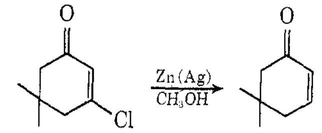
Communications

See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

The Reduction of β-Halo-α,β-Unsaturated Ketones

Summary: β-Chloro-α,β-unsaturated ketones are reduced to α,β-unsaturated ketones by silver-promoted zinc dust in methanol.

Sir: We have found that silver-promoted zinc dust in methanol is an efficient reagent for the reduction of β-halo-α,β-unsaturated ketones to the corresponding α,β-unsaturated ketones; *i.e.*, **1** → **2**. The reducing agent is prepared by a modification of Conia's procedure.[1] A procedure for the conversion of **1** to **2** follows.



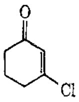
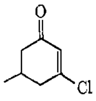
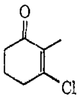
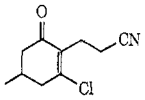
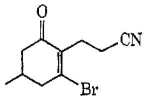
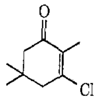
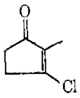
1 **2**

Zinc dust (Mallinckrodt Analytical Reagent, 2.1 g) is stirred for 4 min with 10 ml of 10% aqueous HCl. The supernatant liquid is decanted and the zinc is washed with acetone (2 × 10 ml) and ether (10 ml). A suspension of 60–70 mg of anhydrous silver acetate in 10 ml of boiling acetic acid is then added. After the mixture is stirred for 1 min, the supernatant is again decanted and the black zinc–silver couple is washed with acetic acid (5 ml), ether (4 × 10 ml), and methanol (10 ml). To the moist couple is added a solution of 1 g of chloroenone **1** in 3 ml of methanol. The reduction is exothermic and glpc analysis shows it to be complete after being stirred vigorously at room temperature for 15–30 min. The spent zinc is filtered off and washed with 30 ml of methanol. The methanol is then evaporated under reduced pressure to give a gel which is partitioned between ether and 10% aqueous HCl. The ether layer is dried and evaporated to yield the crude enone **2**. Distillation of the combined product from five similar runs yielded 3.17 g (81%) of enone **2** as a clear liquid. In a large-scale run (21 g of zinc dust, 10 g of chloroenone **1**), the reaction was much slower, requiring about 6 hr for completion.

Other β-haloenones are also reduced by the procedure. When there is an alkyl substituent in the α position, the reduction is much slower but is complete in about 1 day at room temperature. One compound, 3-chloro-2,5,5-trimethylcyclohexenone (**8**), is reduced to the extent of only 58% after 37 hr. Data are collected in Table I.

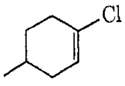
TABLE I

REDUCTION OF β-HALOENONES

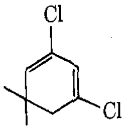
Reactant	No.	Reaction time	Yield,[a] %
	**3**	1.5 hr[b]	75
	**4**	30 min	75
	**5**	40 hr	77
	**6**	24 hr	93
	**7**	30 min	81
	**8**	37 hr	*c*
	**9**	26 hr	65

[a] Isolated yield. [b] Reaction carried out at 0°. At room temperature, the chloroenone reacts with methanol. [c] After 37 hr, glpc analysis shows that the original chloroenone is 58% reduced.

The simple vinyl chloride **10**, the dichlorodiene **11**, *p*-bromoethylbenzene, and α-bromobenzoic acid are not reduced to any noticeable extent after 24 hr.



10



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β-Chloroenones **3**, **4**, **5**, **6**, **8**, and **9** were prepared by treating a suspension of the corresponding 1,3-diketone with oxalyl chloride in benzene or chloroform. β-Bromoenone **7** was prepared from the 1,3-diketone and phosphorus tribromide.

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[1] J. M. Denis, C. Girard, and J. M. Conia, *Synthesis*, **5**, 549 (1972).

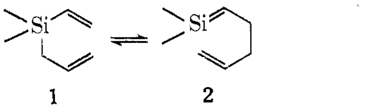
Silicon-Cope Rearrangement. Reversible Formation of a Silicon-Carbon Double Bond

Summary: Evidence has been adduced for a Cope rearrangement in propenylallyldimethylsilanes involving the intermediacy of (what has been regarded as a high energy) double bonded silicon intermediate.

Sir: Currently there is considerable interest in compounds possessing a silicon–carbon double bond. Although no such stable, isolable compounds[1] have been reported, their intermediacy has been implicated in a number of examples. The trapping of $(CH_3)_2Si{=}CH_2$ generated by (1) the pyrolysis of 1,1-dimethyl-1-silacycylobutane[2-4] and (2) the retroene reaction of allyltrimethylsilane[5a] has been reported.[5b-d] The formation of $(Ph)_2Si{=}CH_2$ by photolysis of 1,1-diphenyl-1-silacyclobutane[6] or pentaphenylmethyldisilane[7] has also been reported. Recently the first spectroscopic observation of a silicon–carbon doubly bonded compound was obtained at −196°.[8] Theoretical aspects of the silicon–carbon π bond have been reviewed.[9]

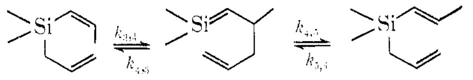
We were interested in whether such silyl olefins could, in general, be generated by concerted, thermal rearrangements. The superior migratory aptitude of silicon in sigmatropic rearrangements has been demonstrated in 5-trimethylsilylcyclopentadiene[10] and 1-trimethylsilylindene[11] and more recently in allylsilanes.[12] The participation of silicon in pericyclic transition states which lead to a doubly bonded silicon has not been reported in the literature.

The reaction selected for study was the [3,3] sigmatropic or Cope rearrangement. The possibility of observing **2** (eq 1) by conventional methods in an equilibrium mixture seemed remote because the equilibrium is expected to greatly favor **1** owing to the greater stability of the carbon–carbon double bond. Therefore, an experiment which could detect the intermediacy of **2** was devised. It was expected that, if the reversible Cope rearrangement occurred, the interconversion (eq 2) of *cis*- and *trans*-propenylallyldimethylsilane (**3** and **5**)[13] would be revealed. The analogous interconversion of *cis*- and *trans*-1,5-heptadiene has already been studied in detail by Frey and Solly.[14]



(1)

1 **2**



(2)

3 **4** **5**

We have found that *cis*- and *trans*-propenylsilanes, **3** and **5**, were interconvertible upon gas phase thermolysis in a gold reactor flow system[15] at temperatures above 500° and reaction times >1 sec. At 560° the equilibrium mixture consisted of 21% **3** and 79% **5**. Reaction kinetics[16] were studied over the temperature range of 500–580°, and least-squares analysis of the kinetic data yielded the following Arhenius parameters: $E_a = 39.2 \pm 0.4$ kcal/mol and $\log A = 9.93 \pm 0.12$. The relatively low preexponential factor is not uncommon for Cope rearrangements.[14,17] Since the calculated activation parameters correlate with the reactions given by $k_{3,4}$ and $k_{5,4}$, it is seen that these reactions require only ~3-kcal/mol greater activation energy than the corresponding all-carbon heptadienes.[14,18] This small activation energy difference may at first glance seem surprising because it does not appear to reflect a much greater energy requirement for the formations of a silicon–carbon double bond. However, coupled with analogous results obtained in these laboratories on the retroene reaction of allyltrimethylsilane (**6**, $E_a = 55.9$ kcal/mol, $\log A = 12.55$) and 3,4-dimethyl-1-pentene (**7**, $E_a = 53.6$ kcal/mol, $\log A = 13.25$), an explanation emerges. The ~10-kcal/mol greater E_a for the all-carbon substrate, **7**, compared with certain oxygenated ones[19] is a reflection of the greater endothermicity of the former reaction (*i.e.*, C=C less stable than C=O).[20,21] In the case of silicon, moreover, preliminary results indicating approximately the same E_a for analogous oxygenated[22] and nonoxygenated[22] substrates appear to reflect the smaller difference in endothermicity between these reactions (*i.e.*, Si=C *vs.* approximately Si=O).[23,24] It could, therefore, be the enhanced ability of silicon to participate in pericyclic transition states which partially compensates the greater energy requirement for the formation of the less stable, multiply bonded silicon.[23] The larger 3p orbitals of silicon may be held responsible for the difference in reactivity.

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[1] Compounds of the type $R_2Si{=}CH_2$ are "unstable" in the reactivity sense, *i.e.*, tend to dimerize.

[2] L. E. Gusel'nikov and M. C. Flowers, *J. Chem. Soc., Chem. Commun.*, 864 (1967).

[3] M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968).

[4] D. N. Roark and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 167 (1973).

[5] (a) W. J. Bailey and M. S. Kaufmann, Abstracts of the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, p Org 55; (b) T. J. Barton and E. Kline, *J. Organometal. Chem.*, **42**, C21 (1972); (c) R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson, and J. Stevenson, *ibid.*, **34**, 53 (1972); (d) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, 782 (1971).

[6] P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 54 (1973).

[7] P. Boudjouk, J. R. Roberts, C. M. Goleno, and L. H. Sommer, *J. Amer. Chem. Soc.*, **94**, 7926 (1972).

[8] T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1973).

[9] C. J. Attridge, *Organometal. Chem Rev.*, **5** (A), 323 (1970).

[10] See, for examples, E. W. Abet, M. O. Dunster, and A. Waters, *J. Organometal. Chem.*, **49**, 287 (1973).

[11] A. J. Ashe III, *Tetrahedron Lett.*, 2105 (1970).

[12] H. Kwart and J. Slutsky, *J. Amer. Chem. Soc.*, **94**, 2515 (1972).

[13] *cis*- and *trans*-propenylallyldimethylsilanes and *cis*- and *trans*-propenyltrimethylsilanes were prepared by the reaction of propenylmagnesium bromide (mixture of cis and trans) in tetrahydrofuran with allyldimethylchlorosilane and trimethylchlorosilane, respectively. Pure samples of each isomer were obtained by preparative glc on a 12-ft 10% Apiezon L column.

[14] H. M. Frey and R. K. Solly, *Trans. Faraday Soc.*, 1858 (1968).

[15] H. Kwart, S. F. Sarner, and J. H. Olsen, *J. Phys. Chem.*, **73**, 4056 (1969).

[16] Kinetic analysis was carried out as follows. Since the concentration of **4** is very much smaller than those of **3** and **5**, **4** is treated as a reactive intermediate. The equilibrium then simplified to

$$3 \underset{k_R}{\overset{k_F}{\rightleftarrows}} 5$$

and the kinetic expression for the simplified equilibrium is

$$\ln\left[(A_0 - A_e)/(A - A_e)\right] = kt$$

where k is the rate constant for the first-order approach to equilibrium $(k_F + k_R)$.

[17] H. M. Frey and D. H. Lister, *J. Chem. Soc. A*, 26 (1967).

[18] M. R. Willcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, **9**, 25 (1972).

[19] Methyl allyl ether ($E_a = 41.6$ kcal/mol), ethyl vinyl ether ($E_a = 44.1$ kcal/mol), 3-buten-1-ol ($E_a = 41.0$ kcal/mol): results of these laboratories.

[20] For example, 1-pentene → propene + ethylene ($\Delta H_R{}^\circ = +2.3$ kcal/mol). Calculated by S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

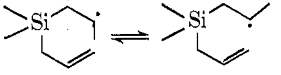
[21] This concept will be elaborated upon in another article which will be submitted for publication in the near future. A referee has questioned the validity of comparing these relative endothermicities. The question of seeing this factor reflected in the activation energy requirements of the respective reactions will be treated in this forthcoming article.

[22] For examples, $R_2HSiOCH_2CH{=}CH_2$ and $R_2HSiCH_2CH_2CH{=}CH_2$.

[23] R. Walsh, *J. Organometal. Chem.*, **38**, 245 (1972).

[24] I. M. T. Davidson and J. M. Thompson, *J. Chem. Soc. D*, 251 (1971).

Alternative mechanisms for the interconversion of **3** and **5** have been considered. It is well known that cis–trans isomerization of olefins[13] occurs upon heating to sufficiently high temperature, presumably *via* a biradical intermediate. To evaluate this possibility, a model compound, *cis,trans*-propenyltrimethylsilane[13] was prepared and thermolyzed. It was found that nearly 100° higher temperatures were required to effect isomerization. This result could have been anticipated if the activation parameters were similar to those of the diradical course of 2-butene thermal isomerization (E_a = 63 kcal/mol, log A = 13.8).[25] It would suggest that a reaction course for isomerization of **3** to **5** passing through the diradical intermediate **8** would have an activation requirement >20 kcal higher than observed. Several other alternative mechanistic possibilities can be regarded as unlikely, and in the interests of brevity will not be discussed.



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This work clearly indicates that the enhanced ability of silicon to participate in pericyclic transition states may lead to the reversible or irreversible formation of multiply bonded silicon.

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(25) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **57**, 1936 (1961).

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Selective Reduction of Aromatic Carboxyl Groups to Methyl in the Presence of Ester Functionality. A New Procedure for the Preparation of Ester-Containing Organosilanes

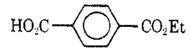
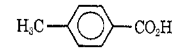
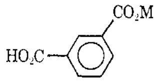
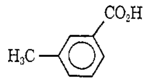
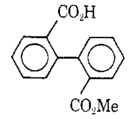
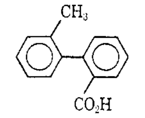
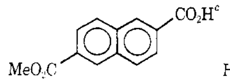
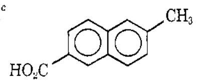
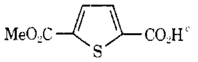
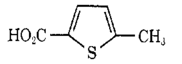
Summary: New synthetic procedures for the selective reduction of the carboxyl group of aromatic half-esters to methyl and for the preparation of benzylic silanes containing ester groups is described.

Sir: It is well documented that ester groups can usually be reduced with relative ease while carboxyl groups are relatively resistant to reduction. Further, reduction of a carboxyl group usually results in the production of aldehydes[1] or alcohols.[2]

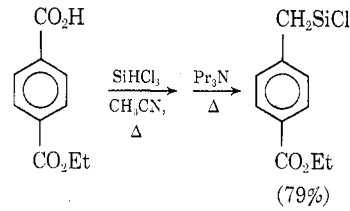
Previously[3] we reported the unprecedented reduction of aromatic carboxyl groups directly to methyl groups by the use of a trichlorosilane–*tert*-amine combination. In an endeavor to extend the scope of this reduction, we attempted to reduce aromatic esters under the same conditions. Surprisingly, esters like ethyl benzoate and phenyl benzoate were totally unreactive and could be recovered virtually unchanged.[4] This immediately raised the possibility that aromatic half-esters might be made to undergo reduction of the carboxyl group to a methyl while the ester group would be left intact. Accordingly the "one-pot" reduction procedure developed earlier[3] was applied to a representative series of aromatic half-esters with the results depicted in Table I. As will be noted from this table the unreduced ester groups were saponified by the base treatment employed to cleave the intermediate benzylic silanes. In the case of ethyl hydrogen terephthalate (entry 1 of table) the intermediate benzylic silane was isolated and characterized in a 79% yield. Benzylic silicon–carbon cleavage of this product was achieved with a slight excess of base in only 0.5 hr. to give a 75% yield of *p*-ethyl toluate. The ester was not saponified under these conditions.

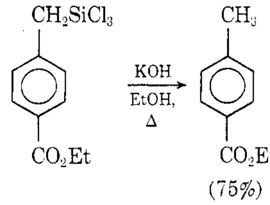
TABLE I

SELECTIVE REDUCTION OF AROMATIC HALF-ESTERS

Entry	Half-ester	Product[a]	Yield[b], %
1			64
2			42
3			41
4			37
5			26

[a] Satisfactory agreement with literature melting points and spectral correlations were obtained for all products. [b] Based on weight of starting half-ester. [c] New compound which gave satisfactory analysis and spectral correlation.





While this investigation is still in its preliminary stages, the results to date suggest that the procedures

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(1) S. Ono and T. Yamauchi, *Bull. Chem. Soc. Jap.*, **25**, 404 (1952); H. A. Staab and H. Braunling, *Justus Liebigs Ann. Chem.*, **654**, 119 (1962).

(2) V. Bazant, *et al.*, *Tetrahedron Lett.*, 3303 (1968); H. S. Broadbent, G. C. Campbell, W. J. Bartley, and J. H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959); H. C. Brown and B. C. Subba Rao, *ibid.*, **22**, 1135 (1957); H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **77**, 3164 (1955); R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

(3) R. A. Benkeser, K. M. Foley, J. M. Gaul, and G. S. Li, *J. Amer. Chem. Soc.*, **92**, 3232 (1970).

(4) Unpublished studies by Robert T. Roche of our laboratory.