1.4–2.1 (2 H, multiplet, CH_2), 0.85–1.15 (3 H, triplet, CH_3).[25] The analysis is in Table II.

Typical Preparation of 1,3-Dialkyl-5-chloropyrazoles. 5-Chloro-3-methyl-1-propylpyrazole (5).—75, 100 g (0.714 mol), was dissolved in 453 g (2.95 mol) of phosphoryl chloride and the mixture was refluxed 24 hr. The reaction mixture was concentrated *in vacuo* at 60° (water bath temperature) and the residue was poured into water. The resulting oil–water mixture was made strongly basic with concentrated ammonium hydroxide with cooling and extracted with diethyl ether. The extracts were dried ($MgSO_4$) and distilled through a Vigreux column, finally under vacuum to yield **5**: 81 g (71%); bp 83–84° (22 mm); nmr ($CDCl_3$) δ TMS 5.82 (1 H, 4-H), 3.8–4.15 (2 H, triplet, 1-CH_2), 2.18 (3 H, singlet, 3-CH_3), 1.6–2.1 (2 H, multiplet, CH_2), 0.75–1.15 (3 H, triplet, CH_3). The analysis is in Table II.

Registry No.—**59**, 29939-11-5; 4,4′-(oxydi-2-thenylidene)bis[5-chloro-1-cyclohexyl-3-methylpyrazole],[26] 29939-28-4.

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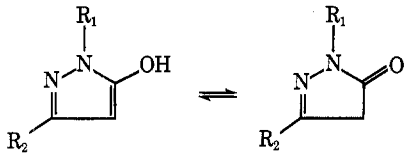
[25] The absorption between 10.2–10.6 and 5.0–5.25 was observed in all of the 1,3-dialkyl-2-pyrazolin-5-ones prepared in this study and was independent of the synthetic route used. It is the result of the equilibrium with the 1,3-dialkylpyrazol-5-ol tautomer in solution.



Thus the absorption between 3.1 and 3.4 due to the hydrogens at position 4 in the 1,3-dialkyl-2-pyrazolin-5-one is diminished proportionally. This was demonstrated by taking the same spectrum in DMSO-d_6. In this solvent the equilibrium is shifted almost exclusively to the 1,3-dialkylpyrazol-5-ol tautomer. The absorption between 10.2 and 10.6 accounts for 0.9 protons and is assigned to the 5-OH as salt-like, the absorption at 5.15 is a singlet accounting for 0.9 protons and is due to the hydrogen at position 4, and the absorption at 3.1–3.4 accounts for 0.2 protons. Equilibration with deuterium oxide in both solvent systems results in rapid removal of the absorption at all three of the given areas.

[26] See Table I, footnote *e*.

Reductions with Organosilicon Hydrides. III. Reduction of Acyl Fluorides to Esters

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The previous paper[1] in this series dealt with the palladium-catalyzed reaction of silicon hydrides with acyl chlorides (eq 1). Since it is known, in contrast to the

$$R_3SiH + RCOCl \xrightarrow{Pd} R_3SiCl + RCHO \qquad (1)$$

other halogens, that carbon–fluorine bonds of fluorocarbons are not cleaved readily by silicon hydrides in the presence of palladium catalysts,[2] it was of interest to discover if this was also true of acyl fluorides.

A mixture of pentanoyl fluoride, triethylsilane, and 5% Pd/C showed no sign of reaction, and this was confirmed by infrared spectrum (the chloride would have reacted vigorously under these conditions). However, it was found that the reaction with the fluoride proceeded thermally to yield pentyl pentanoate (eq 2),

$$2n\text{-}C_4H_9COF + 2Et_3SiH \longrightarrow n\text{-}C_4H_9CO_2C_5H_{11}\text{-}n + 2Et_3SiF \qquad (2)$$

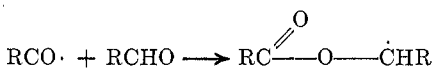
with no trace of pentanal in the product mixture (a test with 2,4-dinitrophenylhydrazine solution was negative). Table I summarizes the results of this and other similar reactions. The reduction of terephthaloyl fluoride yielded a polymer, whose pmr and infrared spectra indicated that it was a polyester of terephthalic acid, *p*-hydroxymethylbenzoic acid, and *p*-bis(hydroxymethyl)benzene. Highly hindered esters can also be prepared, as exemplified by the high yield of 2,2-dimethylpropyl 2,2-dimethylpropionate obtained. However, a silicon dihydride, diphenylsilane, yielded only a complex mixture of carbonyl compounds.

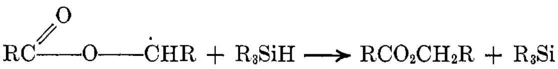
The reaction products could be altered by the addition of other compounds, such as aldehydes. Reduction of pentanoyl fluoride in the presence of equimolar hexanal led to the formation of hexyl pentanoate. As judged from chromatography, no pentyl pentanoate was formed. As noted in Table I, benzonitrile seemed to have no effect upon the reaction. The aldehydes had another effect on the reaction, that of increasing the rate. This was especially true of crotonaldehyde, but only a mixture of carbonyl compounds was isolated from this reaction (a referee has pointed out that this very rapid reaction may not necessarily be the reduction to the ester).

These data are strikingly similar to those obtained in the analogous reductions of tin hydrides.[3] In those reductions of acyl fluorides, esters are also the only products.[4] Based on the mechanism developed for tin hydrides,[3] the steps involved in the present reaction are probably as shown in eq 3–6. The unpaired species

$$R_3Si\cdot + RCOF \longrightarrow RCO\cdot + R_3SiF \qquad (3)$$

$$RCO\cdot + R_3SiH \longrightarrow RCHO + R_3Si\cdot \qquad (4)$$


$$RCO\cdot + RCHO \longrightarrow RC(=O)\text{—O—}\dot{C}HR \qquad (5)$$


$$RC(=O)\text{—O—}\dot{C}HR + R_3SiH \longrightarrow RCO_2CH_2R + R_3Si\cdot \qquad (6)$$

(radicals) represented in eq 3–6 may or may not actually exist (they may only be transition states) but they are useful in visualizing the mechanism. There are two other experiments which tend to substantiate this pathway. After 19 hr at 75°, equimolar amounts of Et_3SiH and pentanoyl fluoride with 0.9 mol % of α,α'-azobisisobutyronitrile contained 19% of the original silicon hydride; a control reaction without the azonitrile initiator contained 43% of Et_3SiH. Thus, as expected, a radical source increased the reaction rate. Another alternate mechanism, addition of the silicon hydride across aldehydic carbonyl, followed by reaction of the resulting alkoxysilane with the acyl fluoride[5] (eq 7), is much less likely because the first step does not

$$R'CHO + R_3SiH \longrightarrow R'CH_2OSiR_3 \xrightarrow{R''COF} R''CO_2CH_2R' + R_3SiF \qquad (7)$$

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[1] For part II, see J. D. Citron, *J. Org. Chem.*, **34**, 1977 (1969).

[2] J. D. Citron, J. E. Lyons, and L. H. Sommer, *ibid.*, **34**, 638 (1969).

[3] E. J. Walsh, Jr., and H. G. Kuivila, *J. Amer. Chem. Soc.*, **88**, 576 (1966).

[4] E. J. Walsh, Jr., *et al.*, *J. Org. Chem.*, **34**, 1156 (1969).

[5] J. D. Citron, *J. Organometal. Chem.*, in press.

Table I

Reductions of Acycl Fluorides by Silicon Hydrides

Silicon hydride (mmol)	Acyl fluoride (mmol)	Other additives (mmol)	Time, hr (temp, °C)	Acyl fluoride derivative, %	Silicon product, %
Et_3SiH (94)	n-C_4H_9COF (95)		24 (115)	n-$C_4H_9CO_2C_5H_{11}$-n, 71	Et_3SiF, 89
$(PhCH_2)_3SiH$ (83)	n-C_4H_9COF (87)		67 (125)	n-$C_4H_9CO_2C_5H_{11}$-n, 47	$(PhCH_2)_3SiF$, 95
Et_3SiH (140)	p-$C_6H_4(COF)_2$ (70)		6 (280)	Polymer,[a] 63	Et_3SiF, 65
Et_3SiH (160)	$(CH_3)_3CCOF$ (160)		8 (160)	$(CH_3)_3CCO_2CH_2C(CH_3)_3$, 74	Et_3SiF, 85
Ph_2SiH_2 (52)	n-C_4H_9COF (100)		10 (220)	Unidentified carbonyl compds	Ph_2SiF_2, 61
Et_3SiH (12)	n-C_4H_9COF (12)	n-$C_5H_{11}CHO$ (12)	27 (115)	n-$C_4H_9CO_2C_6H_{13}$-n[b]	Et_3SiF[b]
Et_3SiH (62)	n-C_4H_9COF (62)	C_6H_5CHO (62)	1 (125)	n-$C_4H_9CO_2CH_2C_6H_5$, 59	Et_3SiF, 87
Et_3SiH (16)	n-C_4H_9COF (16)	C_6H_5CN (15)	96 (125)	n-$C_4H_9CO_2C_5H_{11}$-n[c]	Et_3SiF[c]

[a] See text. [b] Identified by glpc and infrared spectrum. [c] By infrared spectrum; there was no evidence of the nitrile reacting.

occur under the reaction conditions, even in the presence of trace amounts of HF. Finally, if the mechanism of eq 3–6 is correct, the fact that no aldehyde is isolated, and that all added aldehyde reacts, indicates that reaction 5 is much faster than reaction 4.

Experimental Section

All of the silanes used were purchased from the Peninsular ChemResearch Corporation. Acyl fluorides were prepared from the corresponding chlorides by reaction with HF and had previously reported physical constants.[6] The physical constants of all products were identical with those in the literature, and the infrared spectra were in accord with their structures. Some typical procedures are given below.

Reaction of Pentanoyl Fluoride with Triethylsilane.—Into a 1.25-in.-i.d. Teflon tube equipped with a magnetic stirrer and under nitrogen was added 9.9 g of pentanoyl fluoride and 15.0 ml of triethylsilane. The solution was stirred and heated at 110–115° for 24 hr. After cooling, the material was distilled on a platinum spinning-band column to yield 12.8 g of Et_3SiF, bp 107–108.5°, and 5.8 g of pentyl pentanoate, bp 200–204.5°, $n^{23}{}_D$ 1.4155.

Reaction of Terephthaloyl Fluoride with Triethylsilane.—An 80-ml bomb was loaded with 12 g of terephthaloyl fluoride and 22.7 ml of triethylsilane, evacuated, and then heated at 280° for 6 hr. The total recovery of a mixture of solid and liquid was 24 g. The material was subjected to a vacuum, and the volatile fraction was distilled to yield 12.4 g of Et_3SiF, bp 108–110.5°.

The solid was placed in a sublimator at 100° and 0.1 mm for 40 hr. The residue, 6.0 g, was, as indicated by pmr and infrared spectra, a polyester of terephthalic acid, 1,4-bis(hydroxymethyl)benzene and p-hydroxymethylbenzoic acid.

Anal. Calcd for $(C_8H_6O_2)_n$: C, 71.7; H, 4.5. Found: C, 71.3; H, 4.2.

Reaction of Pentanoyl Fluoride with Triethylsilane in the Presence of 2-Butenal.—Into a 50-ml round-bottom flask under nitrogen were charged 9.7 g of pentanoyl fluoride, 14.8 ml of triethylsilane, and 7.7 ml of 2-butenal. The liquid was heated slowly and stirred. When the oil bath reached *ca.* 70° a violent reaction took place; the mixture refluxed rapidly enough to fill the condenser tube with a solid column of liquid. After the reaction subsided, the flask was heated at 70–80° for an additional 10 min and then the contents were transferred to a spinning-band column and distilled. The distillate consisted of 12.7 g of Et_3SiF, bp 107–111°, and several fractions (9.7-g total) of a mixture of carbonyl compounds. Infrared and pmr spectra indicated these were mixtures of ester and a small amount of carboxylic acid. Some of the ester appeared to be one or more of the butenyl pentanoates.

Registry No.—n-$C_4H_9CO_2C_5H_{11}$-n, 2173-56-0; $(CH_3)_3CCO_2CH_2C(CH_3)_3$, 5340-26-1; n-$C_4H_9CO_2C_6H_{13}$-n, 1117-59-5; n-$C_4H_9CO_2CH_2C_6H_5$, 10361-39-4; Et_3SiF, 358-43-0; $(PhCH_2)_3SiF$, 429-76-5; Ph_2SiF_2, 312-40-3; polyester of terephthalic acid, 1,4-bis(hydroxymethyl)benzene, and p-hydroxymethyl benzoic acid, 30135-79-6.

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[6] G. Olah and J. Kuhn, *Org. Syn.*, **45**, 3 (1965).

The Catalytic Dehydrator for Rapid Ester Synthesis

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We wish to report a potentially important modification in the use of ion exchange resins (acid polymers) as catalysts, *i.e.*, the combination of an acid polymer with a drying agent, the catalytic dehydrator, for the purpose of promoting acid-catalyzed, equilibrium reactions which have water as one of the products.

The advantages of the catalytic dehydrator over conventional esterification techniques are (1) the reaction can be done at room temperature or lower, a factor which may prove valuable for heat sensitive compounds; (2) the reaction apparatus is simple; (3) theoretically the catalytic dehydrator can be reused;[1] (4) it can be made quantitative in many cases; (5) it is a one-step reaction from the acid and the alcohol; and (6) the reaction work-up is simple since both of the components of the catalytic dehydrator are insoluble in the reaction media.

The catalytic dehydrator was used in two ways, first, in a column with the acid and alcohol flowing through it and, second, as a component in a stirred mixture of the alcohol and acid. The latter proved more valuable for this study because the exposure time could be more carefully controlled although both were successful. The data in Table I were obtained by the second procedure.

The two reactions studied in detail were chosen on the basis of their equilibrium points and adaptability to glpc analysis. As a control, the extent of esterification at a given time using p-toluenesulfonic acid as the catalyst was given in entries 1–4 and 12 on Table I. Although rate studies using the acid polymer were not undertaken, it was quite apparent from the data of Table I that the esterification rate of 1-butanol was much slower than that of methanol which was in ac-

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[1] N. G. Polyanskii, *Russ. Chem. Rev.*, **39**, 244 (1970).