Tetrahedron Letters,Vol.24,No.43,pp 4727-4728,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

# A CONVENIENT AND NOVEL SYNTHESIS OF 1,1-DICHLOROALKENES USING α-LITHIATED DICHLOROMETHYLTRIMETHYLSILANE AND ALDEHYDES[1]

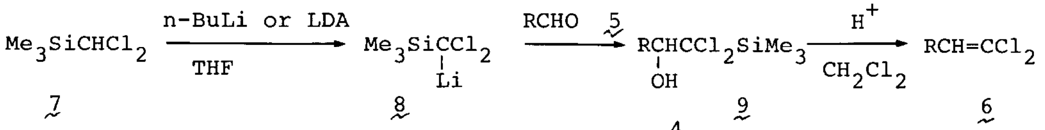
Akira Hosomi,* Masahiro Inaba, and Hideki Sakurai*
Department of Chemistry, Faculty of Science
Tohoku University, Sendai 980, Japan

*Summary:* Various 1,1-dichloroalkenes can be prepared by the reaction of α-lithiated dichloromethyltrimethylsilane with aldehydes followed by hydrolysis.

1,1-Dichloroalkenes can be prepared by the dichloroolefination of carbon-oxygen double bond of carbonyl compounds with a Wittig-type reagent (4), obtained from organophosphine (1) and tetrahalomethane (2).[2] (eq. 1)

$$\underset{1}{2R_3P} + \underset{2}{XCCl_3} \xrightarrow{-R_3XP^+Cl^-\ \ 3} \underset{4}{R_3P{=}CCl_2} \xrightarrow[-R_3P=O]{RCHO\ \ 5} \underset{6}{RCH{=}CCl_2} \qquad (1)$$

However, in the method, at least two equivalents of 1 are necessary for the preparation of the reagent (4), because one mole of 1 is required to the formation of the phosphonium salt (3) which can cause sometimes undesirable side-reactions.[2a,c] We now report a convenient and new route to 1,1-dichloroalkenes (6) using the (trimethylsilyl)dichloromethyl anion (8)[3] as shown in eq. 2. The results are summarized in Table 1.

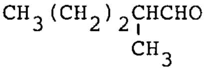
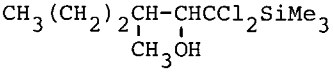
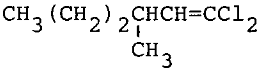


$$\underset{7}{Me_3SiCHCl_2} \xrightarrow[THF]{n\text{-BuLi or LDA}} \underset{8}{\underset{Li}{Me_3SiCCl_2}} \xrightarrow{RCHO\ \ 5} \underset{9}{\underset{OH}{RCHCCl_2SiMe_3}} \xrightarrow[CH_2Cl_2]{H^+} \underset{6}{RCH{=}CCl_2} \qquad (2)$$

(Trimethylsilyl)dichloromethyllithium (8),[4] readily prepared from dichloromethyltrimethylsilane (7)[5] and butyllithium or lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at temperature lower than -100°C for 0.5-1 h, reacts with aldehydes (5) to afford the corresponding β-hydroxysilanes (9) selectively after careful hydrolysis with aqueous ammonium chloride-methanol (1:9) at temperature lower than -80°C. (Procedure is shown in the caption of Table 1.) It is very important that hydrolysis should be conducted at low temperature for avoiding the contamination of homo-Brook rearrangement products (10) of 9. In fact, $RCH(OX)CCl_2H$ (10, $X=SiMe_3$ or H) was obtained exclusively by hydrolysis at -20°C.[6]

The addition of hexamethylphosphoric triamide (HMPA) in the synthesis of 9 also promotes the rearrangement of the silyl group. 9, thus obtained, can be readily converted to 1,1-dichloroalkenes (6) by the treatment with boron trifluoride-etherate or sulfuric acid in dichloromethane[7] in good yield.

Table 1. Synthesis of 1,1-dichloroalkenes (6)[a]

| Entry | Aldehyde (5) | β-Silyl alcohol (9)[b] (% yield)[c] | | 1,1-Dichloroalkene (6)[d] (% yield)[c] | |
|---|---|---|---|---|---|
| 1 | PhCHO | $PhCH(OH)CCl_2SiMe_3$ | (75) | $PhCH=CCl_2$ | (77)[e] |
| 2 | $CH_3(CH_2)_4CHO$ | $CH_3(CH_2)_4CH(OH)CCl_2SiMe_3$ | (56) | $CH_3(CH_2)_4CH=CCl_2$ | (97) |
| 3 | $(CH_3)_2CHCH_2CHO$ | $(CH_3)_2CHCH_2CH(OH)CCl_2SiMe_3$ | (61) | $(CH_3)_2CHCH_2CH=CCl_2$ | (80) |
| 4 |  $CH_3(CH_2)_2\underset{CH_3}{CH}CHO$ |  $CH_3(CH_2)_2\underset{CH_3}{CH}-\underset{OH}{CH}CCl_2SiMe_3$ | (46) |  $CH_3(CH_2)_2\underset{CH_3}{CH}CH=CCl_2$ | (64) |
| 5 | $Ph(CH_2)_2CHO$ | $Ph(CH_2)_2CH(OH)CCl_2SiMe_3$ | (51) | $Ph(CH_2)_2CH=CCl_2$ | (73) |
| 6 | $p-ClC_6H_4CHO$ | $p-ClC_6H_4CH(OH)CCl_2SiMe_3$ | (46) | $p-ClC_6H_4CH=CCl_2$ | (85) |

a) All compounds obtained in this work gave satisfactory elemental analysis and spectral data. b) Metalation of 7 (1.2 mmol) was conducted with n-BuLi-n-hexane (1.0 mmol) or LDA (1.0 mmol) in THF (3 ml) at temperature lower than -100°C for 0.5-1 h and an aldehyde (1.1 mmol) was added. The mixture was stirred for 3-4 h at temperature lower than -80°C and hydrolyzed with 10 ml of aq ammonium chloride-MeOH (1:9) at -80°C. After work-up as usual, the oil was purified by silica gel TLC. c) Yield after isolation by TLC. d) The reaction of 9 (1.0 mmol) was carried out at room temperature for 1.5-2 h in the presence of conc. sulfuric acid (0.1 ml) in dichloromethane (3 ml). e) The reaction was conducted in the presence of $BF_3 \cdot OEt_2$ (0.1 ml) for 8 h.

It should be noted that the reaction proceeds in a different mode from the reaction of aldehydes with (trimethylsilyl)chloromethyllithium which gives α-silyl epoxide by the intramolecular substitution reaction.[8]

*Acknowledgment. The work was supported by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research No. 57118002).*

References and Notes

(1) Chemistry of Organosilicon Compounds 160.

(2) (a) R. Rabinowitz and R. Marcus, J. Am. Chem. Soc., 84, 1312 (1962); (b) W. Reeve, R. Brown, and T. F. Steckel, ibid., 93, 4607 (1971); (c) B. E. Cross and R. E. Markwell, Chem. Commun., 442 (1972); (d) J. C. Combert and J. Villieras, Tetrahedron Lett., 1035 (1971); (e) W. G. Salmond, ibid., 1239 (1977).

(3) (a) D. Seyferth, E. M. Hanson, and F. M. Armbrecht, Jr., J. Organomet. Chem., 23, 361 (1970); (b) G. L. Larson, and O. Rosario, ibid., 168, 13 (1979).

(4) Previously, 8 was prepared in $Me_2O$-THF at -105°C. See ref. 3a.

(5) 7 is commercially available and can also be prepared readily by the photochlorination of trimethylchlorosilane followed by methylation. See J. L. Speier et al., J. Am. Chem. Soc., 70, 1400 (1948); 73, 824 (1951).

(6) It has been observed that 9 rearranges to 10 quantitatively in the presence of NaH and KH in THF at room temperature. c.f. P. F. Hudrlik, and A. K. Kulkarni, J. Am. Chem. Soc., 104, 6809 (1982).

(7) P. F. Hudrlik, D. Peterson and R. J. Rona, J. Org. Chem.. 40, 2263 (1975).

(8) (a) F. Cooke, G. Roy, and P. Magnus, Organometallics, 1, 893 (1982); (b) C. Burford, F. Cooke, E. Ehlinger, and P. Magnus, J. Am. Chem. Soc., 99, 4536 (1977).

(Received in Japan 8 July 1983)