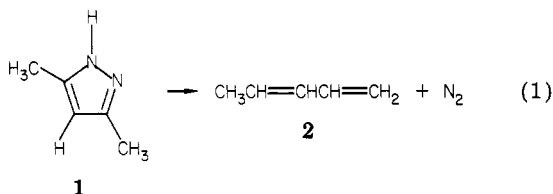


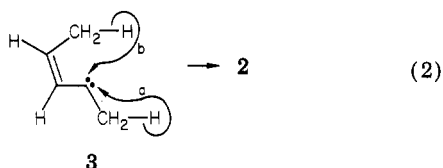
Evidence for a 1,4 Hydrogen Shift in a Deuterium-Labeled Vinyl Carbene Intermediate in the Formation of 1,3-Pentadiene from 3,5-Dimethylpyrazole

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.

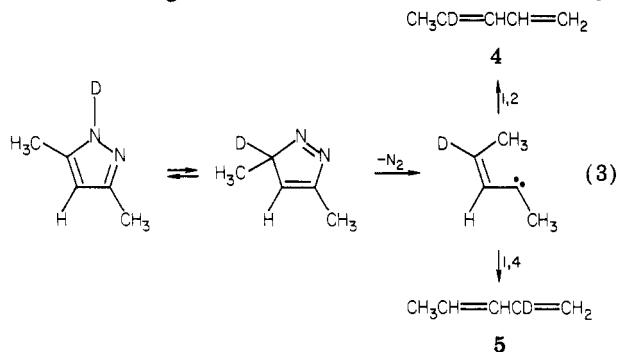
Sir: We have previously reported the results on the thermal behavior of some isoxazoles in the gas phase.¹ Continuing with our studies we carried out preliminary reactions with 3,5-dimethylpyrazole (1) using a flow system previously described^{1b} and found that at 800 °C, 10⁻² s, and 0.1 torr, 1 loses nitrogen to afford 1,3-pentadiene (2) as the only reaction product² [NMR (C₆D₆) δ 1.70 (d, 3 H), 5 (m, 3 H), 6 (m, 2 H)] (eq 1).



According to the reported reactions of Δ¹-pyrazolines,³ 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.⁴ It has been reported⁵ 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 ¹H NMR). NMR analysis of the reaction products obtained from deuterated 1 in C₆D₆ afforded the doublet at δ 1.70 expected of compound 5, confirming the 1,4 hydrogen shift as proposed in the pyrolysis of methylcyclopropenes⁶ (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.

Acknowledgment. This research is supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas and Subsecretaría de Ciencia y Tecnología (Argentina).

Registry No. 1, 67-51-6; 1-d, 81360-83-0; 2, 504-60-9; 5, 81360-84-1.

(7) Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina).

Jorge D. Pérez,* Gloria I. Yranzo⁷
Departamento de Química Orgánica
Facultad de Ciencias Químicas
Universidad Nacional de Córdoba
Estafeta 32-5000 Córdoba, Argentina
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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 reported¹ as examples of surfactants designed specifically for application in organic synthesis.² 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.

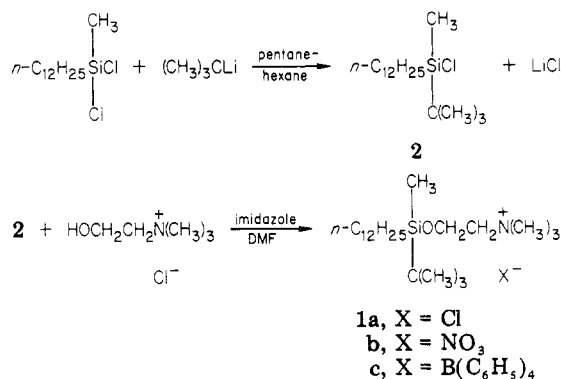
We report herein the synthesis, characterization, and application of "destructible" surfactants 1, which are the first examples based on a silicon-oxygen bond. They have different overall stability/lability characteristics than those of the ketal-based systems,¹ and they were prepared as follows. Reaction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

(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.

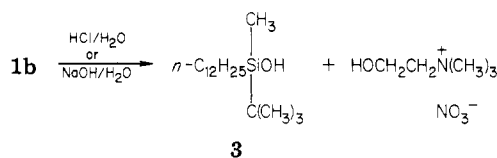
(3) The ¹H NMR, IR, and mass spectra (neutrals only) were consistent with the structural assignment; acceptable high-resolution measurement of M⁺ or carbon and hydrogen analyses (±0.4%) were obtained.

bp 88–90 °C (0.03 mmHg). The reaction⁴ of **2**, choline chloride, and imidazole (1:1.5:1.5 molar ratio, respectively) in dimethylformamide (DMF) at 50 °C yielded **1a**. The DMF was removed from the reaction mixture by distillation at 20 mmHg, and the resultant solid was extracted with chloroform, which was rotary evaporated. The residue was extracted with hexane, and rotary evaporation left crude **1a**, which by ¹H NMR contained traces of imidazole and choline chloride. Column chromatography of this material on neutral alumina (pH 7.4) packed in chloroform with mixtures of ethanol–chloroform containing 1% (v/v) concentrated aqueous ammonia as eluant⁵ gave (66%) of **1a** as a very hygroscopic solid, which was pure by ¹H analysis (270 MHz, CDCl₃ with CHCl₃ internal standard and chemical shifts relative to Me₄Si): δ 4.00 (m, 2 H, CH₂N⁺), 3.80 (m, 2 H, CH₂O), 3.45 (s, 9 H, (CH₃)₃N⁺), 1.18 (s, 20 H, (CH₂)₁₀), 0.82 (s, 12 H, (CH₃)₃C, CH₃), 0.49 (m, 2 H, CH₂Si), 0.02 (s, 3 H, CH₃Si).



The extreme hygroscopic character of **1a** precluded its full characterization and would complicate its application, so it was converted into its nitrate (**1b**) and tetraphenylborate (**1c**) analogues. After addition of an aqueous ethanol solution of 1 molar equiv of AgNO₃ to an ethanol solution of **1a**, AgCl was removed by filtration. Rotary evaporation left crude **1b**, which was dried at 80 °C (0.03 mmHg) and purified by extraction into chloroform and then filtration of an ethanol solution through a column of neutral alumina. Recrystallization of resultant material from hexane at –10 °C gave **1b**:³ mp 65–66 °C; ¹H NMR δ 4.04 (m, 2 H, CH₂N⁺), 3.64 (m, 2 H, CH₂O), 3.30 (s, 9 H, (CH₃)₃N⁺), 1.20 (s, 20 H, (CH₂)₁₀), 0.83 (s, 12 H, (CH₃)₃C, CH₃), 0.58 (m, 2 H, CH₂Si), 0.03 (s, 3 H, CH₃Si). The critical micelle concentration of **1b** at room temperature in 0.01 M NaHCO₃ was 2.8 × 10^{–5} M as determined by a plot (without hysteresis) of relative surface tension (du Nöuy ring) vs. the log of concentration. On mixture of aqueous solutions of **1a** and sodium tetraphenylborate, a white solid precipitated which was dried at 80 °C (0.03 mmHg) and recrystallized from methanol at –10 °C to give **1c**:³ mp 175–176 °C.

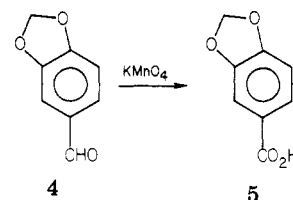
As is described below, **1b** is stable for extended periods in aqueous solution at room temperature over a wide pH range but hydrolyzes in hydrochloric acid and in aqueous sodium hydroxide to *n*-dodecylmethyl-*tert*-butylsilanol (**3**)³ and choline nitrate. Thus, **1b** can be used as a surfactant catalyst at intermediate pH values and then converted to nonsurfactant products at high or low pH values in order to facilitate reaction mixture workup.⁶



The stability of a 0.02 M solution of **1b** in D₂O was monitored by ¹H NMR; after 14 days there was no detectable hydrolysis of **1b**. Likewise, three 0.02 M solutions of **1b** in D₂O containing 0.2 M NaHCO₃ (pH 8.3),⁷ 0.2 M Na₂CO₃ (pH 11.8), and 0.2 M CD₃CO₂D (pH 2.7) were stable for 38,⁸ 38,⁸ and 96 h, respectively. The hydrolysis of 0.02 M **1b** in D₂O containing 3.3 M DCl (pH –0.5) was followed by ¹H NMR. After 10 min, conversion to **3** and choline nitrate was 70% complete, and within (but certainly before) 2 h, 100% complete. In another demonstration of its acid lability, a solution of 73.9 mg of **1b** in 50 mL of 1.1 M hydrochloric acid was stirred overnight; 46.6 mg (96%) of silanol **3** was recovered. The hydrolysis of 0.02 M **1b** in D₂O containing 0.2 M NaOD (pH 13.3) was about 47% and 65% complete after 90 and 280 min, respectively, by ¹H NMR. A solution of 71.7 mg of **1b** in 50 mL of 1.1 M sodium hydroxide was stirred overnight; 35.1 mg (75%) of silanol **3** was isolated.

Both the acid- and base-catalyzed hydrolyses of **1b** most likely proceed by attack at silicon.^{4,9} In the latter, nucleophilic substitution at carbon is an unlikely possibility¹⁰ as is β-elimination. No vinyltrimethylammonium nitrate was detected by ¹H NMR, and choline nitrate was formed without deuterium incorporation.¹¹

The catalytic ability of **1b** under micellar-emulsion conditions was assessed with use of the potassium permanganate oxidation of piperonal (**4**) to piperonylic acid (**5**) at 50–60 °C as in the previous study¹ of destructible



surfactants. In two runs,¹² yields of 44% and 45% of **5**, mp 229–230 °C (lit.¹³ mp 230–232 °C), were obtained, as compared to a 29% yield in a parallel reaction without surfactant. In the context of other comparisons¹ for this reaction, **1b** has about the same catalytic ability as HTABr.

Acknowledgment is made to the U.S. Army Research Office, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to

(4) The method of Corey and Venkateswarlu (Corey, E. J.; Venkateswarlu, A. J. *Am. Chem. Soc.* 1972, 94, 6190) for synthesis of *tert*-butyldimethylsilyl ethers was used.

(5) The elution order was imidazole, **1a**, and choline chloride with 15%, 40%, and 50% ethanol, respectively.

(6) An organic product must be separated from the hydrolysis products, however. An acidic or basic product can be separated from silanol **3** and choline nitrate by appropriate extractions. A neutral organic product would be separated from **3** by other methods such as distillation or chromatography.

(7) This and other pH values are calculated values for the corresponding protio systems.

(8) The solutions were then diluted with D₂O to 0.1 M NaHCO₃ and 0.1 M Na₂CO₃. After an additional 5 days, **1b** had undergone about 17% and 24% hydrolysis in the NaHCO₃ and Na₂CO₃ solutions, respectively.

(9) Baker, R.; Bott, R. W.; Eaborn, C.; Jones, P. W. *J. Organomet. Chem.* 1963, 1, 37.

(10) Crosby, J.; Stirling, C. J. M. *J. Chem. Soc. B* 1970, 671.

(11) Deuterium incorporation at the α-position would be expected as the result of E1 elimination and/or nucleophilic addition of hydroxide to vinyltrimethylammonium nitrate.

(12) The monitored pH of the reaction mixture was 7–8 throughout the 165-min reaction period.

(13) Gulland, J. M.; Macrae, T. F. *J. Chem. Soc.* 1932, 2231.

the Marathon Oil Co. for support of this research.

Registry No. 1a, 81372-17-0; 1b, 81372-19-2; 1c, 81372-20-5; 2, 81372-21-6; 3, 81372-22-7; 4, 120-57-0; 5, 94-53-1; *n*-dodecylmethyl-dichlorosilane, 18407-07-3; choline chloride, 67-48-1; choline nitrate, 26511-31-9.

David A. Jaeger,* Mary Darlene Ward

Department of Chemistry
University of Wyoming
Laramie, Wyoming 82071
Received December 29, 1981

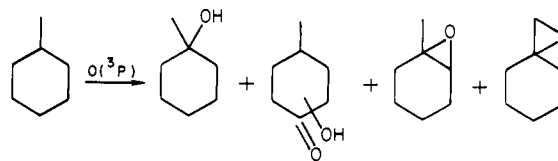
Preparative Oxidation of Cycloalkanes with O(³P) Atoms. Microwave Discharge of CO₂ as a Source of O(³P) Atoms

Summary: Reaction of O atoms produced by CO₂ discharge with cycloalkanes leads to their hydroxy, keto, and epoxy derivatives. The main products of oxidation of isomeric 1,2-dimethylcyclohexanes and *cis*-decalin were their respective tertiary alcohols formed with a high retention of configuration. This oxidation proceeds via radical mechanism, and the alcohols are formed by radical combination in a solvent cage. The influence of temperature and of O₂ on the relative product distribution was investigated.

Sir: Low-pressure photolysis of CO₂ produces O(¹D) atoms which are deactivated, resulting in O(³P) atoms.¹ It was proposed that microwave discharge of CO₂ also produces O(³P) atoms.^{2,3} We have used this method as a convenient source of O(³P) atoms for oxidation of organic compounds. The formation of O(³P) atoms by CO₂ discharge is inferred by the fact that identical results are obtained by this method and by N₂O/N₂ discharge.⁴ Moreover, the new technique is an improvement over the latter one,^{4,5} since it is simpler and easier to perform and proved to be advantageous over O₂ discharge as the oxygen atoms formed are free from oxygen molecules.⁵

We have utilized the CO₂ discharge to oxidize a number of cycloalkanes in neat liquid using a technique similar to that recently described.⁵ The reactions were performed in a flow system at 2 torr with the substrate placed in a flask with an efficient cooling condenser.⁶ The reaction times varied between 15 min and 2 h, the reaction temperatures between -78 and 25 °C, and the conversions between 20% and 50%. The main reaction products were hydroxycycloalkanes accompanied by epoxy derivatives and ketones. Thus oxidation of methylcyclohexane results in methylcyclohexanols, methylcyclohexanones, and two tertiary epoxides (Scheme I). The oxidations proceeded with a high degree of regioselectivity as indicated in Table I. This is in contrast to oxidations of cycloalkanes with O(¹D) atoms which result in a statistical distribution of primary, secondary, and tertiary alcohols.⁷

Scheme I



The relative yields of O(³P) oxidation products were independent of the reaction time but dependent on reaction temperatures: the yield of epoxides was lowest at low temperature and that of alcohols (including the derived ketones) highest (Table I). On the other hand, the regioselectivity of the formation of tertiary alcohols did not change appreciably with temperature.

The main products of the oxidation of isomeric 1,2-dimethylcyclohexanes and *cis*-decalin were the respective tertiary alcohols formed with high retention of configuration, which was temperature dependent: the highest retention was observed at low temperatures.

Since the reaction of O(³P) with saturated hydrocarbons proceeds via a radical mechanism,⁸ the formation of alcohols with high retention of configuration requires a radical combination in a solvent cage.⁹ The formation of epoxides may be explained, on the other hand, by the escape of radicals from the cage, leading to olefins which undergo a fast reaction with O(³P) atoms to give epoxides.^{5,10} This assumption was substantiated by the results of oxidation in the presence of O₂, i.e., when the source of O(³P) atoms was O₂ discharge. In this case the yield of epoxides was considerably lowered, and hydroperoxides were formed.¹¹ Their reduction with Ph₃P led to secondary and tertiary alcohols, the latter being formed with lowered stereoselectivity.

However, the fact that the yields of epoxides are not completely suppressed by O₂ points to an alternative pathway for their formation, namely, disproportionation inside the solvent cage.¹²

The following reaction scheme for O(³P) atom oxidations is suggested (Scheme II): O(³P) atoms abstract H atoms from the substrate, forming a pyramidal cycloalkyl and hydroxyl radical pair (in a triplet state) in a solvent cage. Direct combination (after intersystem crossing) leads to alcohols with retention of configuration. In addition, pyramidal radicals may undergo pseudorotation to give more planar radicals, which after cage combination result in partially inverted alcohols.¹³ Disproportionation inside the cage leads to olefins (and H₂O), which in turn react efficiently with O(³P) atoms to give epoxides. Another competing process involves diffusion of radicals out of cage to form cycloalkyl and hydroxyl free radicals, which in turn abstract H atoms from the substrate, also forming cycloalkyl radicals. Disproportionation of the latter results in olefins, the precursors of epoxides.¹⁴

(8) Andersen, P.; Lunz, A. C. *J. Chem. Phys.* 1980, 72, 5842, 5851. Paraskevopoulos, G.; Cvetanovic, R. J. *J. Phys. Chem.* 1977, 81, 2598. Wright, F. J. *J. Chem. Phys.* 1963, 38, 950.

(9) Koenig, T.; Fischer, H. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, pp 157-190. The intermediacy of a solvent cage in the reactions of O(³P) atoms with alkanes was originally proposed in ref 7a.

(10) Small amounts of ketones may also be formed via H migration.⁵ (11) Mayo, F. R. *Acc. Chem. Res.* 1968, 1, 193. Ingold, K. V. *Ibid.* 1969, 2, 1.

(12) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* 1970, 92, 867.

(13) (a) Greene, F. D.; Lowry, N. N. *J. Org. Chem.* 1967, 32, 875. (b) Miyajima, S.; Simamura, O. *Bull. Chem. Soc. Jpn.* 1975, 48, 526.

(14) No dimers were detected among the reaction products of O(³P) with tertiary hydrocarbons. However, a small yield of bicyclopentyl was found in the oxidation of cyclopentane (Table I).

(1) Moll, N. G.; Clutter, D. R.; Thompson, W. E. *J. Chem. Phys.* 1966, 45, 4469.

(2) Gollnick, K.; Schade, G. *Tetrahedron Lett.* 1973, 857.

(3) In addition to the O(³P) atoms, O₂(¹Δ_g) is formed (ref 2).

(4) Ung, A. Y.-M. *Chem. Phys. Lett.* 1975, 32, 351.

(5) Zadok, E.; Amar, D.; Mazur, Y. *J. Am. Chem. Soc.* 1980, 102, 6369.

(6) He/CO₂, 12:1; total flow rate, 0.7 L/min.

(7) (a) Varkony, T. H.; Pass, S.; Mazur, Y. *J. Chem. Soc., Chem. Commun.* 1975, 457. (b) DeMore, W. B. *J. Phys. Chem.* 1969, 73, 391. This behavior is explained by the fact that the excited O(¹D) atom is much more reactive and, hence, less selective than the ground-state O(³P) atom. The difference in energy between the two species amounts to 45 kcal/mol (cf. Wagner, H. S.; Wolfrum, J. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 604).