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Synthesis of Alkenyl- and Alkynylcyclopropenes

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Abstract: Fluoride anion promoted dehalosilation of 2-(chlorocyclopropyl)trimethylsilanes in the gas-phase was used to prepare a variety of monosubstituted cyclopropenes containing additional unsaturations. The cyclopropylsilanes were constructed easily from common intermediates.

The area of strained organic molecules continues to be one of intense research.¹ Perhaps the best known example of compounds in this discipline is the cyclopropenes,² a family of highly reactive hydrocarbons. We have recently begun investigating the reaction of organometallics with simply-substituted cyclopropene derivatives and desired a route to highly unsaturated analogues. We report herein the preparation of several new alkenyl- and alkynylcyclopropenes via fluoride anion induced elimination of (2-chlorocyclopropyl)trimethylsilanes in the gas phase.³

The traditional synthesis of the requisite cyclopropylsilanes has been addition of an excess of chlorocarbene to an appropriate alkenyltrimethylsilane. This method, however, suffered two drawbacks: 1) each cyclopropylsilane required preparation of a different alkenylsilane precursor. 2) Multiple unsaturations in the alkenylsilane led to a mixture of products separable only by preparative gas chromatography as the carbene added preferentially to the less-hindered (non-silated) double bond, furnishing the desired regioisomer in poor yield. Thus it appeared the general "shotgun" approach of the carbene hitting the silane target would not work for our highly unsaturated molecules. Our solution to these problems was addition of the carbene first to form a common intermediate followed by manipulation of the latent unsaturated molecules.

The key intermediate in the synthesis of the 3-monosubstituted alkenyl and alkynyl derivatives was aldehyde $1,^4$ which was prepared readily from (*E*)-3-trimethylsilyl-2-propen-1-ol (2)⁵ (Scheme 1). Protection of 2 as the THP ether followed by addition of chlorocarbene furnished cyclopropane 3. Hydrolysis of 3 and subsequent oxidation with PCC gave 1 as a moderately stable liquid (52% yield from 2). In turn, compound 1 was converted smoothly to several unsaturated analogues: 1) thermolysis of Cp_2TiMe_2 in a refluxing THF solution⁶ of 1 afforded vinylcyclopropane $4;^7$ 2) Wittig olefination with chloromethylenetriphenyl-phosphorane⁸ gave 5 as a 5:1 *E:Z* mixture; and 3) use of the Corey-Fuchs procedure⁹ readily furnished alkyne 6. Molecule 6 was transformed to a 1:6 *E:Z* mixture of bromoalkene 7 by the three step, one pot procedure of Brown and Gupta.¹⁰ Finally, Hay oxidative dimerization of 6 provided butadiyne 8.¹¹



Reagents: a) DHP, PPTs, CH_2Cl_2 , 96%; b) MeLi, CH_2Cl_2 , 73%; c) HCl, MeOH, 88%; d) PCC, CH_2Cl_2 , 83%; e) Cp_2TiMe_2 , THF, Δ , 22%; f) $Ph_3P=CHCl$, 35%; g) $Ph_3P=CBr_2$, 89%; h) i] MeLi, ii] H_2O , 75%; i) i] catecholborane, ii] Br_2 , CH_2Cl_2 , iii] MeONa, MeOH, 65%; j) CuCl, O_2 , DBU, pyridine, 68%; k) CsF, DMSO.

Passage of **4-6** over tetrabutylammonium fluoride supported on glass helices³ at 25 °C and 30 mtorr resulted in clean formation of cyclopropenes **9-11**. Suprisingly, under the same conditions elimination of **7** gave exclusively **11**.¹² On cooling to -20 °C, however, **12** became the predominant product. The yields of **9-12**, based on isolated Diels-Alder adducts of cyclopentadiene, were generally greater than 70%. Although derivatives of 3-ethenyl^{2,13} and 3-ethynylcyclopropene¹⁴ are known, only recently has a low yield synthesis of **8** been reported;⁷ functionalized vinyl- and parent alkynylcyclopropenes have remained elusive. Gas-phase elimination of **8** was not possible due to low volatility. Elimination in DMSO with CsF did provide small amounts of **13**. Attempts at isolation yielded a polymeric gum which ignited upon removal with a spatula.

$$\begin{array}{cccc} Y & & & & Y \\ Me_{3}Si & Cl & & & & \\ \hline & & & & \\ & & & & \\ 4 & & & (Y = CH = CH_{2}) & 9 \\ 5 & & & & (Y = E - CH = CHCl) & 10 \\ 6 & & & & (Y = C = CH) & 11 \\ 7 & & & & (Y = Z - CH = CHBr) & 12 \end{array}$$

The spectral and physical properties of C_5H_4 hydrocarbon 11 were typical of the 3-monosubstituted molecules. The ¹H NMR spectrum (CDCl₃) contained three signals at δ 7.12 (d, *J*=1.4 Hz), 1.96 (br d, *J*=1.4 Hz), and 1.68 (d, *J*=1.8 Hz), attributed to the cyclopropenyl, cyclopropyl, and alkynyl protons, respectively. In the IR spectrum the cyclopropene and alkyne C-H stretching bands occurred at 3125 and 3306 cm⁻¹, respectively. Alkyne 11 is remarkably stable, exhibiting no noticable decomposition after a week in CDCl₃ solution at -20 °C. Slow decomposition is observed only above 0 °C and yielded a light yellow polymeric mass, presumedly through multiple ene reactions.

SCHEME 2



Reagents: a) DHP, PPTs, CH₂Cl₂, 86%; b) MeLi, CH₂Cl₂, 66%; c) HCl, MeOH, 98%; d) PCC, CH₂Cl₂, 75%; e) Cp₂TiMe₂, THF, Δ , 41%; f) Ph₃P=CBr₂, 76%; g) i] MeLi, ii] H₂O, 69%; h) Bu₄NF, 30 mtorr, 25 °C.

When 2-trimethylsilyl-2-propen-1-ol $(14)^{15}$ was subjected to the same reaction sequence used for 2, the corresponding 1-ethenyl- (15) and 1-ethynyl-2-chlorocyclopropylsilanes (16) were prepared (Scheme 2). Dehalosilation produced cyclopropenes 17 and 18, respectively. In stark contrast to compounds 9-12, 17 and 18 were extremely reactive, even at -78 °C. Molecule 17 was trapped with cyclopentadiene in low yield (>10%) as it readily underwent the dimerization process described previously by Billups and Lin.¹⁶ Cyclopropene 18 eluded detection either as the free species or as the cyclopentadiene cycloadduct; only an insoluble white mass presumedly composed of polymerized 18 was obtained upon careful warming of the liquid nitrogen cold trap.

Preliminary exploration of the thermal chemistry of 9 and 11 revealed a striking difference between the two molecules. Flash vacuum pyrolysis of 9 at 250 °C gave cleanly and quantitatively cyclopentadiene (the product of ring expansion), ^{13a,b} whereas 11 remained unchanged under the same conditions. Incorporation of the pendant unsaturation in 11 might lead to highly reactive, energetically unfavorable molecules (*e.g.*, 19). Only above 500 °C did skeletal rearrangement of 11 take place and gave a 5:1 mixture of 20:21 as products;¹⁷ no materials corresponding to or arising from ring expansion (19) were detected.



In conclusion, we have developed an efficient route to a variety of alkenyl- and alkynylcyclopropenes. Our "rational" design of the precursor molecules avoids the pitfalls associated with the traditional "shotgun" approach and provides the various 2-halocyclopropylsilanes in moderate overall yields. Fluoride anion induced dehalosilation readily furnishes the cyclopropenes, most of which are unknown or very difficult to prepare by traditional methods. We are currently exploring the reactivity of these cyclopropenes with organometallic complexes. These results will be reported in due course.

Acknowledgement. We gratefully acknowledge the University of Oregon for support of this work.

References and Notes

- For recent examples, see: a) Chem. Rev. 1989, 89, issue 5; b) Advances in Strain in Organic Chemistry; Halton, B. (ed.); JAI Press: London, Vols. 1-3; c) "Strain and Its Implication in Organic Chemistry", NATO ASI Series, de Meijere, A.; Blechert, S. (eds.); Kluwer Academic Publishers: Dordrecht, 1989.
- For recent reviews of cyclopropenes, see: a) Halton, B.; Banwell, M. G. "Cyclopropenes", in *The Chemistry of the Cyclopropyl Group*, Rappaport, Z. (ed.); Wiley: New York, 1987, p. 1223; b) Baird, M. S. "Functionalised Cyclopropenes as Synthetic Intermediates," in *Topics in Current Chemistry, Vol. 144*, de Meijere, A. (ed.); Springer-Verlag: Berlin, 1988, p. 137.
- 3. For a recent review, see: Billups, W. E.; McCord, D. J. Angew. Chem. Int. Ed. Engl. 1994, 33, 1332.
- 4. All new compounds exhibited satifactory ¹H and ¹³C NMR, IR, MS, and HRMS data. All silanes were isolated as mixtures of stereoisomers and thus corresponding ¹H NMR data (300 MHz, CDCl₃) are for mixtures unless otherwise specified. Selected data for 1 (major isomer): 9.19 (d, 1H, *J*=6.0), 3.40 (t, 1H, *J*=6.4), 1.85 (dd, 1H, *J*=7.3, 6.8), 1.18 (dd, 1H, *J*=7.3, 6.4), 0.05 (s, 9H); 3: 4.74-4.60 (m, 1H), 4.03-3.10 (m, 5H), 1.95-1.20 (m, 7H), 0.12, -0.01 (2s, 9H); 5: 6.16-6.02 (m, 1H), 5.86-5.18 (m, 1H), 3.40-3.14 (m, 1H), 2.10-1.55 (m, 1H), 0.35-0.20 (m, 1H), 0.20-0.00 (4s, 9H); 6 (major): 3.25 (dd, 1H, *J*=8.4, 3.0), 1.93 (d, 1H, *J*=1.8), 1.58-1.50 (m, 1H), 0.45 (dd, 1H, *J*=8.4, 3.0), 0.14 (s, 9H); 7 (*Z*-isomer 1): 6.17 (d, 1H, *J*=7.5), 5.56 (dd, 1H, *J*=8.5, 7.5), 3.14 (dd, 1H, *J*=8.0, 3.1), 2.17 (dt, 1H, *J*=8.5, 3.1), 0.32-0.23 (m, 1H), 0.17 (s, 9H); (*Z*-isomer 2) 6.26 (d, 1H, *J*=7.2), 6.07 (dd, 1H, *J*=7.9, 7.2), 3.26 (t, 1H, *J*=6.0), 1.99 (dd, 1H, *J*=7.9, 6.0), 0.32-0.23 (m, 1H), 0.05 (s, 9H); 10: 7.19 (s, 2H), 5.96 (d, 1H, *J*=13.4), 5.58 (dd, 1H, *J*=13.4, 7.7), 2.13 (t, 1H, *J*=7.7); 12: 7.20 (d, 2H, *J*=1.4), 6.00 (d, 1H, *J*=6.9), 5.55 (dd, 1H, *J*=8.1, 6.9), 2.51 (d, 1H, *J*=8.1); 15 (major): 5.96 (dd, 1H, *J*=17.1, 10.1), 4.99 (d, 1H, *J*=10.1), 4.87 (d, 1H, *J*=17.1), 3.12 (dd, 1H, *J*=7.1, 4.0), 1.22 (dd, 1H, *J*=7.1, 5.4), 1.05 (dd, 1H, *J*=5.4, 4.0), 0.13 (s, 9H); 16: 3.52-3.02 (m, 1H), 1.93, 1.77 (2s, 1H), 1.46-1.11 (m, 2H), 0.21, 0.08 (2s, 9H).
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- 17. Cyclopropenes are known to rearrange readily to substituted allenes and propynes upon pyrolysis or thermolysis; see reference 2, p. 1272.