

AN EFFICIENT AND MILD CONDITIONS SYNTHESIS OF 2-AZA-1,3-DIENES FROM PHOSPHA- $\lambda^5$ -AZENES.

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SUMMARY: Aza-Wittig reaction of N-acrylic phospho- $\lambda^5$ -azenes with aldehydes gives 3-ethoxycarbonyl 2-aza-1,3-dienes in very high yields.

Compounds containing the 2-aza-1,3-diene group represent a very important class of derivatives as a result of their potential as key intermediates in organic synthesis. Particularly significant is the Diels-Alder reactivity of these substances<sup>1</sup> for the construction of heterocycles.

Previously, several procedures of synthesis<sup>2-4</sup> and some reactions of electronically neutral 2-aza-dienes<sup>3</sup>, as well as 3,4-electron-withdrawing substituted 2-aza-dienes<sup>4</sup> have been reported. However, there is little information about the corresponding 3-substituted electron poor heteradienes, probably owing to the lack of general methods of synthesis of these compounds; in this context, the very reactive N-benzylidenehydroalaninmethyl ester<sup>5</sup> and the 1,1-dimethyl derivative<sup>6</sup> were described.

Moreover, we have recently used phospho- $\lambda^5$ -azenes as starting materials in the preparation of primary enamines<sup>7</sup> and phosphorus containing heterocycles<sup>8</sup>. Continuing our interest in the reactivity of phospho- $\lambda^5$ -azenes and in the synthesis of 2-azadienes, we described here a very easy and mild conditions synthesis of them through aza-Wittig reaction of phospho- $\lambda^5$ -azenes and aldehydes<sup>9</sup>.

Thus, the reaction of N-vinylphospho- $\lambda^5$ -azenes 1, obtained by Staudinger reaction<sup>10</sup> of azidoacrylates<sup>11</sup> and phosphines, with aldehydes (see table) gave very high yields of 3-ethoxycarbonyl-2-aza-1,3-dienes<sup>12</sup> 3, as viscous oils isolated by means of short column chromatography<sup>13</sup>. Spectral data are in agreement with structure 3. Thus, mass spectrum of 3a showed molecular ion peak, while the iminic proton (carbon) resonates at  $\delta = 8.56$  (164.4) ppm, in <sup>1</sup>H- and <sup>13</sup>C-NMR, respectively. Phenyl isocyanate reacts with 1 at room temperature in a similar way leading to the carbodiimide 4.

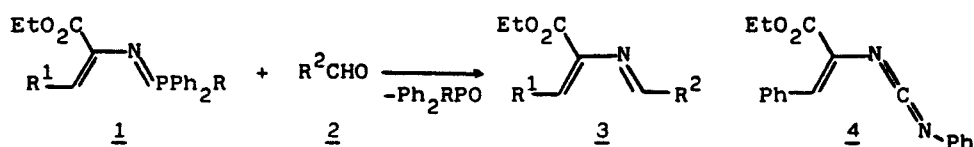


Table of compounds 3 and 4 obtained

Compound*	R <sup>1</sup>	R <sup>2</sup>	Reaction Time(h)	T(°C)	Solvent	Yield(%)
3a	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	18	60	CCl <sub>4</sub>	92
3b	C <sub>6</sub> H <sub>5</sub>	4-Cl-C <sub>6</sub> H <sub>4</sub>	18	60	CCl <sub>4</sub>	91
3c	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH=CH	20	60	CCl <sub>4</sub>	89
3d	C <sub>6</sub> H <sub>5</sub>	2-Thienyl	24	60	CH <sub>3</sub> CN	90
3e	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> )H	40	60	CH <sub>3</sub> CN	86
3f	C <sub>6</sub> H <sub>5</sub> CH=CH	C <sub>6</sub> H <sub>5</sub>	46	25	H <sub>2</sub> CCl <sub>2</sub>	88
4	C <sub>6</sub> H <sub>5</sub>	-	38	25	H <sub>2</sub> CCl <sub>2</sub>	92

\* Obtained from 1(R=Ph) except 3f from 1(R=Me).

The synthesis described in this communication provides an easy entry to N-alkyliden and N-arylidene-aminoacrylic acid derivatives 3, making use of readily available starting materials and under mild reaction conditions. These systems could be key intermediates in the synthesis of new aminoacids derivatives<sup>14</sup> and six membered heterocycles<sup>4</sup>.

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12. All new compounds reported here gave satisfactory elemental analysis. Spectral data for 3a: IR(nujol):  $\nu=1720(\text{CO}), 1630(\text{C}=\text{N}) \text{ cm}^{-1}$ .  $\delta_{\text{H}}$ (80 MHz, CDCl<sub>3</sub>) = 1.35(t, 3H, CH<sub>3</sub>), 4.31(q, 2H, OCH<sub>2</sub>), 7.30-8.01(m, 10ArH+CH=), 8.56(s, 1H, CH=N).  $\delta_{\text{C}}$ (20 MHz, CDCl<sub>3</sub>) = 14.1(CH<sub>3</sub>), 61.2(OCH<sub>2</sub>), 126.7-137.6(C<sub>Arom.</sub> + C<sub>3</sub>+C<sub>4</sub>), 164.2(C=N), 164.5(CO) ppm. MS(70eV): m/z: 273(M<sup>+</sup>, 45).
13. Triphenyl- and diphenylmethyl-phosphine oxides were removed by stirring the crude reaction in ether; after removing the bulk of the phosphine oxide by filtration, the solution was passed through a short silica gel column with ether and evaporated to dryness.
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