

Transhalogenation of Mucohalic Acids by Grignard Reagents

By Emanuel Beška and Pavel Rapoš,* Research Institute of Agrochemical Technology, 810 04 Bratislava, Czechoslovakia

The reaction of alkylmagnesium halides with mucohalic acids (2,3-dihalogenomalealdehydic acids) in aprotic solvents results in an exchange between the 2-halogen of the mucohalic acid and the halogen of the Grignard reagent. The mechanism is discussed.

THE reaction of alkylmagnesium halides with mucohalic acids is reported^{1,2} to lead to 5-alkyl-3,4-dihalogenofuran-2(5H)-ones. We now describe another mode of reaction of mucohalic acids with Grignard reagents, involving exchange between the α -halogen atom of the former and the halogen of the latter; this takes place provided that the Grignard reagent is added to the mucohalic acid (*i.e.* inverse addition), and the halogen of the Grignard reagent is a stronger nucleophile than that attached to the α -position of the mucohalic acid used.

Transhalogenations of various compounds by Grignard reagents are known.^{3,4} Nevertheless, the present reaction is not a direct halogen-halogen exchange. The

first step is a reaction with active hydrogen, *i.e.* neutralization of the mucohalic acid with the Grignard reagent, leading to the halogenomagnesium salt. The next stage is the nucleophilic substitution of the α -halogen of the mucohalic acid by the halogen of the halogenomagnesium salt according to the Scheme. This mechanism was confirmed by studying the rate of reaction of the acid (1) with methylmagnesium iodide to give the acid (4).

In the present reaction only the α -halogen of the mucohalic acids is substituted. This was confirmed by the reactions of the acids (2) and (3) with methylmagnesium iodide: both gave the same compound (5).

The i.r. and n.m.r. spectra of the acids (4) and (5)

¹ H. Simonis, E. Marben, and E. Mermod, *Ber.*, 1905, **38**, 3983.

² E. J. Vinogradova and M. M. Shemyakin, *Zhur. obshchei Khim.*, 1946, **16**, 709.

³ J. Thessing, S. Klüssendorf, P. Ballach, and H. Mayer, *Chem. Ber.*, 1955, **88**, 1295.

⁴ N. S. Popov, *Zhur. obshchei Khim.*, 1940, **10**, 1141.

confirm their lactol structure, as known for the other mucohalic acids (1)—(3).⁵⁻⁷

EXPERIMENTAL

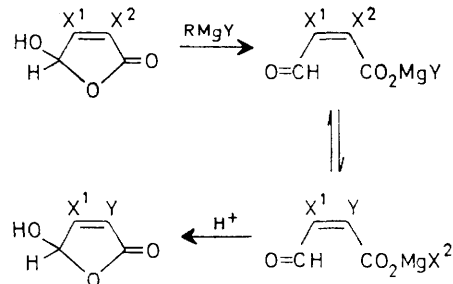
I.r. spectra were determined with a double beam UR-10 Zeiss spectrophotometer, u.v. spectra with a Unicam SP 8000 instrument, and n.m.r. spectra with a Tesla BS 487 spectrometer (80 MHz) with tetramethylsilane as internal standard. M.p.s were determined with a Reichert microscope.

3-Chloro-2-iodomalealdehydic Acid (4).—A 50% solution of methylmagnesium iodide (42.0 g) in ether was added dropwise to a stirred solution of the acid (1) (42.0 g) in sodium-dried ether (150 ml) under reflux during 2 h. After a further 3 h heating the mixture was set aside for 3 days, and thoroughly decomposed with dilute sulphuric acid. The organic phase was separated, washed with aqueous sodium hydrogen sulphite and with water, dried, and evaporated. The residue was crystallized from benzene to yield the acid (4) (28.0 g, 43.0%), m.p. 156—157 °C (Found: C, 18.5; H, 0.8; Cl, 13.7; I, 48.5. $C_4H_2ClIO_3$ requires C, 18.45; H, 0.8; Cl, 13.6; I, 48.7%); ν_{max} ($CHCl_3$) 1 615 (C=C), 1 778 and 1 798 (C=O), and 3 100—3 400 cm^{-1} (OH); λ_{max} (MeOH) 205 and 248 nm (ϵ 5 130 and 6 400); δ [$(CD_3)_2SO$] 8.37 (1 H, s, OH) and 6.12 (1 H, s, CH). From the benzene mother liquor 3,4-dichloro-5-methylfuran-2(5H)-one,¹ b.p. 93 °C and 10 mmHg (16.2 g), n_D^{20} 1.503 0, was obtained.

3-Bromo-2-iodomalealdehydic Acid (5).—(i) A 10% solution of methylmagnesium iodide (16.6 g) in ether was added dropwise during 1.5 h to the acid (2) (24.5 g) in dry ether (150 ml). The temperature was maintained at 30 °C. After 2 days, isolation as described for the acid (4) gave the

⁵ E. Kuh and R. L. Shepard, *J. Amer. Chem. Soc.*, 1953, **75**, 4597.

acid (5) (8.1 g, 26.6%), m.p. 143—144 °C (from benzene) (Found: C, 15.9; H, 0.65; Br, 26.65; I, 42.3. $C_4H_2BrIO_3$ requires C, 15.7; H, 0.7; Br, 26.2; I, 41.6%); ν_{max} ($CHCl_3$) 1 604 (C=C), 1 770, 1 790 (C=O), and 3 050—3 450 cm^{-1}



- (1) $X^1 = X^2 = Cl$, $Y = I$ (4)
 (2) $X^1 = X^2 = Br$, $Y = I$ (5)
 (3) $X^1 = Br$, $X^2 = Cl$, $Y = I$ (5)

R = alkyl

SCHEME

(OH); λ_{max} (MeOH) 206 and 252 nm (ϵ 4 400 and 4 200); δ [$(CD_3)_2SO$] 8.37 (1 H, s, OH) and 6.08 (1 H, s, CH).

(ii) The acid (5) was similarly obtained (31.3%) from the acid (3) (21.3 g) with ethylmagnesium iodide (18.0 g); m.p. 143—144 °C (from benzene) (Found: C, 15.5; H, 0.6; Br, 26.6; I, 41.4%).

[6/502 Received, 15th March, 1976]

⁶ Y. Hachihama, T. Shono, and S. Ikeda, *J. Org. Chem.*, 1964, **9**, 1371.

⁷ Dong Han Kim and D. N. Harpp, *Chem. Ind.*, 1965, 183.