Journal of Organometallic Chemistry, 172 (1979) C20—C22
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Preliminary communication

OXIDATION OF ORGANOBORANES CONTAINING PRIMARY ALKYL GROUPS WITH PYRIDINIUM CHLOROCHROMATE. A DIRECT SYNTHESIS OF ALDEHYDES FROM TERMINAL ALKENES

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(Received February 27th, 1979)

Summary

Organoboranes derived from terminal olefins are oxidized by pyridinium chlorochromate to aldehydes in good yields.

A recent communication on the conversion of organoboranes derived from cyclic olefins to the corresponding ketones using pyridinium chlorochromate [1] prompted us to report our own research on the convenient preparation of aldehydes by oxidizing with this reagent organoboranes from terminal olefins (eq. 1).

$$RCH{=}CH_2 \xrightarrow{BH_3 \cdot SMe_2} (RCH_2CH_2)_3B \xrightarrow{Py \cdot HCl \cdot CrO_3} RCH_2CHO \qquad (1)$$

The convenient conversion of a terminal olefin into the corresponding aldehyde should be a highly useful synthetic transformation. One possible method for such a transformation is the hydroboration of a terminal olefin, oxidation of the resulting organoborane with alkaline hydrogen peroxide to the corresponding primary alcohol [2], followed by oxidation with pyridinium chlorochromate to the corresponding aldehyde [3] (eq. 2, 3).

$$RCH{=}CH_2 \xrightarrow{BH_3 \cdot SMe_2} (RCH_2CH_2)_3B \xrightarrow{NaOH/H_2O_2} RCH_2CH_2OH \qquad (2)$$

$$RCH_2CH_2OH \xrightarrow{Py \cdot HCl \cdot CrO_3} RCH_2CHO \qquad (3)$$

There would be obvious advantages to a direct oxidation of such organoboranes to aldehydes. The direct oxidation of organoboranes with a variety of oxidizing agents has been extensively studied in this laboratory [2]. Organoboranes containing secondary alkyl groups can be directly converted to ketones utilizing aqueous chromic acid [4]. However, application of this procedure for the synthesis of aldehydes did not meet with the desired success [5]. During an investigation of the selective transformation of trialkylboranes into borinate, boronate and borate esters, we observed that borate esters are rapidly oxidized by pyridinium chlorochromate to aldehydes and ketones [6]. Accordingly, we undertook to explore this direct synthesis of aldehydes from terminal olefins via the corresponding organoboranes.

The terminal olefins were transformed into the corresponding organoboranes by treatment with borane-methyl sulfide (BMS) in methylene chloride [7] and the resulting organoboranes without isolation were oxidized with excess pyridinium chlorochromate in the same solvent to obtain the corresponding aldehydes in good yields (Table 1). Since the regioselectivity in the hydroboration of straight chain terminal alkenes with BMS is 94/6, the organoboranes contain approximately 6% of the secondary alkyl groups. These give rise to methyl ketones on oxidation (Table 1).

TABLE 1

OXIDATION OF ORGANOBORANES WITH PYRIDINIUM CHLOROCHROMATE

Alkene	Product^a	Product^b distribution	Yield^c
1-Hexene	Hexanal	95	72
	2-Hexanone	5	
1-Octene	Octanal	94	70
	2-Octanone	6	
1-Decene	Decanal	95	74
	2-Decanone	5	
1-Dodecene	Dodecanal	94	78
	2-Dodecanone	6	
3,3-Dimethyl-1-butene	3,3-Dimethylbutanal	98	64
	3,3-Dimethyl-2-butanone	2	
Methylenecyclohexane	Cyclohexylcarboxaldehyde	99	71
	1-Methylcyclohexanol	1	

^{a}The aldehydes were identified by comparison of ^{1}H NMR spectra, b.p., n_D^{20} and GLC retention times with those of authentic samples ^{b}Determined by GLC analysis on a 12 ft × 1/8 in column packed with 5% QF-1 on Varaport-30 using a Varian 1400 Gas Chromatograph. ^{c}Overall isolated yields based on the starting olefins; all reactions were carried out on 60 mmol of olefins.

The oxidation of organoboranes with pyridinium chlorochromate proceeds via the formation of borate esters as observed by the ^{11}B NMR spectrum of aliquots from an incomplete reaction. This has been further substantiated by observation of the facile oxidation by the reagent of trialkylborates to aldehydes [6].

The high yields, anhydrous reaction conditions, and easy workup procedure make this a highly convenient, one-pot method for the conversion of terminal olefins into aldehydes. The following experimental procedures are representative.

Procedure A

In an oven-dried, nitrogen-flushed, 100-ml round bottom flask fitted with a septum inlet, magnetic stirring bar and a connecting tube leading to a mercury bubbler, were placed 2.04 ml of BMS (20 mmol, neat reagent was 9.8 *M* in BH_3) and 20 ml of methylene chloride. To this solution was added 9.4 ml of 1-octene (60 mmol) dropwise with vigorous stirring. The reaction mixture was stirred for 1 h at room temperature, and then the solvent and methyl sulfide were removed using a water aspirator. The resulting trialkylborane was added dropwise to a well-stirred suspension of 38.3 g of pyridinium chlorochromate (180 mmol) in 150 ml of methylene chloride, taken in a 500-ml round bottom flask fitted with a septum inlet, a magnetic stirring bar and a reflux condenser with a connecting tube leading to a mercury bubbler. After the initial vigorous reaction subsided, the mixture was refluxed for 4 h with stirring. It was then cooled to room temperature, diluted with 200 ml of dry ethyl ether and filtered through 100 g of 100—200 mesh Florisil contained in a 350-ml sintered glass funnel. The residue in the flask was triturated with ether (3 × 50 ml) and the solvents removed on a rotary evaporator. The resulting liquid, on distillation under reduced pressure, gave 5.4 g (70% yield) of octanal (containing ~ 5% of 2-octanone), b.p. 65—66°C/15 mmHg, n_D^{20} 1.4185 [lit.[8] b.p. 171°C/760 mmHg, n_D^{20} 1.4183].

Procedure B

The oxidation reaction was carried out in the same manner as described in Procedure A. To the reaction mixture, after refluxing for 4 h, was added 50 ml of water. Steam distillation provided a condensate consisting of methylene chloride, aldehyde, and water. The organic layer was separated, dried over anhydrous magnesium sulfate, and solvent removed. Distillation under reduced pressure afforded 5.3 g (69% yield) of octanal (containing ~ 5% of 2-octanone), b.p. 65—66°C/15 mmHg, n_D^{20} 1.4185.

Acknowledgement

We acknowledge the financial support from Exxon Research and Engineering Co., and the National Institutes of Health (Grant GM 10937-16).

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