

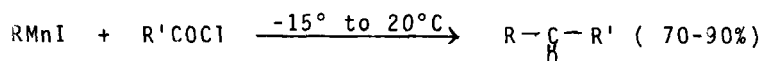
REACTIVITY OF ORGANOMANGANESE(II) REAGENTS. REACTION WITH CARBONYL COMPOUNDS, SELECTIVE PREPARATION OF KETOLS FROM KETO-ALDEHYDES.

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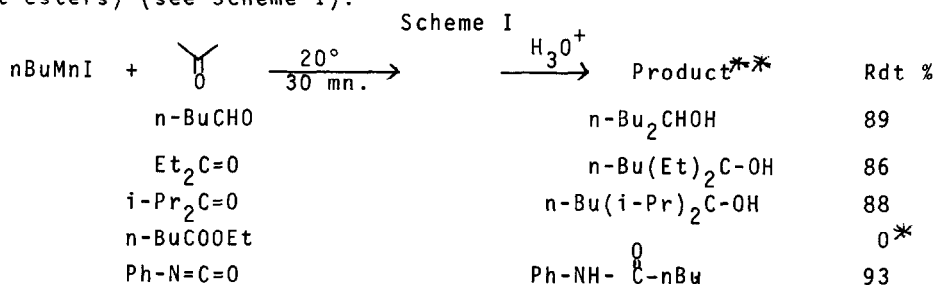
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We have recently shown that organomanganous derivatives are very useful reagents for the preparation of ketones from acid chlorides (1):



Stoichiometric amounts of these reagents lead only to the desired ketone uncontaminated by alcoholic by products as is the case with organo-magnesium or organolithium compounds.

However, we have now obtained evidence that this high selectivity is due to the large difference in the reaction rates of the competing starting acid halide and the ketone formed, and not to the complete inertness of the latter. Organomanganous iodides do react with aldehydes, ketones, isocyanates, (but not esters) (see Scheme I).

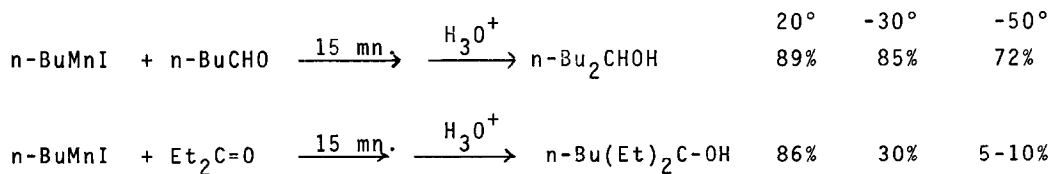


\* No reaction after 6h.

\*\* All physical data are in good agreement with those of the literature.

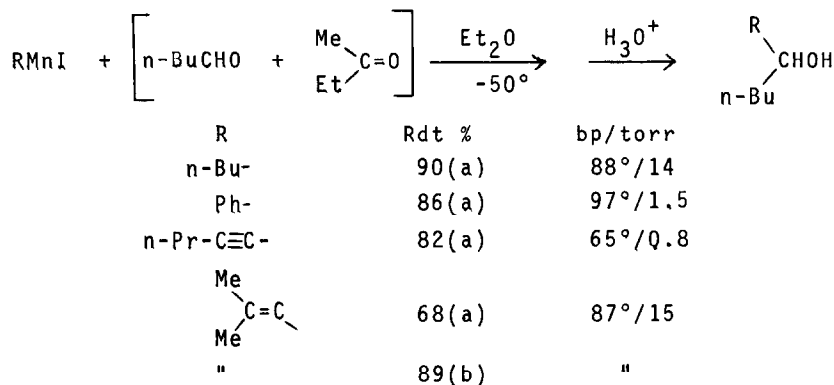
The reaction is fast at room temperature, but shows interesting discrepancies when the temperature is lowered, as far as aldehydes and ketones are concerned (see Scheme II).

## Scheme II



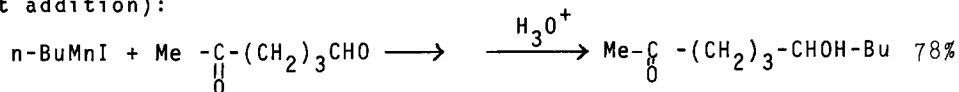
Competitive experiments performed at -50° lead to an almost selective attack of the aldehyde moiety (see Scheme III).

## Scheme III



- a) Addition of the mixture of carbonyl compounds to RMnI; at once: -50° for 30min., then raise temperature to +20° over 1h.  
 b) Addition of RMnI to the mixture: slowly, same conditions as in a).

As an example, we have prepared a keto-alcohol from a keto-aldehyde (direct addition):



In conclusion, organomanganous iodides allow a selective condensation on aldehydes even in the presence of non protected keto groups. Other aspects of the selective reactivity of these manganese reagents are being actively studied.

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## Reference:

- 1) G. CAHIEZ, D. BERNARD, J. F. NORMANT, *Synthesis*, 1977, 130.