Tetrahedron Letters No. 22, pp 1995 - 1998.
©Pergamon Press Ltd. 1979. Printed in Great Britain.
0040-4039/79/0522-1995$02.00/0

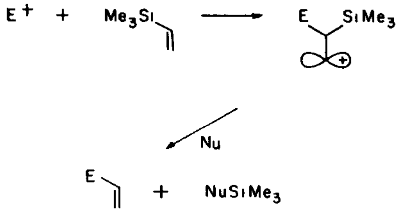
SILICON IN SYNTHESIS. C_2-C_3 ANNULATION USING VINYLTRIMETHYLSILANE AS AN ETHYLENE EQUIVALENT FOR BICYCLO[n.3.0]ENONE SYNTHESIS

Frank Cooke, James Schwindeman and Philip Magnus*

Evans Chemistry Laboratory
Ohio State University
140 West 18th Avenue
Columbus, Ohio 43210

Summary. Vinyltrimethylsilane reacts with cyclic α,β-unsaturated acid chlorides in the presence of stannic tetrachloride to give bicyclo[n.3.0]enones.

The ability to conduct intermolecular Friedel-Crafts reactions with simple alkenes such as ethylene is at best limited.[1] This can be attributed to the high energy intermediates involved which have primary carbonium ion character. The trimethylsilyl group can stabilize a carbonium ion situated β- to it, provided the geometrical requirements of vertical stabilization (hyperconjugation) are fulfilled.[2] This enables the generation of intermediates that although normally associated with high energy processes, are stabilized, and can undergo discrete and useful chemistry. The scheme below illustrates this concept.

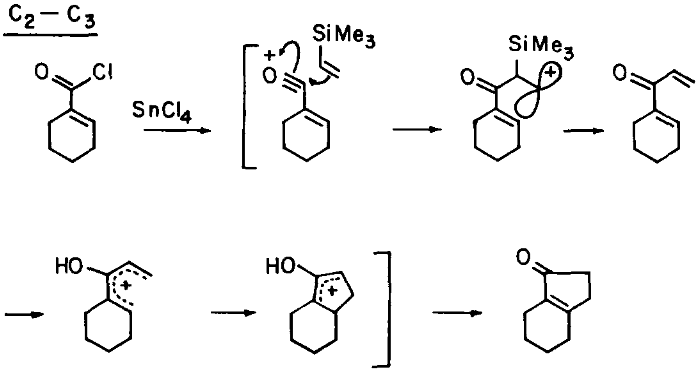


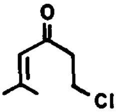
SCHEME

The current interest in cyclopentenones via C_2-C_3 annulation reactions,[3] and recent developments in vinylsilane chemistry,[4] can be combined with the classical Nazarov reaction[5] (see below) to provide a convenient synthesis of certain useful bicyclo[n.3.0]enones. The use of silicon-based reagents to accomplish carbon-carbon bond forming reactions is part of our recent research in developing organosilicon reagents for synthesis.[6] Vinyltrimethylsilane[7] (b.p. 55° cf. ethylene -104°) provides a convenient reagent that functions as an ethylene equivalent in the aliphatic Friedel-Crafts-Kondakov reaction.[8] When the cyclic acid chlorides listed in the TABLE were treated with vinyltrimethylsilane in the presence of stannic tetrachloride, under the conditions specified, the bicyclo[n.3.0]enones were formed in the yields indicated. While the yields of the single step procedure are by no means as good as one would like, it should be borne in mind that previous routes to the enones (entries a, b and c) involved multistep and very low yield procedures.[9,10,11,12] Consequently the one-step procedure described here provides convenient access to a variety of useful bicyclo[n.3.0]enones, and illustrates that trimethylvinylsilane can serve as an ethylene equivalent in the Friedel-Crafts-Kondakov reaction.

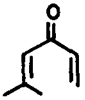
Attempts to convert 3,3-dimethylacryloyl chloride into 4,4-dimethylcyclopent-2-enone **3** using trimethylvinylsilane and stannic tetrachloride or aluminum trichloride gave either the β-chloro-adduct **1** or the diene **2**. No discernable amount of **3** could be detected under the

$C_2 - C_3$

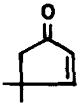




1

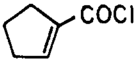
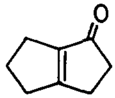
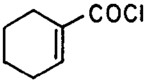
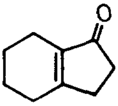
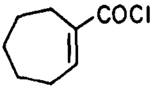
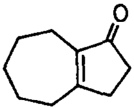
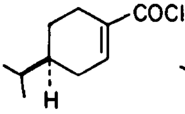
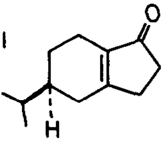
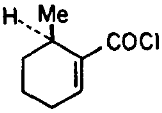
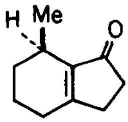


2



3

TABLE

SUBSTRATE	PRODUCT	YIELD
	 9	52.5 %
	 10	46 %
	 11	32 %
		56 %
		63.5 %

described reaction conditions. Attempts to prepare simple monocyclic cyclopentenones using acryloyl chloride, crotonyl chloride and cinnamoyl chloride gave no useful results.

The roles of reagent and substrate may be reversed in this annulation procedure and this consequence is described in the following paper.[14]

Cyclopentene carboxylic acid chloride (12.0 g.) in freshly distilled dichloromethane (100 ml.) at -78° was treated with vinyltrimethylsilane (10.13 g.) and warmed to -30°. Stannic tetrachloride (26.35 g.) was added slowly to the above mixture, keeping the temperature at -30°. After stirring for 1 hr. at -30° the mixture was warmed to 20° and the reaction monitored by ir. When the ir absorption at 1765 cm^{-1} disappeared and the absorption at 1690 cm^{-1} reached a maximum (ca. 6h.) the reaction mixture was worked-up by quenching in water (100 ml.). The quenched mixture was extracted with dichloromethane (100 ml.) and the extract washed with saturated aqueous sodium bicarbonate (100 ml.). Drying (Na_2SO_4), evaporation and distillation gave bicyclo[3.3.0]-Δ^7-octen-1-one (5.90 g. 52.5%), b.p. 114-115°/13 mm Hg. (95% pure glc).

Acknowledgements

The NSF and NIH is thanked for financial support of this work. Steve Kroll is thanked for preparing some of the α,β-unsaturated acid chlorides.[13] Dr. Malcolm Nobbs is thanked for experiments pertinent to 1 and 2.

References

1. Olah. G., "Friedel-Crafts and Related Reactions," Vol. 3, Pt. 2, p. 1033. Nenitzescu and Balaban, A. T.; Deno, N. C.; and Chafetz, H., J. Am. Chem. Soc., 1952, 74, 3940; Norris, J. F. and Couch, H. B., Ibid., 1920, 42, 2329 Matsumoto, T.; Nishida, T.; Hata, K.; J. Org. Chem., 1958, 23, 106; Taylor, H. T.; J. Chem. Soc., 1958, 3922.

2. Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; and Braun, R. S., J. Am. Chem. Soc., 1971, 93, 5713; Traylor, T. G.; Berwin, H. J.; Jetkunica, J.; and Hall, M. L.; Pure Appl. Chem., 1972, 30, 599; Jarvie, A. W. P.; Organometallic Chem. Rev. (A), 1970, 6, 153; Cooke, M. A.; Eaborn, C.; and Walton, D. R. M.; J. Organometallic Chem., 1970, 24, 30; Bourne, A. J. and Jarvie, A. W. P.; Ibid., 1970, 24, 335.

3. Jung, M. E. and Hudspeth, J. P.; J. Am. Chem. Soc., 1977, 99, 5508 and references cited therein; Trost, B. M. and Kelley, D. E.; Ibid., 1976, 98, 248; Ellison, R. A.; Synthesis, 1973, 397; Hiyama, T.; Shinoda, M.; and Nozaki, H.; Tetrahedron Letters, 1978, 771; Karpf, M.; and Drieding, A. S.; Helv. Chim. Acta., 1976, 59, 1226; Hoffman, W. and Muller, N.; Tetrahedron Letters, 1976, 3585. Jacobson, R. M.; Raths, R. A.; McDonald, J. H., J. Org. Chem., 1977, 42, 2545.

4. Pillot, J-P.; Dunogues, J.; and Calas, R.; Compt.rend. , 1974, 278, C. 787, 789; Indem, Bull. Soc. Chim. France, 1975, 2143; Fleming, I. and Pearce, A.; J.C.S. Chem. Comm., 1975, 633; Chen, T. H.; Lau, P. W. K.; and Mychajlowskij, W.; Tetrahedron Letters, 1977, 3317.

5. Nazarov, I. N. and Zaretskaya, I. I.; Zh. Obsh. Khim., 1957, 27, 693; Nazarov, I. N.; Uspekhi, Khim., 1949, 18, 377; Nazarov, I. N. and Torgov, I. V.; Bull. Acad. Sci. USSR Classe Sci. Chim., 1947, 495, CA 42, 7735; Nazarov, I. N. and Zaretskaya, Ibid., 1942, 200; Matsoyan, S. G.; Avetyan, M. G.; and Darbinyan, E. G.; Izv. Akad. Nauk. Arm. SSR. Khim. Nauk., 1964, (4)17. CA, 45, 6572; Woodward, R. B. and Hoffman, R.; "The Conservation of Orbital Symmetry," Verlag Chemie, Weinham/Bergstv Germany, 1970; Sorensen, T. S.; J. Am. Chem. Soc., 1967, 89, 3782; Deno, N. C.; Pittman, Jr., C. V.; Turner, J. O.; Ibid. 1964, 87, 2153; Ohloff, G.; Schulte, K. H.; and Demole, E.; Helv. Chim. Acta., 1971, 54, 2813.

6. Burford, C.; Cooke, F.; Ehlinger, E.; and Magnus, P. D.; J. Am. Chem. Soc., 1977, 99, 4536; Cooke, F. and Magnus, P. D.; J.C.S. Chem. Comm., 1977, 513; Ayalon-Chass, D.;

Ehlinger, E.; and Magnus, P. D.; Ibid., 1977, 772; Magnus, P. D. and Roy, G.; Ibid., 1978, 297; Bundy, G.; Cooke, F.; and Magnus, P. D.; Ibid., 1978, 714.

7. Vinyltrimethylsilane is commercially available from Petrarch Systems.

8. Kondakov, I. L.; J. Russ. Phys. Chem. Soc., 1892, **24**, 309; Indem., Bull. Soc. Chim. France, 1892, **7**, 576.

9. Jones, N. and Taylor, H. T.; J. Chem. Soc., 1959, 4017; Dev. S.; J. Indian. Chem. Soc., 1957, **34**, 169; Dev. S. and Rai. C.; Ibid., 1957, **34**, 266. Kulkarni, S. B. and Dev. S.; Tetrahedron, 1968, 545.

10. Dev. S.; Chem. and Ind., 1955, **32**, 255; Mathieson, D. W.; J. Chem. Soc., 1951, 177; 1953, 3248; Johnson, W. S.; Davis, C. E.; Hunt, R.H.; and Stork, G.; J. Am. Chem. Soc., 1948, **70**, 3021; Bishop, R. and Parker, W.; Tetrahedron Letters, 1973, 2375.

11. Buchi, G. and Plattner, P. A.; Helv. Chim. Acta., 1946, **29**, 1608.

12. References to the synthesis of cyclopentenones using inter- or intra-molecular Friedel-Crafts reactions - Baddeley, G.; Taylor, H. T.; and Pickles, W.; J. Chem. Soc., 1953, 124; Chuang, C-K.; Tien, Y-L.; Ma, C-M.; Ber., 1936, **69**, 1494, Dev. S.; J. Indian. Chem. Soc., 1956, **33**, 703; Conia, J-M. and Leriverend, M-L.; Tetrahedron Letters, 1968, 2101; Martin, G. J.; Rabiller, Cl.; and Mabon, G.; Ibid., 1970, 3131; Martin, G. J. and Daviand, G.; Bull. Soc. Chim. France, 1970, 3098; Jacquier, R.; Mousseron, M.; and Boyer, S.; Ibid., 1956, 1653; Schegolev, A. A.; Smit, W. A.; Roitburd, G. V.; and Kucherov, V. F.; Tetrahedron Letters, 1974, 3373.

13. References to α,β-unsaturated acids - Dev. S.; J. Indian. Chem. Soc., 1956, **33**, 769; McElvain, S. M.; and Starn, Jr., R. E.; J. Am. Chem. Soc., 1955, **77**, 4571; Assony, S. J.; and Kharach, N.; Ibid., 1958, **80**, 5978. The α,β-unsaturated acids were converted into the corresponding acid chlorides using conventional literature procedures. Bosshard, H. H.; Mory, R.; Schmid, M.; and Zollinger, Hch.; Helv. Chim. Acta., 1959, **42**, 1653.

14. Fristad, W. E.; Dime, D. S.; Bailey, T. R.; Paquette, L. A.; Tetrahedron Letters, accompanying paper.

(Received in USA 2 February 1979)