NOTES *Bull. Chem. Soc. Jpn.*, **63**, 290—292 (1990)

Novel Reduction of Carbonyl Compounds with $Al/NH_3/Halide$ under Irradiation of Ultrasonic Wave

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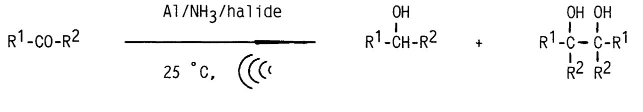
(Received May 30, 1989)

Synopsis. Various carbonyl compounds, such as benzophenones and acetophenones, were reduced by $Al/NH_3/$halide under ultrasonic wave irradiation to give the corresponding monohydric alcohols and/or pinacols in satisfactory yields. The addition of inorganic halides improved the selectivity in the formation of monohydric alcohols and pinacols.

So far, there have been numerous reports concerning the reduction of organic compounds with chemically active metals such as sodium, potassium, and calcium.[1] Recent efforts have, however, been centered on an improvement of such reduction so as to overcome various difficulties: for example, problems in the handling of such metals, reactivity control, and increasing the selectivity.[2] Much interest concerning reduction using metal has been directed to the development of a new process using other metals which are both inexpensive and readily available.[3] We have recently found that many aromatic and aliphatic disulfides are effectively and selectively reduced to the corresponding thiols by $Al/NH_3/$halide.[4] We now wish to report on a novel reduction of carbonyl compounds (**1**) to the corresponding monohydric alcohols (**2**) and/or pinacols (**3**), the latter being coupling products, using $Al/NH_3/$halide under ultrasonic wave irradiation[5] (Scheme 1).



Scheme 1.

Experimental

Melting points are uncorrected. IR spectra were obtained on a Hitachi 295 spectrophotometer and ^1H NMR spectra were obtained on a Hitachi R-22 spectrometer using tetramethylsilane as an internal standard. Mass spectra and high-resolution mass spectra were taken with a Hitachi RMU-6M mass and Hitachi M-2000 spectrometers, respectively. Elemental analyses were carried out with a Yanagimoto MT-3. Ultrasonic waves were produced using a Sono cleaner 100-a (80 W-30 KHz) by Kaijo Denki Ltd.

Materials. All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., Ltd., or Aldrich Chemical Co. The reagents were used without further purification. Wako gel C-200 was employed as silica gel for column chromatography.

General Procedure. Liquid ammonia (10 ml) (ca. 10 kg cm^{-2}) was charged from a Pyrex glass tube into an evacuated Pyrex glass tube containing **1** (0.5 mmol), aluminum (4 mg-atom), and sodium chloride (0.5 mmol) through a needle valve under cooling with ice–water. Ultrasonic waves were irradiated to the mixture at 25 °C. The time required for the completion of the reaction was determined by repeating a few runs. The mixture obtained by evaporation of ammonia was extracted with chloroform (30 ml); the solvent was then removed in vacuo. The residue was chromatographed on silica gel using $CHCl_3$ to give **2** and **3**. The obtained products were identified by comparing the spectra and physical data with those of authentic samples (Table 2). The ratio of *dl*/meso isomers in the obtained pinacols, **3h**, **3i**, and **3j**, were determined to be 6/1, 6/1, and

Table 1. Reduction of Benzophenones with $Al/NH_3/$Halide

Run[a]	Amine	Additive	Conditions	React. time	Yield of product	
				h	**2**/%	**3**/%
1	NH_3	—	Stir[b]	12	0	0
2	NH_3	NaCl	Stir	24	54	11
3	NH_3	NaCl	Stir[c]	24	0	0
4	NH_3	—	U.S.[d]	8	0	0
5	NH_3	NaCl	U.S.	2	60	12
6	NH_3	LiCl	U.S.	4	53	13
7	NH_3	KBr	U.S.	4	69	11
8	NH_3	$AlCl_3$	U.S.	4	65	12
9	NH_3	$MgCl_2$	U.S.	4	0	0
10	NH_3	$ZnCl_2$	U.S.	4	0	0
11	NH_3	I_2	U.S.	4	70	16
12	NH_3	NH_4Cl	U.S.	4	98	0
13	CH_3NH_2	I_2	U.S.	12	15	0
14	$H_2NCH_2CH_2NH_2$	I_2	U.S.	4	66	17

a) Benzophenone, 0.5 mmol; Al, 4.0 mg-atom; amine, 10 ml; additive, 0.5 mmol; react. temp, 25 °C. b) Stirred with magnetic mixer. c) Diphenylpicrylhydrazyl (DPPH) (1.0 mmol) was added. d) Under irradiation of ultrasonic wave.

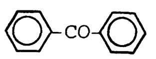
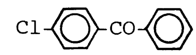
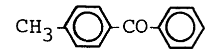
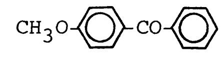
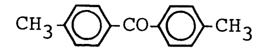
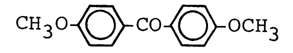
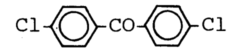
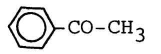
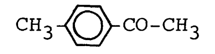
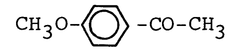
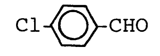
3.4/1, respectively by ^{1}H NMR, while the ratio for other pinacols could not be obtained.

Results and Discussion

As shown in Tables 1 and 2, we succeeded to produce novel reductions of various carbonyl compounds, such as benzophenones and acetophenones, with a new reduction system using metallic aluminum, inorganic halide, and liquid ammonia under ultrasonic wave irradiation. In this reduction system, the effects of ultrasonic wave irradiation and the addition of halides were noticeable (Table 1, Runs 1—5). For example, ultrasonic wave irradiation shortened the reaction period from 24 h to 2 h (Runs 2 and 5). Since it is well-known that the surface of metal aluminum is usually covered with an aluminum oxide layer, the surface should be activated by either ultrasonic wave irradiation or additives. However, no significant effect regarding the selectivity of **2**/**3** was observed through changes in the added metal ion (Runs 5—8); the addition of $MgCl_2$ and $ZnCl_2$ resulted in no reaction (Runs 9 and 10). Iodine (I_2) was also a useful additive, comparable with sodium chloride (Runs 11, 13, and 14). The use of ammonium chloride as an additive remarkably affected the selectivity, as shown in Run 12. Thus, only benzhydrol was obtained in quantitative yield. Although methylamine as a solvent amine did not give a favorable result.(Run 13), the use of ethylenediamine together with iodine afforded **2** (66%) and **3** (17%) in satisfactory yields (Run 14).

As shown in Table 2, many benzophenones were examined under similar conditions using sodium chloride as an additive to give mainly benzhydrols in high yields accompanied by minor amounts of benzopinacol, which are reductive coupling products (Runs 1, 3, 5, 8—10). Benzhydrols, however, were exclusively obtained by reduction with $Al/NH_3/NH_4Cl$ (Runs 2, 4, 6, and 7). The reduction of other carbonyl compounds, such as acetophenones (**1h**—**1j**), under the same conditions also proceeded smoothly to give interesting results (Runs 11—14). Thus, in the presence of NaCl, reductive coupling products, pinacols **3**, were predominantly obtained (Runs 11, 13, and 14). On the other hand, the addition of NH_4Cl instead of NaCl gave a mixture of **2** and **3** (Run 12). These contrasting results for selectivity are thought to be due to the stability of intermediate. It

Table 2. Reduction of Various Carbonyl Compounds

Run[a]	Substrate		Additive	Yield and mp of products	
				2/% θ_m/°C (lit)	**3**/% θ_m/°C (lit)
1		**1a**	NaCl	62 **2a** 67 (68)[7]	10 **3a** 178 (186)[15]
2			NH_4Cl[b]	98	0
3		**1b**	NaCl	40 **2b** 59 (62)[8]	37 **3b** 168 (168)[16]
4			NH_4Cl[b]	85	0
5		**1c**	NaCl	41 **2c** 46 (51)[9]	14 **3c** 169 (164)[16]
6			NH_4Cl[b]	90	0
7		**1d**	NaCl	19 **2d** 65 (68)[10]	60 **3d** 155 (158)[16]
8			NH_4Cl[b]	98	0
9		**1e**	NaCl	71 **2e** 70 (69)[11]	24 **3e** 174 (180)[17]
10		**1f**	NaCl	65 **2f** 70 (72)[12]	27 **3f** 172 (182)[17]
11		**1g**	NaCl	36 **2g** 92 (94)[13]	48 **3g** 174 (175)[17]
12		**1h**	NaCl	0	90 **3h** 121 (120)[18]
13			NH_4Cl	37 **2h** oil[14]	28
14		**1i**	NaCl	0	84 **3i** 134 (135)[18]
15		**1j**	NaCl	0	71 **3j** 118 (122)[19]
16		**1k**	NaCl	0	0

a) Substrate, 0.5 mmol; Al, 4.0 mg-atom; additive, 0.5 mmol; NH_3, 10 ml; react. temp, 25 °C; irradiation time of ultrasonic wave, 4 h. b) NH_4Cl, 2.0 mmol.

should be noted that the carbonyl group of aldehyde (**1k**) was not reduced under these conditions (Run 15). This result suggests a synthetically useful chemoselectivity[6] of the present reduction system.

Since the addition of diphenylpicrylhydrazyl (DPPH) inhibited the reaction (Table 1, Run 3) and pinacols were formed as a product,[3,20] the reaction seems to proceed through an intermediate anion radical.[21] Further applications of the present reduction system are now in progress in our laboratory.

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