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A New Synthesis of Aldehydes and Aldehydes-*d* from Grignard Reagents

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Synopsis. Aldehydes were prepared from Grignard reagents in high yields using pentacarbonyliron as the carbonylating agent. This reaction was also found to be applicable to the synthesis of aldehydes-*d*.

Although there have been some reports on the synthesis of aldehydes by the use of Grignard reagents, these processes have been restricted to the hydrolysis of an intermediate derived from the reagent, and it is impossible to synthesize an aldehyde-*d*.[1)] In this note, we wish to report an alternative and useful method for synthesizing aldehydes and aldehydes-*d* from Grignard reagents using pentacarbonyliron.

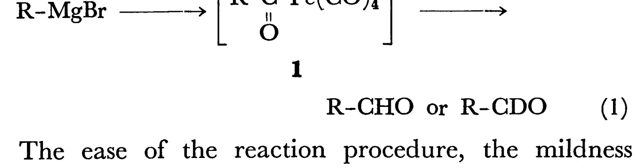
A representative reaction procedure was as follows. To a tetrahydrofuran solution of hexylmagnesium bromide derived from hexyl bromide and magnesium, an equimolar amount of pentacarbonyliron was injected by means of a syringe, after which the mixture was stirred for 2 h at room temperature under an argon atmosphere. Acetic acid was then added to the solution, and stirring was continued for a further 5 min. The mixture was washed with 1 mol dm^{-3} hydrochloric acid and then 0.1 mol dm^{-3} aqueous sodium hydroxide saturated with sodium chloride; it was subsequently extracted with diethyl ether, dried, and filtered, and the ether was removed with a rotary evaporator. The residue was purified by distillation under reduced pressure. The product was identified as heptanal by means of IR, NMR, MS, and GLC. The yield was 91% on the basis of the Grignard reagent (GLC). When CH_3COOD was used instead of CH_3COOH, heptanal-1-*d* was obtained in the same yield. The results are listed in Table 1.

TABLE 1. SYNTHESIS OF ALDEHYDES FROM GRIGNARD REAGENTS

Run	RMgBr R	AcOH or AcOD	Product	Yield/%[a)]
1	$CH_3(CH_2)_5$-	AcOH	$CH_3(CH_2)_5CHO$	91 (44)
2		AcOD	$CH_3(CH_2)_5CDO$	(43)
3	$CH_3(CH_2)_4$-	AcOH	$CH_3(CH_2)_4CHO$	99
4	C_6H_5-	AcOH	C_6H_5CHO	94
5		AcOD	C_6H_5CDO	(33)
6	C_6H_{11}-[b)]	AcOH	$C_6H_{11}CHO$	40
7		AcOD	$C_6H_{11}CDO$	(14)

a) Determined by GLC. Yields in parentheses are those of substances isolated by fractional distillation.
b) Cyclohexyl.

In these reactions, the acyltetracarbonylferrates **1** are assumed to be intermediates,[2)] which are hydrogenated or deuterated to give aldehydes or aldehydes-*d* (Eq. 1).



$$\text{R-MgBr} \xrightarrow{\text{Fe(CO)}_5} \left[\begin{array}{c}\text{R-C-Fe(CO)}_4\\ \overset{\Vert}{\text{O}}\end{array}\right]^- \xrightarrow{\text{H}^+ \text{ or D}^+} \text{R-CHO or R-CDO} \quad (1)$$

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The ease of the reaction procedure, the mildness of the reaction conditions, and the high yields of the products may make it possible to utilize this reaction for the syntheses of aldehydes and aldehydes-*d* from Grignard reagents.

Experimental

The infrared spectra were recorded on a Hitachi 260-10 Infrared Spectrophotometer, the NMR spectra were measured on a Hitachi R-600 FT-NMR Spectrometer, and the mass spectra were measured on a Hitachi RM-50 GC-MS. Gas chromatography was carried out on a Yanagimoto G-8 Model equipped with a stainless column packed with Silicone gum SE-30 on chromosorb. All the experiments were carried out under an atmosphere of argon. The tetrahydrofuran was dried by distillation from lithium aluminum hydride. The pentyl bromide, hexyl bromide, bromobenzene, and cyclohexyl bromide were all commercial products and were distilled before use. The pentacarbonyliron was purchased from a commercial source and was used without further purification. The acetic acid, acetic acid-*d*, and magnesium for the Grignard reaction were also commercial products of the highest available purity.

Representative Synthesis of Heptanal-d. Into the tetrahydrofuran solution (30 ml) of hexylmagnesium bromide derived from hexyl bromide (22 mmol) and magnesium (44 mg-atom), pentacarbonyliron (3 ml, 22 mmol) was injected by means of a syringe, after which the mixture was stirred for 2 h at room temperature under argon. Acetic acid-*d* (26 mmol) was then added to the solution, and stirring was continued for further 5 min. The mixture was washed with 1 mol dm^{-3} hydrochloric acid and then 0.1 mol dm^{-3} aqueous sodium hydroxide saturated with sodium chloride, and subsequently extracted with diethyl ether. The organic layer was dried over sodium sulfate, and the solvent was removed with a rotary evaporator. The residue thus obtained was purified by distillation *in vacuo*, giving heptanal-1-*d* (1.09 g): bp 46—49 °C/17 Torr (1 Torr≈133.322 Pa); NMR ($CDCl_3$) δ 0.93 (3H, t, $-CH_3$), 1.13—2.07 (8H, m, $-(CH_2)_4-$), 2.48 (2H, t, $-CH_2CO-$); IR (neat) 2070, 1710 cm^{-1}; MS *m/e* (%) 115 (M^+, 4), 97 (27), 85 (27), 82 (23), 70 (100).

*Benz(aldehyde-*d*).* Bp 70 °C/17 Torr; NMR ($CDCl_3$) δ 7.42—8.16 (5H, C_6H_5-); IR (neat) 2110, 1695 cm^{-1}; MS *m/e* (%) 107 (M^+, 100), 105 (96), 77 (89).

*Cyclohexane(carboaldehyde-*d*).* Bp 45 °C/10 Torr; NMR ($CDCl_3$) δ 0.82—2.83 (11H, m, $C_6H_{11}-$); IR (neat) 2050, 1710 cm^{-1}; MS *m/e* (%) 113 (M^+, 8), 95 (21), 83 (56), 71 (21), 68 (36), 55 (100).

The hexanal, heptanal, benzaldehyde, and cyclohexane-carboaldehyde were identified by a comparison of their IR, NMR, and mass spectra with those of authentic samples.

References

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