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FURAN SERIES ORGANOSILICON COMPOUNDS

IX. Organosilicon Pyromucates, 3-(2-Furyl)Acrylates, and Cinnamates*

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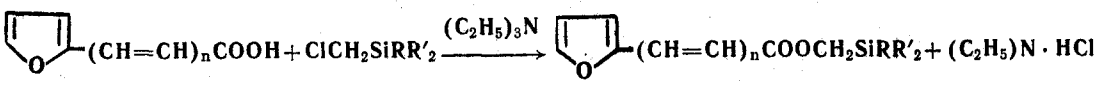
Six new organosilicon esters of pyromucic, 3-(2-furyl)acrylic, and cinnamic acids were synthesized by reacting these acids with chloromethylalkylsilanes and chloromethylalkoxysilanes in the presence of triethylamine.

Organosilicon esters of pyromucic and 3-(2-furyl)acrylic acids containing a C–O–Si bond have previously been described [2]. The present paper describes the synthesis of organosilicon esters of pyromucic and 3-(2-furyl)acrylic acids, and also of cinnamic acid, containing the group C–O–C–Si. They were prepared by refluxing toluene or xylene solutions of the corresponding acids with chloromethyltrimethylsilane, chloromethylmethyldimethoxysilanes, chloromethyldiethoxysilane, and chloromethyltrimethoxysilane in the presence of triethylamine for 12-24 hr. The general equation for the reaction is:



$$(CH{=}CH)_nCOOH + ClCH_2SiRR'_2 \xrightarrow{(C_2H_5)_3N} (CH{=}CH)_nCOOCH_2SiRR'_2 + (C_2H_5)N \cdot HCl$$

$R = CH_3;\ CH_3O;\ R' = CH_3;\ CH_3O;\ C_2H_5O;\ n = 0,1.$

The comparatively low ester yields (30-60%) were due to resinification during distillation. The esters were colorless liquids with a characteristic odor, and turned yellow on standing. Table 1 gives physical constants and analytical data for them.

The methyldimethoxysilylmethyl ester of cinnamic acid $C_6H_5CH{=}CHCOOCH_2Si(OCH_3)_2CH_3$ was prepared similarly in 30% yield.

Experimental

Methyldimethoxy(furoxymethyl)silane. A solution of 11.2 g (0.1 mole) pyromucic acid, 15.5 g (0.1 mole) chloromethylmethyldimethoxysilane and 12.1 g (0.12 mole) triethylamine in 50 ml dry toluene was stirred vigorously and refluxed for 13 hr. After cooling the precipitate of triethylamine hydrochloride was filtered off, and washed with toluene, and the toluene and excess triethylamine distilled off from the filtrate under a waterpump vacuum. Two distillations gave 13.7 g (59.5%) methyldimethoxyfuroxymethylsilane bp 112-115° (1 mm).

The rest of the esters listed in Table 1 were prepared similarly; ratios of reactants, synthesis conditions, and product yields are given in Table 2, on the next page.

REFERENCES

1. E. Ya. Lukevits and M. G. Voronkov, KhGS, 179, 1965.
2. E. Ya. Lukevits, Izv. AN Latv. SSR, ser. khim., 111, 1963.

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*For Part X see [1].

Table 1

Organosilicon esters of carboxylic acids.

Compound	Bp, °C (pressure mm)	n_D^{20}	d_4^{20}	MR_D		Molecular formula	Si, %	
				Found	Calculated		Found	Calculated
 $COOCH_2Si(CH_3)_3$	84 (1.5)	1.4785	1.0215	54.98	53.90	$C_9H_{14}O_3Si$	14.02; 14.09	14.16
 $COOCH_2Si(OCH_3)_2CH_3$ . . .	112—115 (1)	1.4742	1.1470	56.45	55.42	$C_9H_{14}O_5Si$	12.28; 12.48	12.20
 $COOCH_2Si(OC_2H_5)_2CH_3$ . . .	126—128 (1)	1.4690	1.0950	65.71	64.68	$C_{11}H_{18}O_5Si$	10.67; 10.73	10.87
 $COOCH_2Si(OCH_3)_3$	127—129 (3)	1.4640	1.1876	57.23	56.18	$C_9H_{14}O_6Si$	11.70; 11.85	11.56
 $CH=CHCOOCH_2Si(OCH_3)_3$.	143—144 (1,5)	1.5157	1.1605	70.84	64.97	$C_{11}H_{16}O_6Si$	10.13; 10.19	10.31
$C_6H_5CH=CHCOOCH_2Si(OCH_3)_2CH_3$	159—161 (3)	1.5321	1.0879	75.88	71.40	$C_{13}H_{18}O_4Si$	10.51; 10.52	10.54

Table 2

Synthesis conditions for the organosilicon esters of pyromucic, 3-(2-furyl)acrylic and cinnamic acids.

Acid*	Quantity		$R'R''_2SiCH_2Cl$	Quantity		$(C_2H_5)_3N$		Toluene, ml	Reaction time, hr	Yield	
	g	mole		g	mole	g	mole			g	%
RCOOH	5.6	0.05	$(CH_3)_3SiCH_2Cl$	6 2	0.05	6.1	0.06	50	24	3.3	33.3
RCOOH	11.2	0.1	$CH_3(CH_3O)_2SiCH_2Cl$	15.5	0.1	12.1	0.12	50	13	13.7	59.5
RCOOH	5.6	0.05	$CH_3(C_2H_5O)_2SiCH_2Cl$	9.2	0.05	6.1	0.06	50	14	4.8	37
RCOOH	16.8	0.15	$(CH_3O)_3SiCH_2Cl$	25.6	0.15	18.2	0.18	175	25	14.5	39.2
RCH=CHCOOH . .	27.6	0.2	$(CH_3O)_3SiCH_2Cl$	34.2	0.2	24.2	0.24	100	12	16.3	30
$C_6H_5CH=CHCOOH$.	13.4	0.09	$CH_3(CH_3O)_2SiCH_2Cl$	15.1	0.1	12.1	0.12	50**	14	8.0	30

*R = 2-furyl.

**Xylene.