BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 1177 (1976)

Olefination of Aldehydes by Methylenedicalcium Diiodide

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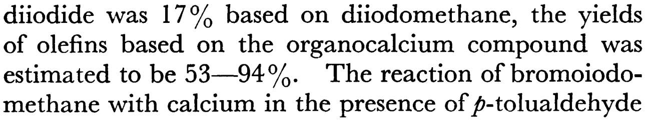
(Received December 15, 1975)

Synopsis. Reaction of diiodomethane with calcium in tetrahydrofuran gave methylenedicalcium diiodide in 17% yield. Reaction of the calcium compound with aldehydes was shown to give the corresponding olefins in estimated yields of 53—94%.

Only a few works are available in the literature on the reaction of organocalcium compounds. We have demonstrated that methylcalcium iodide is a useful organometallic reagent in several organic reactions.[1,2] This paper describes the reaction of methylenedicalcium diiodide with carbonyl compounds. *gem*-Dimetallic compounds of lithium,[3] magnesium,[4] and zinc[5] are known to olefinate carbonyl compounds, but no information is available in the literature on the reaction of methylenedicalcium dihalides with carbonyl compounds.

Reaction of diiodomethane with calcium in tetrahydrofuran at −30 °C gave methylenedicalcium diiodide in 17% yield. Gas chromatographic analysis showed that diiodomethane was not remained in the reaction mixture. The yield was determined based on the amount of methane evolved by the addition of methanol. The geminal dimetallic nature of the organocalcium compound was confirmed by carboxylation, which gave malonic acid in 12% yield based on diiodomethane (71% based on methylenedicalcium diiodide).



Reaction of diiodomethane with calcium in the presence of aldehydes at room temperature in tetrahydrofuran was found to give the corresponding olefins in 9–16% yields based on diiodomethane as is shown in Table 1. Since the yield of methylenedicalcium diiodide was 17% based on diiodomethane, the yields of olefins based on the organocalcium compound was estimated to be 53—94%. The reaction of bromoiodomethane with calcium in the presence of *p*-tolualdehyde gave *p*-methylstyrene though in a lower yield, but dibromomethane and dichloromethane did not react with calcium under the conditions. The reaction of diiodomethane with calcium in the presence of ketones did not give the corresponding olefins.

Experimental

Diiodomethane and aldehydes were purified by distillation. Bromoiodomethane was prepared by a conventional method.[6] Tetrahydrofuran and nitrogen were purified, and metallic calcium was rasped as described in our previous papers.[7,8] Methylenedicalcium diiodide was prepared from 0.26 g (6.50 mmol) of calcium and 0.74 g (2.76 mmol) of diiodomethane in 5.0 ml of tetrahydrofuran at −30 °C according to our previous procedure[8] with minor modifications. Carboxylation of methylenedicalcium diiodide was carried out at −70 °C according to our previous procedure[2] with minor modifications. Olefination of aldehydes was carried out by the addition of dihalomethane to a mixture of metallic calcium and aldehyde in tetrahydrofuran at room temperature under a nitrogen atmosphere. The reaction mixture was allowed to remain at room temperature for an additional 1 h, and worked up in the usual manner. Yields were determined by gas chromatographic analyses of the reaction mixture.

References

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TABLE 1. OLEFINATION OF ALDEHYDES BY METHYLENEDICALCIUM DIHALIDE[a)]

Calcium (mmol)	Dihalomethane	(mmol)	Aldehyde	(mmol)	Olefin (Yield, %)[b)]
3.24	CH_2I_2	0.74	C_6H_5CHO	0.57	11
8.16	CH_2I_2	4.08	*p*-$CH_3C_6H_4CHO$	4.08	16
7.41	CH_2BrI	4.63	*p*-$CH_3C_6H_4CHO$	3.47	5
6.09	CH_2I_2	3.33	*trans*-$CH_3CH=CHCHO$	3.23	9
9.88	CH_2I_2	2.37	$CH_3(CH_2)_3CHO$	2.06	10

a) Reactions were carried out at room temperature in 5.0 ml of tetrahydrofuran under a nitrogen atmosphere.
b) Based on dihalomethane.

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