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DEHALOGENATION OF α-HALOCARBONYLS USING DECABORANE AS A TRANSFER HYDROGEN AGENT IN METHANOL

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ABSTRACT

Decaborane reduces α -halocarbonyl compounds to the corresponding dehalogenated products in the presence of Pd/C in methanol at room temperature efficiently and chemoselectively.

The reductive dehalogenation reaction has been received considerable attention in organic chemistry and could be accomplished with many reducing agents.¹ The choice of a reducing agent usually depends on what other functional groups are present. There are several reagents that reduce only the halogen of α -haloketones, leaving the carbonyl group intact. Several reagents have recently been reported for the reductive dehalogenation of α -halo ketones without affecting the carbonyl group.²

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Decaborane ($B_{10}H_{14}$) is a boron cluster, which is nontoxic and stable white solid. It is a well-known reagent for the synthesis of *ortho*-carboranes.³ It is more electron-deficient than borane(BH₃), and therefore less reactive as a reducing agent. However, it was found out to have a reducing power and generated hydrogen gas slowly in protic solvent, which was identified to be synthetically useful.⁴ In connection with our works of decaborane as a hydrogen transfer agent, dehalogenation of α -haloacetophenones using decaborane in methanol was studied and α -haloacetophenones were found to be smoothly converted into the corresponding dehalogenated ketones in the presence of 10% Pd/C under nitrogen atmosphere at room temperature.

Here we wish to report the efficient reducing systems based on the combination of decaborane with palladium-on-carbon in methanol under mild condition (Scheme 1).



Scheme 1.

In a typical experimental procedure, to a solution of α -halocarbonyls in methanol were added decaborane and 10% palladium-on-carbon under a nitrogen atmosphere. The solution was stirred at room temperature until the reaction is complete (monitored by TLC). The decomposed decaborane was easily removed by filtration through a short silica gel pad. The reaction mixture was chromatographed to give acetophenones in excellent yield, which shows identical spectroscopic properties with authentic materials.

As shown in Table 1, the carbonyl groups of all substrates (entries 1–7) were remained unaffected under our reduction condition. The other bromo substituent (of bromoalkyl or bromoaryl) was leaved intact under the reaction condition (entries 4 and 8). The nitro group of the substrate (entry 5) was survived under the condition. The reactions are reasonably fast and high-yielding. The reduction of α -halosubstituted carbonyls into dehalogenated ketones using hydrogen gas and transition metal had been reported by Denton, et al.⁵ The catalytic hydrogenations were generally required base, because the reaction was inhibited by the halogen acid released.⁶ However, under our condition, the reaction was proceeded smoothly in high yield without any base.

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DEHALOGENATION OF α-HALOCARBONYLS

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Entry	Substrate	t/h	Product	Yield(%) ^a
1	CI	5		94
2	Br	3		96
3	Br	3		96
4	Br	1.5	Br	95
5	O ₂ N Br	12	O ₂ N	91
6	H ₃ C	1	H ₃ C	97
7	H ₃ CO Br	2	H ₃ CO	99
8	Br	12	No Reaction	

Table 1. Reduction of α -Halo Ketones by Using Decaborane

In conclusion, the reaction of α -halo ketones with decaborane under our mild condition chemoselectively gave the corresponding carbonyl compounds in excellent yields.

EXPERIMENTAL

All starting materials were purchased from Aldrich Chemical Company and were used without any further purification. The ¹H NMR spectra were recorded on a Varian 300. Silica gel 60 (230–400 mesh, Merk) was used for column chromatography, and silica gel $60F_{254}$ plates (0.25 mm, Merk) were used for TLC.

Typical Procedure for Reduction of *α*-Halo Ketones

To a solution of 2-bromo-4'-methylacetophenone (100 mg, 0.469 mmol) in methanol (15 ml) under a nitrogen atmosphere was added decaborane



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^aAll yields refer to isolated products fully characterized by spectral data.

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(5.7 mg, 0.047 mmol) and 10% Pd/C (10 mg). The solution was stirred at room temperature. The reaction monitored by TLC, was complete within 1 h, as indicated by the complete disappearance of starting material. The solution was removed under reduced pressure and then traces of decomposed decaborane was removed by chromatography on silica gel (ethyl acetate:hexane = 1:4) to afford 4'-methylacetophenone (62 mg, 98%) as a colorless syrup, identical in every respect with authentic sample.

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