selective olefination of aldehydes and ketones with a diazo group involves catalysis by metalloporphyrins (Mirafzal *et al.*, 2002; Chen *et al.*, 2003; Lee *et al.*, 2003), but the mechanism was not verified. We have captured an intermediate using an acyl-stabilized diazo compound as the starting material. We report here the crystal structure of the intermediate, *viz*. the title compound, (I).



(I)

Selected bond distances and angles are listed in Table 1. The compound crystallizes in the monoclinic space group $C2/c$ with one molecule in the asymmetric unit. The molecular structure is shown in Fig. 1. There are no notable interactions between molecules.

Experimental

Triphenylphosphine (262 mg, 1.0 mmol) and Fe(TPP)Cl (6 mg, 0.01 mmol) (TTP = *meso*-tetrakisphenylporphyrin) were dissolved in toluene (10 ml) in a round-bottomed flask, and a solution of 4-nitrobenzyl 2-diazo-3-oxobutanoate (263 mg, 1.0 mmol) in toluene (3 ml) was then added dropwise with vigorous stirring; the mixture was further heated to 353 K. After 24 h, the reaction mixture was cooled to room temperature and the solvent was removed *in vacuo*. The residue was then purified by flash column chromatography (SiO_2, 3:1 hexane/EtOAc) to give the desired product (yield 82%). Colorless crystals were obtained by slow evaporation of an ethyl acetate solution over a period of 6 d. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (*d*, 2H), 7.62 (*m*, 6H), 7.50 (*m*, 3H), 7.40 (*m*, 6H), 7.0 (*d*, 2H), 4.80 (*s*, 2H), 2.48 (*s*, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.9, 167.6, 147.4, 144.7, 133.3, 131.9, 128.8, 128.4, 127.0, 126.2, 123.5, 63.3, 29.8. ESI–MS: 498.0 (M^+H), 520.0 (M^+Na).

Crystal data

$C_{29}H_{24}NO_5P$
$M_r = 497.46$
Monoclinic, $C2/c$
$a = 39.826$ (3) Å
$b = 8.1857$ (6) Å
$c = 15.1786$ (10) Å
$\beta = 93.928$ (10)°
$V = 4936.6$ (6) Å^3
$Z = 8$
$D_x = 1.339$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15308 reflections
$\theta = 6.2$–55.1°
$\mu = 0.15$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.3 × 0.1 × 0.1 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.955$, $T_{max} = 0.985$
22380 measured reflections
5612 independent reflections
3278 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 27.5°$
$h = -51 \rightarrow 49$
$k = -10 \rightarrow 9$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.107$
$S = 1.06$
5612 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0028P)^2 + 8.1979P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—C9	1.740 (2)	O3—C8	1.364 (3)
P1—C12	1.803 (2)	O3—C7	1.434 (3)
P1—C24	1.807 (3)	O4—C8	1.213 (3)
P1—C18	1.814 (2)	O5—C10	1.244 (3)
C9—P1—C12	115.0 (1)	C10—C9—P1	111.4 (2)
C9—P1—C24	108.2 (1)	C8—C9—P1	120.6 (2)
C12—P1—C24	109.9 (1)	O5—C10—C9	118.6 (2)
C9—P1—C18	113.7 (1)	O5—C10—C11	118.6 (2)
C12—P1—C18	103.7 (1)	C17—C12—P1	119.2 (2)
C24—P1—C18	106.0 (1)	C13—C12—P1	121.2 (2)
C8—O3—C7	115.9 (2)	C23—C18—P1	121.4 (2)
O3—C7—C4	108.9 (2)	C19—C18—P1	119.7 (2)
O4—C8—O3	120.1 (2)	C25—C24—P1	122.9 (2)
O4—C8—C9	126.1 (2)	C29—C24—P1	117.4 (2)
O3—C8—C9	113.8 (2)		

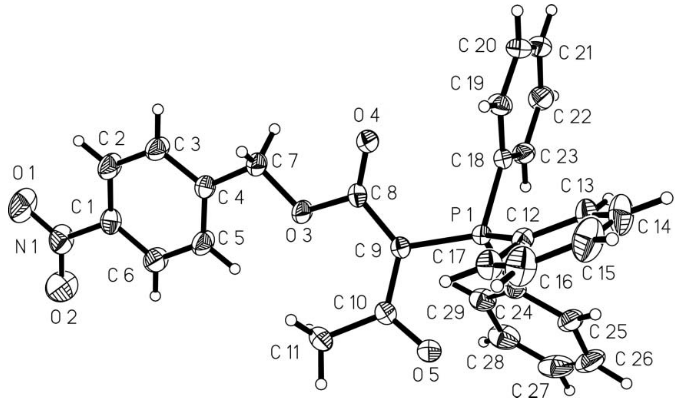


Figure 1
A perspective view of the molecular structure of (I). Displacement ellipsoids are drawn at the 25% probability level.

All H atoms were positioned geometrically (C—H = 0.93–0.96 Å) and refined as riding, with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2003).

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