

## A C-Phosphono-keten Imine as a Novel Annellation Reagent

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*Summary* N-Ethyl(diethylphosphono)methylketen imine, a new type of keten imine, was easily prepared in high yield, and reacted with the sodium salts of salicylaldehyde and 2-formylpyrrole to afford the benzopyran and pyrrolizine derivatives, respectively.

synthetic applications. Introduction of a phosphoryl group bonded directly to the keten unit would be expected to increase not only the reactivity of the keten imine but also its value as a synthetic reagent. A few examples of keten imines with phosphorus substituents are known,<sup>2</sup> but the synthesis of C-phosphono-keten imines has not been reported. We report here a simple preparation of the C-phosphono-keten imine (**1**), a new type of keten imine, and also that this compound acts as an annellation reagent.

WHILE keten imines are expected to be useful reagents in organic chemistry,<sup>1</sup> little attention has been paid to their

The keten imine (**1**) was obtained in 82% yield as a colourless liquid (b.p. 86–90 °C at 1 Torr) from the reaction of the amide (**2**)<sup>3</sup> with triphenylphosphine-bromine and triethylamine in CH<sub>2</sub>Cl<sub>2</sub> at room temperature according to the established procedure;<sup>4</sup>  $\nu_{C=N}$  2030 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 1.32 (t, 9H, MeCH<sub>2</sub>O, MeCH<sub>2</sub>N,  $J_{HH}$  7.0 Hz, overlapping signals), 1.69 (d, 3H, MeC=,  $J_{HP}$  13.6 Hz), 3.51 (dq, 2H, MeCH<sub>2</sub>N,  $J_{HH}$  7.0,  $J_{HP}$  4.8 Hz), and 4.07 (dq, 4H, MeCH<sub>2</sub>OP,  $J_{HH} = J_{HP} = 7.0$  Hz);  $m/e$  219 ( $M^+$ ).

The synthetic utility of the keten imine (**1**) was studied in annulations to form heterocyclic compounds. The sodium salt of salicylaldehyde was treated with (**1**) at 80 °C in dimethylformamide (DMF) to afford the benzopyran (**3**)<sup>†</sup> in 52% yield (b.p. 78–81 °C at 1 Torr);  $\nu_{C=N}$  1650 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 1.20 (t, 3H, MeCH<sub>2</sub>), 2.07 (s, 3H, Me), 3.56 (q, 2H, MeCH<sub>2</sub>), 6.76 (s, 1H, H<sub>a</sub>), and 6.83–7.23 (m, 4H, ArH);  $m/e$  187 ( $M^+$ ). In this reaction the anionic species attacks the centre carbon atom of the keten imine (**1**) activated by the phosphoryl group, and intramolecular Horner–Emmons reaction proceeds smoothly because of stabilization of the negative charge in the intermediate by the imino group. The sodium salt of 2-formylpyrrole similarly gave the pyrrolizine (**4**)<sup>†</sup> in 51% yield (b.p. 85–90 °C at 3 Torr);  $\nu_{C=N}$  1650 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 1.41 (t, 3H, MeCH<sub>2</sub>), 1.96 (s, 3H, Me), 3.57 (q, 2H, MeCH<sub>2</sub>), 5.76 (d, 1H, H<sub>a</sub>), 6.05 (m, 1H, H<sub>b</sub>), 6.46 (m, 1H, H<sub>c</sub>), and 6.90 (d, 1H, H<sub>d</sub>);  $m/e$  160 ( $M^+$ ).

† Satisfactory elemental analyses were obtained.

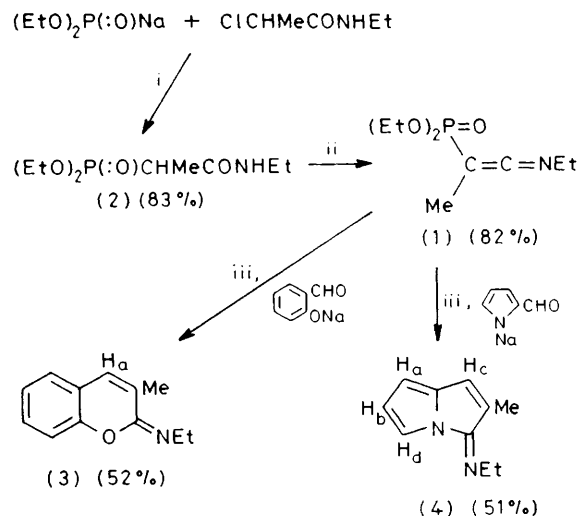
<sup>1</sup> G. R. Krow, *Angew. Chem. Internat. Edn.*, 1971, **10**, 435.

<sup>2</sup> R. D. Partos and A. J. Speziale, *J. Amer. Chem. Soc.*, 1965, **87**, 5068; A. Foucand and R. Leblanc, *Tetrahedron Letters*, 1965, 509; H. J. Bestmann and G. S. Schmid, *Angew. Chem.*, 1974, **86**, 274.

<sup>3</sup> *N*-Substituted carbamoylmethylphosphonates have been prepared by the Arbuzov reaction: A. J. Speziale and R. C. Freeman, *J. Org. Chem.*, 1958, **23**, 1883; the amide (**2**) was prepared by a Michaelis–Becker reaction.

<sup>4</sup> H. J. Bestmann, J. Lienert, and L. Mott, *Annalen*, 1968, **718**, 24.

<sup>5</sup> Annulations with vinylphosphonates are described by W. A. Kleshick and C. H. Heathcock, *J. Org. Chem.*, 1978, **43**, 1256; T. Minami, H. Suganuma, and T. Agawa, *Chem. Letters*, 1978, 285.



Reagents/conditions: i, tetrahydrofuran, room temp., 2 h; ii, PPh<sub>3</sub>, Br<sub>2</sub>, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, room temp., 6 h; iii, DMF, 80 °C, 2 h.

Thus, the keten imine (**1**) acts chemically as a vinylphosphonate<sup>5</sup> activated by the cumulated imino-group, and is a novel annulation reagent for the synthesis of heterocyclic compounds having endocyclic imino-groups.

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