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-A1 *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.

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THE WHITMORE LABORATORY
SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.

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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.

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).