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LETTERS

Trimethylsilylated 1,3-Dienes or Styrenes from the Reaction between Trimethylsilyldiazomethane and Vinyl or Aryl Ketenes

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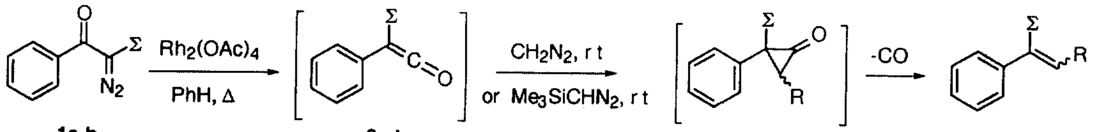
Abstract: The reaction between trimethylsilyldiazomethane and aryl or vinyl ketenes **2** and **7**, bearing an electron withdrawing group on the ketene moiety, gave rise in moderate to good yields to the trimethylsilylated styrenes **3-5** or 1,3 dienes **8a-d** resulting from the decarbonylation of presumed intermediate cyclopropanones.

Keywords : diazo compounds, ketenes, cyclopropanones, decarbonylation.

The formation of cyclopropanones by addition of diazoalkanes to ketenes has been described more than thirty years ago by the groups of de Boer and Turro.[1] If applied to conjugated ketenes the same reaction would lead to cyclopentenones resulting from the rearrangement of intermediate cyclopropanones.[2] To our knowledge, no example of the reaction between diazo compounds and vinylketenes has been reported and only a few examples have been given with arylketenes. With the latter species, depending on the nature of the ketene moiety, the formation of either a cyclopentenone[3], indanone derivatives[4] or a cyclobutanone[5] was observed. As part of our continuing interest in the reactivity of functionalized vinyl or aryl ketenes[6], we have examined the reaction between these species and diazomethane or its trimethylsilylated derivative.

We initiated our study from arylketene **2a**, prepared by rhodium catalyzed Wolff rearrangement[6c] of diazo compound **1a**. When **2a** was submitted to the action of diazomethane, it did not lead to the expected indanone but to the styrene 3, in low yield. When trimethylsilyldiazomethane was used[7] the corresponding silylated styrene 4 was now formed in reasonable yield.[8] Similarly arylketene **2b** led to styrene 5.



1a-b **2a-b** **3, 4, 5**

a $\Sigma = PO(OMe)_2$
b $\Sigma = SO_2Ph$

3 $\Sigma = PO(OMe)_2$ R = H (12%)
4 $\Sigma = PO(OMe)_2$ R = $SiMe_3$ (44%)
5 $\Sigma = SO_2Ph$ R = $SiMe_3$ (60%)

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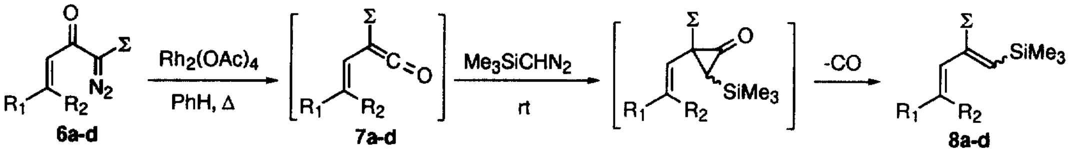
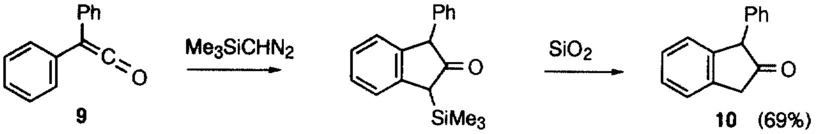
Vinyl ketenes **7a-d** showed a similar behaviour and gave rise to a mixture of stereoisomeric dienes **8a-d**, in indicated yields.



a R_1 = Ph R_2 = H Σ = PO(OMe)$_2$ (74%) **c** R_1 = Ph R_2 = H Σ = SO_2Ph (71%)
b R_1 = Me R_2 = H Σ = PO(OMe)$_2$ (69%) **d** R_1 = Ph R_2 = OMe Σ = PO(OMe)$_2$ (62%)

The importance of the phosphonate or sulfone group on the course of the reaction was underlined when trimethylsilyldiazomethane was reacted with diphenylketene 9[9]. In this case, in agreement with the literature[4], the reaction did not give rise to a styrene, but to the indanone **10** in 69% yield.[10]



Thus, by adding trimethylsilyldiazomethane to functionalized ketenes 2 and 7, neither indanones nor cyclopentenones were formed but only compounds resulting from the decarbonylation of presumed intermediate cyclopropanones. This process may take place thermally or photochemically.[11] However, under the former conditions, it has only been observed so far at rather high temperatures ranging from 110°C to 600°C. In our case, the presence of a withdrawing group on the ketene that may increase the stability of the diradical or zwiterionic intermediate species during the decarbonylation, would facilitate the loss of carbon monoxide.[12, 13]

We are currently exploring the further possibilities of this new preparation of dienes.

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13. Rhodium acetate did not interfere in the decarbonylation of the cyclopropanone since diene **8d** was formed in a similar yield from the ketene **7d** obtained by the thermolysis of diazo **6d** in refluxing toluene without catalyst.