Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

SHORT COMMUNICATION

The benzylcadmium reagent

Although organocadmium reagents have been widely used in synthesis[1], their structures in solution remain unknown; and they have only rarely been isolated and purified. Hence, the criteria for their existence in solution are generally based on indirect evidence: (*1*) the failure of the "Gilman test[2]" for the presence of Grignard reagent, from which organocadmium compounds are always prepared; and (*2*) the reaction of the reagent with acid chlorides and acid anhydrides or various activated carbonyl compounds to form, respectively, ketones or α-hydroxy carbonyl products[1]. Recently, Kollonitsch[3] has shown that *in situ* organocadmium reagents react additively with aldehydes and ketones; this property is also a potential criterion for the existence of an organocadmium reagent, although it alone would not serve to distinguish between organocadmium and organomagnesium compounds.

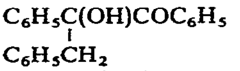
Benzyl-type cadmium reagents have apparently rarely been investigated with regard to structure or reactivity[1]. In fact, Elderfield and Meyer[4] reported that both the benzyl reagent and the *p*-methoxybenzyl reagent decomposed with formation of metallic cadmium, the former at reflux temperature, the latter even at 0°.

The benzylcadmium reagent was of great interest not only because of the dearth of information about its properties but also because of the possibility of rearrangement products, such as those formed from benzylmagnesium chloride[5]. We, therefore, undertook the preparation of the benzylcadmium reagent by conventional means, with a view to testing for its existence and examining its behavior. Its synthesis was carried out by way of benzylmagnesium chloride in ether; the Gilman test was positive before the addition of cadmium chloride and negative after its addition and a one-hour reflux period. There was no visible indication of decomposition or formation of metallic cadmium during the refluxing.

The *in situ* reagent so formed was treated with benzil, which is known to undergo monoaddition with organocadmium reagents. The product mixture was analyzed by NMR spectroscopy, with toluene as an internal standard. The results are shown in Table 1. The expected addition product, benzylbenzoin, is formed in major amount.

TABLE 1

NMR ANALYSIS OF PRODUCT MIXTURE FROM BENZYLCADMIUM REAGENT AND BENZIL

Product	*% in air*	*% in nitrogen*
 $C_6H_5\underset{\underset{C_6H_5CH_2}{\vert}}{C}(OH)COC_6H_5$	52.5	70.3
$C_6H_5CH(OH)COC_6H_5$	9.0	11.7
$(C_6H_5CH_2)_2$	9.0	11.7

Benzoin, a reduction product, was unanticipated and warranted further examination. With the possibility that oxygen was involved in forming cadmium benzyloxide, which in turn was serving as a reducing agent[6], the experiment was repeated in a nitrogen atmosphere. Clearly, the reduction product is formed equally effectively in the absence of oxygen. It is striking to note the parallel formation of coupling product, bibenzyl, and reduction product, benzoin. The only obvious effect of the exclusion of oxygen is an increase in the amount of addition product. In both experiments benzil was recovered unchanged, but in greater amount in the first case.

Our conclusion from this investigation is that the benzylcadmium reagent is formed by conventional means, if one accepts the usual criteria for the existence of organocadmium compounds. It is reasonably stable and reacts normally with benzil. If rearrangement products (*o*-, *m*-, or *p*-tolyl derivatives) are present in the reaction mixture, their concentrations must be minute, for they were undetected by NMR spectroscopy.

Experimental

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Melting point are corrected. Infrared spectra were determined as halocarbon and Nujol mulls with a Perkin–Elmer 337 grating spectrophotometer. The NMR spectra, determined with a Varian A-60 spectrometer, are reported in ppm downfield from tetramethylsilane as internal standard. Coupling constants (J) are expressed in cps.

Preparation of the benzylcadmium reagent. The Grignard reagent was prepared in ether from 9.7 g (0.4 mole) of magnesium and 50 g (0.4 mole) of benzyl chloride. After the addition was complete, the mixture was heated at reflux for 15 min; the Gilman test was positive. Then, 73 g (0.4 mole) of anhydrous cadmium chloride was added slowly, with stirring. The mixture was heated at reflux for one hour, at which time the Gilman test was negative.

Reaction of the benzylcadmium reagent with benzil. To the organocadmium reagent was added an ethereal solution of 84 g (0.4 mole) of benzil, while excess ether was removed by distillation. After addition was complete, the mixture was heated at reflux for 4–5 h and then was decomposed with ice-cold, 20% sulfuric acid. A light yellow solid (A), which precipitated out of the two-phase hydrolysis mixture, was removed and dried in air. By separation of the organic layer and removal of the solvent after drying, a second, dark yellow solid (B) was obtained. (A) and (B) were handled separately in the subsequent product analyses. The crude solid was taken up in chlorobenzene, to which a known amount of toluene was added. The following peaks were integrated relative to that of toluene at 2.2; a singlet at 5.85 (benzoin); an AB multiplet centered at 3.63 ($\delta_B - \delta_A = 16$–17 cps; $J_{AB} = 14$–15 cps; benzylbenzoin); a singlet at 2.85 (bibenzyl). By correction for the number of protons associated with each peak and correlation with the known quantity of toluene in the sample, the absolute amounts of the three components could be calculated. The values in the Table are the combined amounts of components in (A) and (B).

Column chromatographic separations on "Baker Analyzed" silica gel of the products from samples of (A) and (B) were carried out, the eluent being petroleum ether gradually enriched with chloroform. Recovery of 77% (by weight) of the samples in the form of pure components was accomplished. The components, in order of elution, are as follows: bibenzyl (1%); benzil (37%); benzylbenzoin (38%), m.p.[7] 119–121°, (Found: C, 83.57; H, 6.13. $C_{21}H_{18}O_2$ calcd.: C, 83.42; H, 6.00%.); benzoin (1%), m.p. 133–134.5°.

The reaction in a nitrogen atmosphere and subsequent NMR analysis were conducted identically. Chromatographic separation was omitted in this latter case.

Acknowledgment

We are grateful to the National Science Foundation for a grant (G-22718) used to purchase the NMR spectrometer.

Department of Chemistry,
University of New Hampshire,
Durham, New Hampshire 03824 (U.S.A.)

PAUL R. JONES
P. DWIGHT SHERMAN, JR.*
KAREN SCHWARZENBERG*

1 J. CASON, *Chem. Rev.* 40 (1947) 15; D. A. SHIRLEY, *Org. Reactions*, 8 (1954) 28.
2 H. GILMAN AND F. SCHULZE, *J. Am. Chem. Soc.*, 47 (1925) 2002.
3 J. KOLLONITSCH, *J. Chem. Soc.*, *A*, (1966) 453.
4 R. C. ELDERFIELD AND V. B. MEYER, *J. Am. Chem. Soc.*, 76 (1954) 1887.
5 R. A. BENKESER AND T. E. JOHNSTON, *J. Am. Chem. Soc.*, 88 (1966) 2220.
6 M. S. KHARASCH AND O. REINMUTH, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, p. 160.
7 G. SCHEUING AND A. HENSLE, *Ann. Chem.*, 440 (1924) 72.

Received June 12th, 1967

---

* National Science Foundation Undergraduate Research Participant.