

## Reaction of Azomethine Oxides with Allenes: a New Synthesis of 3-Pyrrolidinones

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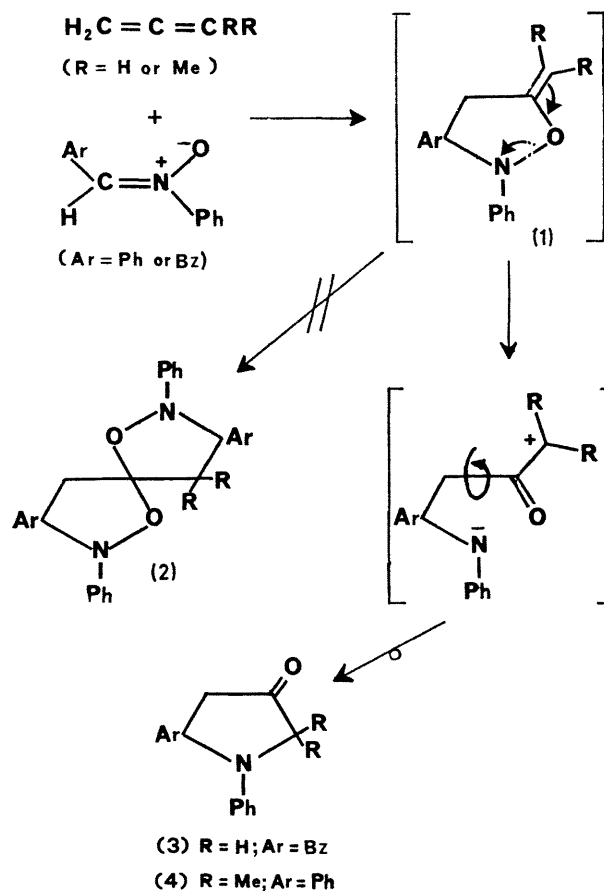
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**Summary** Azomethine oxides add to allene and 1,1-dimethylallene by a reaction pathway which may involve an initial 1,3-dipolar cycloaddition, followed by intramolecular rearrangement leading to 3-pyrrolidinones.

It is known that azomethine oxides undergo 1,3-dipolar cycloaddition reactions with several olefinic double bonds, to form isoxazolidine derivatives.<sup>1</sup> Our interest in these compounds<sup>2</sup> led us to extend this reaction to the highly reactive cumulated double bond system of allenes as a dipolarophile; by analogy with the behaviour of other classes of dipoles, such as nitrile oxides, towards the same substrate,<sup>3</sup> the synthesis of spiro-compounds of type (2) was attempted using azomethine oxides. We found, however, that the reaction follows a different path, leading to 3-pyrrolidinones.

When allene is recycled for 24 h at room temperature through a solution of *N*-benzoyl-*N*-phenylazomethine oxide in Me<sub>2</sub>CO, (3), C<sub>17</sub>H<sub>15</sub>O<sub>2</sub>N, is isolated in 85% yield (m.p. 119°, *M* 265). This assignment of structure is supported by elemental analysis and spectrometric data. The u.v. spectrum displays the characteristic absorption pattern of *N*-phenyl-substituted 3-pyrrolidinones:<sup>4</sup> λ<sub>max</sub> (cyclohexane) 282 (log ε 3.50) and 246 nm (4.36). The i.r. spectrum shows two strong carbonyl stretching frequencies at ν<sub>max</sub> (Nujol) 1714 (cyclic CO) and 1686 cm<sup>-1</sup> (Bz). The <sup>1</sup>H n.m.r. spectrum indicates the presence of a >CH-CH<sub>2</sub>- group and of an isolated methylene group in the molecule: δ (CDCl<sub>3</sub>, 60 MHz) 8.1–6.6 (m, 10H, ArH), 5.34 (dd, 1H, J<sub>54</sub> 5.6, J<sub>54'</sub> 11.5 Hz, 5-CH), 4.28 and 3.59 (*gem* AB quartet, 2H, J<sub>32'</sub> 14.5 Hz, 2-CH<sub>2</sub>), and 2.81 p.p.m. (ddd, 2H, J<sub>44'</sub> 12.6, J<sub>45</sub> 5.6, J<sub>45'</sub> 11.5 Hz, 4-CH<sub>2</sub>) (dd and ddd constitute an ABX system). The mass spectrum exhibits the following main peaks: *m/e* 265, 160, 132, 130, 117, 105, 91, and 77. The high-resolution mass measurements and the presence of the corresponding metastable peaks indicate the fragmentation pattern *M*<sup>+</sup> (*m/e* 265)  $\xrightarrow{-\text{Bz}^+}$  *m/e* 160  $\xrightarrow{-\text{CO}}$  *m/e* 132, thus confirming the cyclic ketonic structure of (3).

Under experimental conditions (72 h at 80° in a sealed tube) different from those leading to (3), *CN*-diphenylazomethine oxide reacts very slowly with 1,1-dimethylallene to yield another 1:1 adduct, C<sub>18</sub>H<sub>19</sub>ON, (m.p. 98°,



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*M* 265), which is assigned the 3-pyrrolidinone structure (4) on the basis of its spectrometric characteristics, which are closely related to the corresponding data for (3): u.v. λ<sub>max</sub> (cyclohexane) 280 (log ε 3.37) and 246 nm (3.95); i.r. ν<sub>max</sub> (Nujol) 1715 cm<sup>-1</sup> (cyclic CO); <sup>1</sup>H n.m.r. δ (CDCl<sub>3</sub>) 7.6–6.4 (m, 10H, ArH), 4.61 (t, 1H, J<sub>54</sub> 7.8, J<sub>54'</sub> 7.2 Hz,

5-CH), 2.95 and 2.73 (ddd, 1H and 1H,  $J_{44}$ , 10.9,  $J_{45}$  7.8,  $J_{4'5}$  7.2 Hz, 4-CH<sub>2</sub>), 1.50 (s, 3H, 2-CH<sub>3</sub>), and 1.40 p.p.m. (s, 3H, 2'-CH<sub>3</sub>). In the mass spectrum, the sequence  $M^+$  ( $m/e$  265)  $\xrightarrow{-Me}$   $m/e$  250  $\xrightarrow{-CO}$   $m/e$  222, confirmed by high-resolution mass measurements and by appropriate metastable peaks, supports the assignment of the structure as (4).

Further evidence in favour of (3) and (4) is provided by their reduction to the corresponding 3-pyrrolidinols on treatment with sodium borohydride.<sup>5</sup>

From our results, it is clear that the reaction between allenes and azomethine oxides differs from the cycloaddition reactions of the same dipolarophile with nitrile oxides,<sup>3</sup> azides,<sup>6</sup> and diazoalkanes;<sup>7</sup> in all these cases stable

spiro-compounds and/or exocyclic alkylidene adducts are formed as primary reaction products. A possible mode of formation of the 3-pyrrolidinones is shown in the Scheme. This involves an initial 1,3-dipolar cycloaddition of the azomethine oxide to one of the cumulated double bonds of the allene, forming the electronically preferred adduct (1); a rearrangement then occurs as shown by means of ring opening and closure in the intermediate isoxazolidine (1), not isolated, leading to the 3-pyrrolidinone (3) or (4).

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