

THE REACTION OF CYANOGEN WITH METHYLMAGNESIUM IODIDE AND METHYLMAGNESIUM BROMIDE*

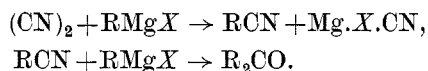
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Blaise (1901) found that 2 moles of ethylmagnesium bromide reacts with 1 mole of cyanogen to form diethyl ketone rather than the expected dipropionyl. This work was later confirmed and expanded by Grignard and co-workers (Grignard 1911 ; Grignard and Bellet 1912), who first reported the isolation of nitriles from the interaction of organomagnesium compounds and cyanogen (in the ratio of 1 mole of each reagent), and later, Grignard, Bellet, and Courtot

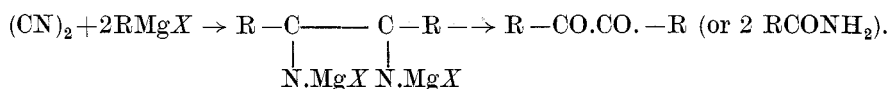
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(1919) found that either nitriles or ketones may readily be produced. Presumably the reaction proceeds as follows :



In order to prepare ^{14}C (carbonyl) labelled diacetyl, the interaction of labelled cyanogen with methylmagnesium halides was considered, since cyanogen may readily be prepared in good yield from K^{14}CN (Lynn, unpublished data). An investigation of the reaction at low temperatures was undertaken, as previous workers used temperatures above 0°C . Among the products isolated were diacetyl and acetamide. These results indicate that the reaction probably proceeds as follows :



Because of the lack of readily available refrigerants in the range -80 to -110°C , and since alternative procedures offered higher yields of diacetyl, experiments were not continued.

Experimental

The experiments were performed with non-radioactive material in a standard vacuum manifold (Calvin *et al.* 1949) working at pressures of the order 10^{-3} to 10^{-4} mm mercury. The cyanogen was generated by heating silver cyanide (Cook and Robinson 1935) on the manifold, the gas obtained being distilled through phosphorus pentoxide twice, then stored until used. The organometallic compounds were prepared as usual, the flasks attached to the vacuum system frozen in liquid oxygen, and evacuated. Methyl bromide and methyl iodide were both investigated in strictly comparable reactions with identical results.

Cyanogen was transferred into the vessel containing 2 moles of the Grignard reagent by means of liquid oxygen (experiments were performed on a 10 m mole scale). This flask was then closed from the rest of the system and allowed to attain dry-ice temperature, after which it was immersed in a bath at -70°C and stirred vigorously with a magnetic stirrer as soon as melting of the reaction mixture occurred. Pressure measurements indicated the completion of the reaction within 30 min of melting, though a further 15 min were allowed before decomposition with ice/hydrochloric acid. Extraction with ether simplified the isolation of the products which were found to be diacetyl (c. 10% yield; oxime, m.p. 245°C), acetamide (c. 0.1 g, 8%, m.p. 82°C , hydrolysis producing acetic acid, *p*-nitrobenzyl ester, m.p. 78°C), and an unidentified residue.

To confirm the presence of diacetyl further, the ethereal extract of a decomposed reaction mixture was dried and treated with an excess of methylmagnesium bromide (Pace 1928), when pinacol was isolated as one product (m.p. $40-41^\circ\text{C}$; acetate, m.p. 64°C) (for each the melting points given above were undepressed on admixture with pure samples).

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