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AN INEXPENSIVE MODIFICATION OF THE SIMMONS–SMITH REACTION: THE FORMATION OF BROMOMETHYLZINC BROMIDE AS STUDIED BY NMR SPECTROSCOPY

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Summary

Bromomethylzinc bromide, prepared from zinc metal and methylene bromide in tetrahydrofuran, gives moderate to good yields of cyclopropanation product when treated with olefins, thus providing an inexpensive alternative to the Simmons–Smith procedure. An NMR study of the reaction between metallic zinc and methylene bromide has been carried out: in addition to bromomethylzinc bromide and dimethylzinc, two further species were observed and tentatively identified as bis(bromomethyl)zinc and a di- or tri-zinc compound.

Introduction

The Simmons–Smith method for the generation of methylene has for many years been an important tool in synthetic organic chemistry [1]. Various modifications of the original procedure have been suggested, and in recent years it has been adapted for use in carbonyl olefination [2]. The "classical" reaction involves the use of a zinc–copper couple, prepared, for example, as described by Le Goff [3], and methylene iodide. Boudjouk [4] has very recently shown that the use of ultrasonic radiation permits the replacement of the couple by metallic zinc.

Results and discussion

We now report that, in contrast to the earlier observations of Le Goff [3], it is also possible to replace methylene iodide by the much less expensive methylene bromide when tetrahydrofuran is used as solvent. The yield of cyclopropanation product is however decreased somewhat, as shown by the following comparative study.

A series of five olefins was treated with three carbene sources: (A) methylene iodide and zinc-copper couple (prepared by the method of Le Goff [3]), (B)

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TABLE 1

RESULTS OF OLEFIN TREATMENT WITH CARBENE SOURCES

Olefin	Yield of cyclopropanation product [a]		
	Method A	Method B	Method C
Cyclohexene	64.2 (61 [b])	59.9 (92)	52.8
Allylbenzene	34.4 (49 [c])	39.6	35.3
Styrene	46.2 (32 [c])	46.1 (69)	43.1
α-Methylstyrene	56.7	60.7	35.2
2,3-Dimethyl-2-butene	61.0 (42 [c])	54.2	41.1

[a] For A, B, C see text. [b] Methylene bromide/Zn–Cu couple [4] [c] Original data of Simmons and Smith [6].

methylene iodide and zinc in the presence of copper(I) chloride (the method described by Rawson and Harrison [5]) and (C) methylene bromide and zinc in tetrahydrofuran.

In order to obtain comparable data, reaction times and conditions and the conditions of work-up were kept similar. The results are given in Table 1.

In our hands (we made no effort to maximise our yields), methods A and B gave comparable yields, while those of our method C are between 3 and 20% lower. Values in parentheses are taken from the literature: it should be noted that the yields quoted by Rawson and Harrison are GLC yields while ours refer to products isolated by distillation from a spinning band column.

Since the species involved in the Simmons–Smith cyclopropanation have not previously been identified with certainty, we have carried out an NMR study of the reaction between zinc or zinc–copper couple and methylene bromide in tetrahydrofuran and octadeuterotetrahydrofuran. With a molar ratio Zn/CH_2Br_2 of 1/1, formation of dimethyl zinc (^1H: δ -0.8, ^{13}C: δ -14.8 ppm) was observed, though not on changing the ratio to 1/4. The reaction was carried out in both cases at 35–40 °C, and ethylene formation was observed. The main product species absorbed at 2.1–2.3 (^1H) and 14.4 (^{13}C) ppm, and is presumably $BrCH_2ZnBr$ or a THF complex thereof: the formation of methyl bromide was also indicated.

Two further species were however observed: at a molar ratio of 1/1 the signal assigned to $BrCH_2ZnBr$ disappeared on standing, to be replaced by one at 3.1 ppm (^1H). By analogy with the corresponding organomercury species, this is assigned to $Zn(CH_2Br)_2$:

$$2\ BrCH_2ZnBr \rightleftharpoons Zn(CH_2Br)_2 + ZnBr_2$$

$BrCH_2HgBr$ absorbs at 2.2 ppm, $Hg(CH_2Br)_2$ at 3.18 ppm [7].

At a ratio Zn/CH_2Br_2 of 3/1 a broad signal was observed at -1.2 (^1H) and -22.7 (^{13}C) ppm. This could well be due to the presence of the di- and/or tri-zinc species proposed by Turnbull [8]:

$$CH_2(ZnBr)_2 \rightleftharpoons Zn(CH_2ZnBr)_2$$

In this connection it is interesting to note that Bickelhaupt [9] has recently reported the formation of methylenedimagnesium dibromide, for which he quotes a broad proton NMR signal ($\nu_{1/2}$ 20 Hz) at -2.75 ppm.

Experimental

All manipulations involving organozinc species were carried out under argon. NMR spectra were recorded using Varian EM-360 (^{1}H) and Bruker AM-300 (^{13}C) spectrometers.

Cyclopropanation using bromomethylzinc bromide

Zinc (13.0 g, 0.2 mol), methylene bromide (69.4 g, 0.4 mol) and olefin (0.1 mol), were stirred at 40 °C for 48 h in tetrahydrofuran (120 ml). After hydrolytic work-up and removal of the solvent by distillation, the residue was fractionally distilled using a spinning band column. The fractions were identified by NMR spectroscopy and gas chromatography (4 m Emulphor and OV-17 columns).

Cyclopropanation using methylene iodide and zinc–copper couple

Zinc–copper couple (6.6 g, 0.1 mol), prepared as described by Le Goff [3], methylene iodide (24.4 g, 0.09 mol) and olefin (0.05 mol) were stirred for 48 h in ether (70 ml) under reflux. The work-up and isolation procedure were as described above.

Cyclopropanation using methylene iodide and zinc/copper(I) chloride

Zinc (9.8 g, 0.15 mol) and copper(I) chloride (1.5 g, 0.015 mol) were heated for 30 min in refluxing ether (70 ml). Olefin (0.05 mol) and methylene iodide (24.4 g, 0.09 mol) were added and the reaction mixture heated for 48 h under reflux. Work-up and isolation were carried out as described above.

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