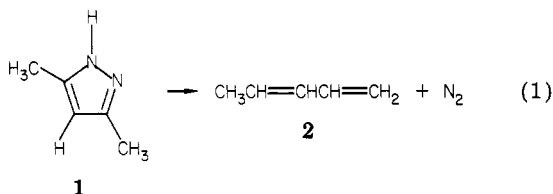


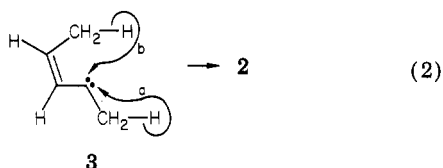
### Evidence for a 1,4 Hydrogen Shift in a Deuterium-Labeled Vinyl Carbene Intermediate in the Formation of 1,3-Pentadiene from 3,5-Dimethylpyrazole

**Summary:** The formation of 1,3-pentadiene via a 1,4 hydrogen shift from a deuterium-labeled vinylcarbene intermediate is demonstrated in the thermolysis of 3,5-dimethylpyrazole.

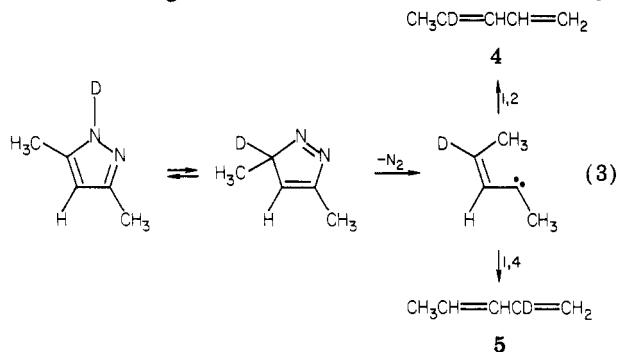
**Sir:** We have previously reported the results on the thermal behavior of some isoxazoles in the gas phase.<sup>1</sup> Continuing with our studies we carried out preliminary reactions with 3,5-dimethylpyrazole (1) using a flow system previously described<sup>1b</sup> and found that at 800 °C, 10<sup>-2</sup> s, and 0.1 torr, 1 loses nitrogen to afford 1,3-pentadiene (2) as the only reaction product<sup>2</sup> [NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.70 (d, 3 H), 5 (m, 3 H), 6 (m, 2 H)] (eq 1).



According to the reported reactions of Δ<sup>1</sup>-pyrazolines,<sup>3</sup> we suggest tautomerization to form an N=N bond, followed by loss of nitrogen to form vinylcarbene (3). Looking at this vinylcarbene, we see that this intermediate is the one proposed in the pyrolysis of cyclopropene derivatives.<sup>4</sup> It has been reported<sup>5</sup> that 1,3-diethylcyclopropene affords 2,4-heptadiene through the vinylcarbene intermediate analogous to 3. However, it is not clear whether these dienes are formed by a 1,2 or 1,4 hydrogen shift (eq 2, a and b, respectively). In an attempt to demonstrate the



reaction pathway unequivocally, we labeled 1, changing NH to ND using deuterium oxide (≥95% 3,5-dimethyl-



(1) (a) Murature D.; Pérez, J. D.; de Bertorello, M. M.; Bertorello, H. *An. Asoc. Quím. Argent.* 1976, 64, 337; *Chem. Abstr.* 1978, 89, 128847m. (b) Pérez, J. D.; de Díaz, R. G.; Yranzo, G. I. *J. Org. Chem.* 1981, 46, 3505. (c) Pérez, J. D.; Yranzo, G. I.; Wunderlin, D. A. *J. Org. Chem.* 1982, 47, 982.

(2) At 900 °C, 1 gives quantitatively 2 (50%) and 1,4-pentadiene (50%).

(3) (a) Hiberty, P. C.; Jean, Y. *J. Am. Chem. Soc.* 1979, 101, 2538. (b) Auff, R. K.; Savins, E. G. *J. Chem. Soc., Chem. Commun.* 1980, 15, 742.

(4) Srinivasan, R. *J. Am. Chem. Soc.* 1969, 91, 6250.

(5) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* 1973, 95, 5680.

(6) Stelch, H. *Ber. Dtsch. Chem. Ges.* 1964, 97, 2681.

pyrazole-1-d by <sup>1</sup>H NMR). NMR analysis of the reaction products obtained from deuterated 1 in C<sub>6</sub>D<sub>6</sub> afforded the doublet at δ 1.70 expected of compound 5, confirming the 1,4 hydrogen shift as proposed in the pyrolysis of methylcyclopropenes<sup>6</sup> (eq 3). Besides, a different pattern is observed in the NMR vinylic region due to the presence of deuterium. Further results, essentially the kinetic parameters involved, will be reported in future papers.

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### Destructible Surfactants Based on a Silicon-Oxygen Bond

**Summary:** A "destructible" surfactant based on the lability of a silicon-oxygen bond, [2-(*n*-dodecylmethyl-*tert*-butylsiloxy)ethyl]trimethylammonium nitrate (1b), has been prepared and characterized along with the corresponding chloride (1a) and tetraphenylborate (1c).

**Sir:** The use of surfactants in organic synthesis to catalyze reactions of water-insoluble organic compounds with water-soluble ionic reagents has been limited, in part, by the formation of troublesome emulsions during reaction mixture workup. Therefore, we have undertaken the preparation of "destructible" surfactants that can be used for catalysis and then decomposed to nonsurfactant products prior to straightforward workup. Two quaternary ammonium chlorides containing an acid-labile ketal group have recently been reported<sup>1</sup> as examples of surfactants designed specifically for application in organic synthesis.<sup>2</sup> They were about as effective as hexadecyltrimethylammonium bromide (HTABr) in catalysis of neutral and basic reactions and were hydrolyzed by the addition of acid before workup.

We report herein the synthesis, characterization, and application of "destructible" surfactants 1, which are the first examples based on a silicon-oxygen bond. They have different overall stability/lability characteristics than those of the ketal-based systems,<sup>1</sup> and they were prepared as follows. Reaction of *n*-dodecylmethyl-dichlorosilane (Petrarch) with *tert*-butyllithium in pentane-hexane at reflux gave (88%) *n*-dodecylmethyl-*tert*-butylchlorosilane (2),<sup>3</sup>

(1) Jaeger, D. A.; Frey, M. R. *J. Org. Chem.* 1982, 47, 311.

(2) Keana and co-workers (Cuomo, J.; Merrifield, J. H.; Keana, J. F. *W. J. Org. Chem.* 1980, 45, 4216) have prepared and characterized destructible nonionic surfactants (unsymmetrical aryl glucosyl disulfides) for use in membrane protein isolation and purification.

(3) The <sup>1</sup>H NMR, IR, and mass spectra (neutrals only) were consistent with the structural assignment; acceptable high-resolution measurement of M<sup>+</sup> or carbon and hydrogen analyses (±0.4%) were obtained.