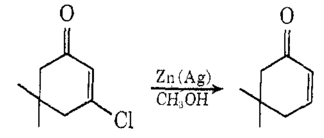
Communications

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.



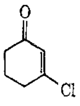
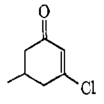
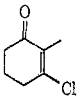
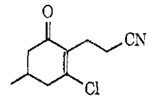
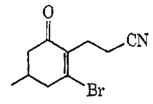
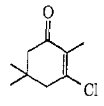
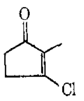
1 **2**

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.

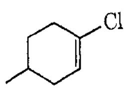
Other β-haloenones are also reduced by the procedure. When there is an alkyl substituent in the α position, the reduction is much slower but is complete in about 1 day at room temperature. One compound, 3-chloro-2,5,5-trimethylcyclohexenone (**8**), is reduced to the extent of only 58% after 37 hr. Data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

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

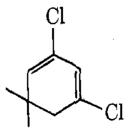
Table I
Reduction of β-Haloenones

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.



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.

Acknowledgment.—This work was supported by a grant from the National Science Foundation, GP 31321X.

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Received July 12, 1973

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.

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