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Ultrasounds in Synthetic Reactions. II. Convenient Methylenation of Carbonyl Compounds with Zinc–Diiodomethane[1)]

Junzo Yamashita,* Yoshio Inoue, Takashi Kondo, and Harukichi Hashimoto
Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Aramaki-Aoba, Sendai 980

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Synopsis. Ultrasonic irradiation facilitates the methylenation of carbonyl compounds with zinc-diiodomethane reagent in tetrahydrofuran at room temperature.

The cyclopropanation of olefins with zinc–diiodomethane complex was first reported by Simmons and Smith,[2)] and the methylenation of carbonyl compounds was also observed with this complex in the presence of an excess of zinc by Miyano, Hida, and Hashimoto of this laboratory.[3)] The preparation of zinc–diiodomethane complex usually needs activated zinc–copper couple, which requires rather tedious procedure. Other methylenation procedures for aldehydes which use reagents involving Ti have been developed and given good yields, but they use highly air sensitive trimethylaluminium.[4,5)] Dibromomethane–zinc–tetrachlorotitanium is a very good methylenation reagent for ketones but not for aldehydes.[5,6)]

Ultrasounds have been successfully applied to accelerate a variety of organic reactions,[7)] particularly those involving metals. We now wish to report that ultrasonic irradiation is also very useful for the methylenation reactions with zinc–iodomethane reagents: no chemical activation of commercial zinc powder is required, the reaction proceeds smoothly and rapidly at room temperature, and the yields are reproducible.

Experimental

Materials. Commercially available aldehydes and ketones were dried over Drierite and distilled under nitrogen atmosphere and stored for use. Tetrahydrofuran was distilled over sodium prior to use. Commercially available zinc powder was used as obtained. Commercially available diiodomethane was purified according to the known procedure.[3)]

Analysis. Reaction products were identified by the retention volume on GLC and mass spectra (JEOL D300 mass spectrometer) compared with the authentic samples. The yields of products were determined by GLC. GLC was performed on a Hitachi 163 gas chromatograph (20 m glass capillary column coated with OV-17) or a Shimadzu GC 3AH gas chromatograph (Silicone DC-550 20 wt% on Diasolid M, squalane 20 wt% on Diasolid M, Silicone GE SE-52 20 wt% on Chromosorb W AW, or FFAP 10 wt% on Chromosorb W AW DMCS).

General Procedures for Methylenation Reactions. Methylenation of Benzaldehyde: To a 50 ml, 3-necked flask, which contained 1.57 g (24 mmol) of zinc powder previously dried at 100 °C for 30 min under vacuum, were added 0.53 g (5 mmol) of benzaldehyde, 2.68 g (10 mmol) of diiodomethane, and 0.335 g (2.5 mmol) of durene (internal standard for GLC analysis) in 20 ml of THF, and irradiated for 20 min under nitrogen atmosphere in the water bath of an ultrasound laboratory cleaner(53 W, 41 kHz), which was maintained at room temperature. The yield of styrene was determined by GLC (FFAP 20 wt% on Chromosorb W AW DMCS at 120 °C).

Results and Discussion

The reactions of aldehydes or ketones with Zn–CH_2I_2 were carried out in THF at room temperature irradiated by ultrasound.

$$R_2C{=}O + CH_2I_2 \xrightarrow[\text{THF, room temp}]{\text{Zn, ultrasound}} R_2C{=}CH_2$$

The results were shown in Table 1. None or very small amount of olefins was detected when the similar reaction was carried out with ordinary magnetic stirrer instead of ultrasonic irradiation, though the longer reaction time afforded the corresponding olefin without the irradiation. The yield may be improved, for the reaction conditions are not optimum. Dibromomethane instead of diiodomethane can be used, but the longer reaction time is necessary (runs 7 and 8). Only low yields are obtained for ketones as indicated by runs 9 and 10, and this reaction is not recommended for ketones. The yields are comparable to those of previously reported procedures (40 °C, 6 h in THF using activated zinc–copper couple), but the precise comparison is impossible, for the latter used 2 mol of carbonyl compounds to 1 mol of diiodomethane and the yields of olefins were based on diiodomethane.

In conclusion, the present method is a very convenient procedure for methylenation of aldehydes.

TABLE 1. ULTRASOUND-ACCELERATED METHYLENATION OF CARBONYL COMPOUNDS WITH ZINC-DIIODOMETHANE IN THF AT ROOM TEMPERATURE[a)]

Run	Carbonyl compounds	Reaction time/min	Products	Yield %
1	Benzaldehyde	20	Styrene	70[b)]
2	*p*-Methylbenzaldehyde	120	*p*-Methylstyrene	73
3	*p*-Methoxybenzaldehyde	90	*p*-Methoxystyrene	50
4	*p*-Chlorobenzaldehyde	15	*p*-Chlorostyrene	69[c)]
5	1-Naphthaldehyde	120	1-Naphthylethene	54
6	Cinnamaldehyde	60	Phenylbutadiene	37
7	Heptanal	20	1-Octene	71
8	Heptanal[d)]	300	1-Octene	58
9	Cyclohexanone	60	Methylenecyclohexane	18
10	Acetophenone	300	α-Methylstyrene	8

a) Reaction conditions; Zn 24 mmol, diiodomethane 10 mmol, substrate 5 mmol, THF 20 ml, room temperature. b) The yield increased to 82% when the reaction time was 60 min. c) Isolated yield was 57%(20 mmol scale). d) Dibromomethane was used instead of diiodomethane.

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