Polar Effects of Organosilicon Substituents in Carboxylic Acids[1]

BY L. H. SOMMER, J. R. GOLD, G. M. GOLDBERG AND N. S. MARANS

The acid strengths of carboxylic acids containing organosilicon substituents close to the carboxyl are of interest in connection with an elucidation of the polar effects of such substituents in organic molecules. We wish to report the synthesis and acid strengths of four silicon-containing carboxylic acids.

TABLE I

Acid	Formula	M. p., °C.	Silicon, % Calcd.	Silicon, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
I	$(CH_3)_3SiCH_2CO_2H$	40	21.2	21.3	132	133
II[a]	$(CH_3)_3SiOSi(CH_3)_2$-CH_2CO_2H	17	27.2	26.7	206	207
III	$(C_6H_5)(CH_3)_2SiCH_2$-CO_2H	90	14.4	14.3	194	193
IV[b]	$(CH_3)_3SiCH_2CH_2CO_2H$	22	19.1	19.1	146	145

[a] Acid II has n^{20}_D 1.4149. [b] Acid IV has b. p. 147° (65 mm.), n^{20}_D 1.4279.

Acids I, II and III were synthesized in yields of 88, 85, and 69%, respectively, by carbonation of the Grignard reagents derived from the appropriate chlorides.[2] The Grignard reagents were added to an excess of Dry Ice in the form of chips and the reaction mixture allowed to stand for twelve hours. Subsequent to treatment with 5% hydrochloric acid, ether was removed from the acids by vacuum distillation at temperatures below 25°. These acids were not distilled. They were purified by two recrystallizations from heptane.[3] Acid IV was synthesized from chloromethyltrimethylsilane by the malonic ester synthesis (66% yield) and from iodomethyltrimethylsilane by the acetoacetic ester synthesis (63% yield). This acid was purified by distillation (65 mm.).

Determination of the acid strengths was made by a potentiometric method using a Leeds and Northrup 7662-Al *p*H Indicator Assembly.[4] Stability of acids I–IV under the conditions used in this procedure was demonstrated by preparation of the sodium salts and regeneration of the acids.

The dissociation constant of *t*-butylacetic acid was determined for comparison with acid I. Propionic acid was run as a check on the accuracy of the method at the concentrations used.

TABLE II

DISSOCIATION CONSTANTS FOR RCH_2CO_2H AT 25°

R	$K \times 10^5$	K/K_{acetic}
$(CH_3)_3Si$	0.60	0.34
$(CH_3)_3SiOSi(CH_3)_2$	.60	.34
$(C_6H_5)(CH_3)_2Si$	.54	.31
$(CH_3)_3SiCH_2$	1.24	.71
$(CH_3)_3C$	1.00	.57
CH_3	1.34[a]	.77
H	1.75	

[a] Value found in this work, 1.32×10^{-5}.

According to current theory,[5] the acid-weakening effects of organosilicon substituents in acids I, II, and III show that *these substituents exert an inductive effect of electron-release relative to alkyl and hydrogen.*

The data for acid IV demonstrates that this effect diminishes rapidly in a saturated carbon chain. Additional theoretical aspects will be discussed in a later publication.

We thank Dr. A. W. Hutchison for valuable advice and Dr. N. C. Cook for the *t*-butylacetic acid.

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[1] Paper XXI in a series on organosilicon chemistry. For paper XX see THIS JOURNAL, **70**, 3512 (1948).

[2] (a) Chloromethyldimethylphenylsilane, b. p. 138° (50 mm.), n^{20}_D 1.5212, Si, 15.1% (calcd. 15.2), was synthesized in 72% yield from chloromethyldimethylchlorosilane and phenylmagnesium bromide; (b) the Grignard reagent derived from chloromethylpentamethyldisiloxane has recently been reported; Bluestein, THIS JOURNAL, **70**, 3068 (1948).

[3] The non-isolation of trimethylsilylacetic acid (I) in a previous preparation resulted from the different procedure used in working up the product; Whitmore, Sommer, Gold and Van Strien, THIS JOURNAL, **69**, 1551 (1947).

[4] For a recent application of this method see Newman, Taylor, Hodgson and Garrett, *ibid.*, **69**, 1784 (1947).

[5] For an excellent summary see Johnson and Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, New York, N. Y., 1943, pp. 1842–1845.

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Grignard Reactions. XIX.[1] Preparation of 2,4,4-Trimethyl-3-pentanone

BY CARLYLE J. STEHMAN,[2] NEWELL C. COOK AND FRANK C. WHITMORE[3]

The limitations of the Grignard reaction in the synthesis of highly branched compounds are well known. Such a synthesis, the reaction of *t*-amylmagnesium chloride with isobutyryl chloride, has previously given little or no ketone.[4,5]

Copper vessels for Grignard reactions have been in use in this Laboratory and others for many years. Crane, Boord and Henne[6] noted slightly better yields in copper than in glass. It has now been found that *t*-amylmagnesium chloride reacts with isobutyryl chloride in copper reactors to give 2,4,4-trimethyl-3-pentanone in yields up to 87%.

Further studies on the copper-catalyzed reaction of acid chlorides with Grignard reagents are in progress.

Experimental

For preparation of the *t*-amylmagnesium chloride, and coupling of the Grignard reagent with isobutyryl chloride,

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[1] XVIII, Whitmore and Sloat, THIS JOURNAL, **64**, 2968 (1942).

[2] Present address: Monsanto Chemical Co., Dayton, Ohio; research work performed during academic leave of absence from Monsanto.

[3] Deceased.

[4] Whitmore, *et al.*, THIS JOURNAL, **63**, 643 (1941).

[5] W. A. Mosher, Doctor's Dissertation, 1940, The Pennsylvania State College.

[6] Crane, Boord and Henne, THIS JOURNAL, **67**, 1237 (1945).

a jacketed copper Grignard reactor (20 liters capacity) developed at Penn State was used. To 608 g. (25 moles) of magnesium and 12,500 ml. of ether was added 2662 g. (25 moles) *t*-amyl chloride; from the product mixture was decanted 20 moles (12,200 ml.) of a clear ether solution of *t*-amylmagnesium chloride. This solution was then added dropwise at the rate of 450 cc. per hour to a mixture of 2150 g. (20 moles) of freshly prepared isobutyryl chloride in 4000 ml. of dry ether, at 16–18° and stirring continued for five days, also at 16–18°. After decomposing the product by pouring onto 10 kg. of ice, the ether layer and water layer were separately distilled. The combined ether layer distillates upon fractionation gave cuts 1–5, 88 g., b. p. 50–76° at 80 mm., $n^{20}\text{D}$ 1.3840–1.4092, containing isobutyraldehyde and isobutyl alcohol; cut 6, 22 g., b. p. 76–82° at 80 mm., $n^{20}\text{D}$ 1.4111; cuts 7–10, 89 g., b. p. 84–87.5° at 90 mm., $n^{20}\text{D}$ 1.4070–1.4081, containing isobutyl isobutyrate; cuts 11–14, 108 g., b. p. 88–94° at 100 mm., $n^{20}\text{D}$ 1.4091–1.4136, containing isobutyl isobutyrate and 2,4,4-trimethyl-3-pentanone; cuts 15–18, 2021 g., b. p. 94° at 100 mm. to 87° at 35 mm., $n^{20}\text{D}$ 1.4214, 2,4,4-trimethyl-3-pentanone; and cut 20, 41 g., residue. Based on isobutyryl chloride, yields were estimated as 73% 2,4,4-trimethyl-3-pentanone, 10% isobutyl isobutyrate, 2% isobutyraldehyde and 1% isobutyl alcohol.

In a second preparation, also on 20-mole scale, in which the rate of addition of Grignard solution (625 cc. per mole) was constant at about 600 cc. per hour, and the temperature was 14–17°, there were obtained yields of 87% 2,4,4-trimethyl-3-pentanone, 5% isobutyl isobutyrate, 0.1% isobutyraldehyde, and 2% isobutyl alcohol.

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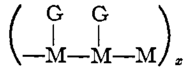
Methylation of Guar Polysaccharide[1]

BY JOHN W. SWANSON

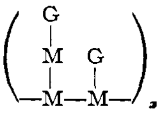
Purified guar polysaccharide, a mannogalactan consisting of 60% mannan and 37% galactan units, has been methylated, subjected to methanolysis, and the resulting glycosides separated into three principal fractions by means of high vacuum fractional distillation. Fraction 1 has been hydrolyzed to the corresponding sugar and identified as 2,3,4,6-tetramethylgalactose, through its crystalline anilide. This derivative was obtained in a yield sufficient to account for 90% of the galactose present in the original polysaccharide. A sample of the unfractionated glycoside mixture was also hydrolyzed and converted to the anilides; only one crystalline anilide has been recovered. This anilide, which was identical with the above, was obtained in sufficient yield to account for 87% of the galactose present. The other two principal fractions (3 and 4 in Table I) correspond to trimethyl and dimethyl sugar units, respectively. These fractions have not been conclusively identified, but they appear to be largely methylated mannose derivatives.

Although insufficient data have been obtained to make any conclusive statements, it is interesting to note that at least 90% of the galactose units appear to be present in the polymer chain as side units and, therefore, possess four free hydroxyl groups. If the other two main fractions are principally trimethyl and dimethyl mannose, respectively, then the following types of units may be present in guar polysaccharide



$$\left(\begin{array}{ccc} \text{G} & \text{G} & \\ | & | & \\ \text{—M—} & \text{M—} & \text{M} \end{array}\right)_x$$

a



$$\left(\begin{array}{cc} \text{G} & \\ | & \\ \text{M} & \text{G} \\ | & | \\ \text{—M—} & \text{M—} \end{array}\right)_x$$

b

G = anhydrogalactose unit
M = anhydromannose unit

Moe, Iwen and Miller[2] have reported that guar mannogalactan in buffered medium consumes one mole of periodic acid per hexose unit. Structures (a) and (b) might also consume an *average* of one mole of periodic acid per hexose unit because each of the side galactose units would presumably consume two moles of periodate and the units located at the branching points would consume no periodic acid, whereas the units from which branching does not occur would consume one mole of periodic acid. Such a reaction with the galactose units would be expected to lead to the formation of a considerable quantity of formic acid. Whistler and co-workers[3] have recently published formic acid data which support the proposed structure as indicated by methylation.

Experimental

Methylation of Guar.—Ten grams of purified guar polysaccharide was dissolved in 500 ml. of water and methylated under nitrogen by the simultaneous dropwise addition during five hours of 100 ml. of dimethyl sulfate and 280 ml. of 30% sodium hydroxide. After complete reaction of the dimethyl sulfate, the excess alkali was carefully neutralized with dilute sulfuric acid and the partially methylated product was salted out with sodium sulfate. The supernatant salt solution was dialyzed, evaporated under vacuum, and the residue combined with the precipitated gum product. The polysaccharide content of this residue was so small after two methylations that this procedure was not deemed necessary for later methylations. The product from the first methylation was then redispersed in water and the methylation repeated. The final product (or part thereof for methoxyl determination) was dissolved in chloroform, dried over anhydrous sodium sulfate, and precipitated with an excess of light petroleum ether. After five to six methylations and reprecipitation to remove ash, the methoxyl content was 45.4% and the ash content 0.8%; yield 11.5 g., 91.2%; $[\alpha]^{23}\text{D}$ + 46.4 ($CHCl_3$, *c* 0.67.)

Methanolysis of Methylated Guar.—Five and one-half grams of the methylated guar was dissolved in 80.5 ml. of anhydrous methanol and 46.5 ml. of methanol–hydrogen chloride was added (final concentration of hydrogen chloride, 3.0%). The high viscosity decreased very rapidly. The mixture was centrifuged to remove 0.02 g. of a dark solid, giving a clear light yellow solution. The optical rotation was followed to a constant value ($[\alpha]^{23}\text{D}$ + 66.5°) at room temperature and then to a constant value of $[\alpha]^{23}\text{D}$ + 74.8° after refluxing on a steam-bath for six and one-fourth hours. The hydrochloric acid was neutralized with silver carbonate and, after filtration, the solution was evaporated under vacuum to a sirup. The

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[1] Presented before the Division of Sugar Chemistry and Technology at the 112th meeting of the American Chemical Society, New York, N. Y., 1947.

[2] O. A. Moe, S. E. Miller and M. H. Iwen, THIS JOURNAL, **69**, 2621 (1947).

[3] R. L. Whistler, *et al.*, *ibid.*, **70**, 3144 (1948).