Oxidation of Halomagnesium *sec*-Alkoxides to Ketones

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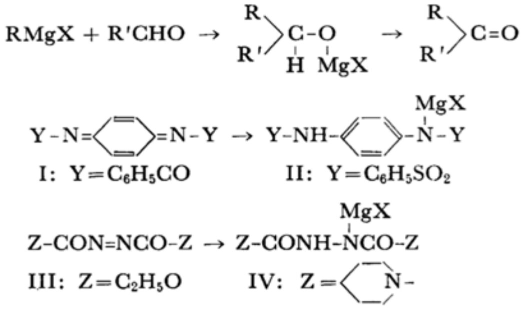
It is well known that alcohols are oxidized by carbonyl compounds such as acetone and cyclohexanone, in the presence of alminum alkoxide (Oppenauer Reaction).¹⁾ It is expected from the above fact that aldehydes will be converted into ketones by oxidation of halomagnesium alkoxides, obtained from the reaction of aldehydes and Grignard reagents, with suitable dehydrogenating reagents.

This communication reports oxidation of halomagnesium alkoxides by the use of various dehydrogenating reagents such as *p*-quinone dibenzimide (I), *p*-quinone dibenzenesulfonimide (II), diethyl azodicarboxylate (III) and azodicarbonpiperidide (IV). When an equimolar amount of I in benzene was added dropwise to an ethereal solution of magnesium alkoxide, resulted by the reaction of phenylmagnesium bromide and benzaldehyde, at room temperature, bromomagnesium salt of *p*-phenylene dibenzamide deposited soon. The corresponding ketone, benzophenone, was produced in 58% yield after the reaction mixture was heated at 60—65°C for 1 hr. In a similar manner, bromomagnesium salts of 1-phenylpentanol and 1-phenyl-1-penten-3-ol, prepared by Grignard reaction, were converted into the corresponding aralkyl ketones. In the case of aliphatic alkoxide, however, the yield of the ketone was low and a large amount of tarry product resulted. For example, 3-octanone was produced in only 29% yield by treating the corresponding bromomagnesium alkoxide in benzene at 60—65°C for 3 hr.

Similar results were observed when bromomagnesium alkoxides were treated with II; the corresponding aromatic ketones were produced in fairly good yields, however, in the case of aliphatic ketone, the yield was comparatively low.



I: $Y=C_6H_5CO$ II: $Y=C_6H_5SO_2$

III: $Z=C_2H_5O$ IV:

Next, it was found that aliphatic ketones were successfully prepared by treating the halomagnesium alkoxides with III, known to be a strong hydrogen abstracting reagent.²⁾ Treatment of butylmagnesium bromide with butyraldehyde, followed by the addition of diethyl azodicarboxylate under ice-cooling gave a brownish precipitate immediately. After keeping the reaction mixture to stand overnight at room temperature, 3-octanone was obtained in 66% yield. Similarly, 7-methyl-4-octanone, benzophenone and valerophenone were obtained in fairly good yields by treating the corresponding bromomagnesium alkoxide with the azo compound.

Furthermore, it was established that IV is also an effective dehydrogenating reagent in this type of reaction (see Table 1.)

Thus it can he noted that this procedure is a useful method for converting aldehydes to ketones *via* a Grignard route without isolating the intermediate alcohols.

TABLE I. THE REACTIONS OF HALOMAGNESIUM ALKOXIDES, PREPARED FROM GRIGNARD REAGENTS (RMgBr) AND ALDEHYDES (R'CHO), WITH OXIDANTS I—IV

Yields (%) of (a) ketones, RR'CO, and (b) the hydrogenated products of the oxidants

R	R'	I		II		III		IV	
		a	b	a	b	a	b	a	b
C_6H_5	C_6H_5	58	60	51	53	67	81	71	75
C_4H_9	C_6H_5	43	59	52	42	50	69	51	73
C_2H_5	$C_6H_5CH=CH$	45	52	62	75	66	87	35	73
C_4H_9	C_3H_7	29	52	15	21	66	82	53	64
i-C_5H_{11}	C_3H_7	—	—	—	—	65	71	67	81

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1) C. Djerassi, "Organic Reactions," Vol. 6, John Wiley & Sons, Inc., New York, N. Y. (1951), p. 257.

2) F. Yoneda, K. Suzuki and Y. Nitta, *J. Org. Chem.*, **32**, 727 (1967).