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(*E*)-α,β-UNSATURATED CARBOXYLIC ESTERS FROM (*E*)-ALKENYLPENTAFLUOROSILICATES BY PALLADIUM-PROMOTED CARBONYLATION[1]

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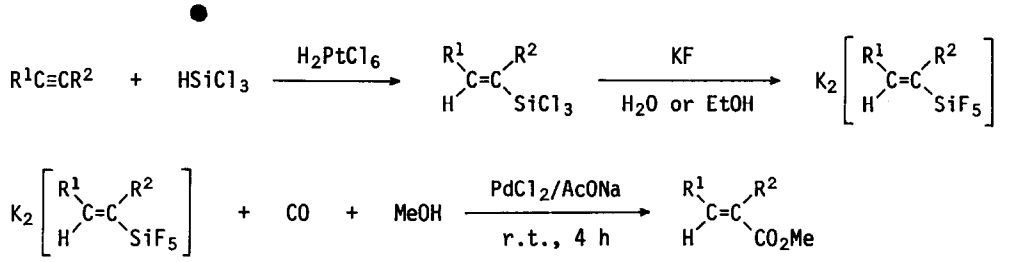
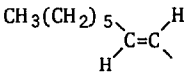
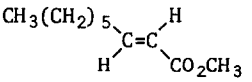
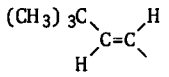
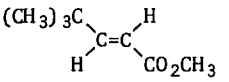
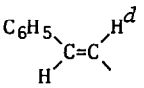
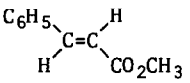
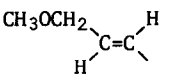
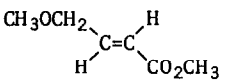
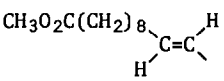
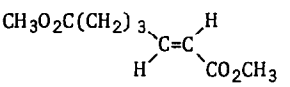
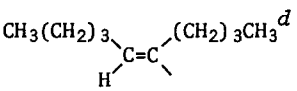
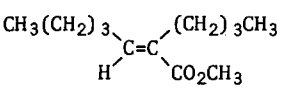
Organopentafluorosilicates, $M_2[RSiF_5]$, have recently been recognized as virsatile intermediates in various organic syntheses.[2] Previously, we have reported that (*E*)-1,4-dienes can be prepared stereoselectively by the reaction of (*E*)-alkenylpentafluorosilicates, readily available by hydrosilylation of alkynes, with allylic halides in the presence of catalytic amounts of palladium salts.[2d] As a further example of virsatility of alkenylpentafluorosilicates in the carbon-carbon bond formation, we present here the carbonylation of alkenylpentafluorosilicates. This reaction is indeed the first case of carbonylation of organosilicon compounds. Thus, we find that (*E*)-alkenylpentafluorosilicates readily react with carbon monoxide (atmospheric pressure) in the presence of palladium salts and sodium acetate in methanol to give (*E*)-α,β-unsaturated carboxylic esters in excellent yields.



The most remarkable feature may be the high stereoselectivity of the carbonylation step. The platinum-catalyzed hydrosilylation of 1-alkynes, excepting *t*-butyl- and phenyl-acetylene, forms terminal (*E*)-1-alkenylsilanes mainly, together with non-terminal adducts as minor products.[3] Since these isomers can be separated by fractional distillation, the present procedure provides

Table I. Carbomethoxylation of $K_2[RSiF_5]$[a]

R in $K_2[RSiF_5]$	Product	Yield (%)[b]
		91 (83)[c]
		90
 [d]		76
		61 (57)[c]
		72
 [d]		88
C_6H_5-	$C_6H_5CO_2CH_3$	trace
$C_6H_5CH_2$-	$C_6H_5CH_2CO_2CH_3$	trace

[a] Carried out on a 1-mmol scale in the same manner as described in the text, unless otherwise noted. [b] Yields were determined by GLC, based on the silicate. [c] A 3-mmol scale reaction, product being isolated by distillation. [d] These silicates were prepared in EtOH, others in H_2O.

the regio- and stereo-selective transformation of alkynes into (*E*)-α,β-unsaturated carboxylic esters. The use of sodium acetate as a base afforded the most satisfactory results; tertiary amines in place of sodium acetate gave only moderate to poor yields, *e.g.*, yield of methyl 2-nonenoate was 40% with Et_3N and 20% with pyridine. While $PdCl_2$ and $PdBr_2$ exhibited similar reactivities, $Pd(OAc)_2$ was somewhat less active and no carbonylation occurred with $PdCl_2(PPh_3)_2$. The carbonylation proceeded smoothly at room temperature (around 25°C), but very slowly at 0°C.

Simplicity and efficiency of the present reaction are demonstrated by the following typical

procedure. To a mixture of $K_2[(E)\text{-}C_6H_{13}CH{=}CHSiF_5]$ (936 mg; 3.0 mmol), sodium acetate (480 mg; 5.9 mmol) and anhydrous methanol (15 ml), through which had been bubbled carbon monoxide during 5 min, was added palladium chloride (585 mg; 3.3 mmol). The mixture was stirred under the carbon monoxide atmosphere (a CO balloon) at room temperature (ca. 25°C) for 4 h. Almost immediately the color changed from brown to black (possibly palladium black). Ether was added and the mixture filtered. The filtrate was washed three times with 10% NaCl aqueous solution, dried over magnesium sulfate, and distilled (bulb-to-bulb) to give 424 mg (83% yield) of methyl (*E*)-2-nonenoate: ^{1}H NMR (100 MHz, CCl_4, TMS) δ 0.92 (t, 3H), 1.33 (br. 8H), 2.20 (br. q, 2H), 3.67 (s, 3H), 5.76 (double t, J = 16Hz, 1Hz, 1H), 6.86 (double t, J = 16Hz, 7Hz, 1H); IR, 1730, 1660, 975 cm^{-1}.

Representative results summarized in Table I were obtained under the same conditions as above. The present procedure —— a sequence of hydrosilylation of alkynes, silicate formation, and carbonylation —— is capable of tolerating some functional groups such as ester and ether. An internal alkenyl-silicate was also carbonylated with equal efficiency, as shown by the preparation of methyl (*E*)-2-butyl-2-heptenoate, the authentic sample of which was prepared by the hydroalumination-carboxylation procedure.[4] Phenyl- and alkyl-silicates, unfortunately, gave only trace amounts of carbonylation products.[5]

Preparation of α,β-unsaturated carboxylic esters via carbonylation of organometallics has so far been known only for alkenylmercurials.[6] While carbonylation of alkenyl halides with nickel carbonyl proceeds with retention of configuration,[7] palladium-catalyzed reactions suffer from rather low stereoselectivity.[8] Our present procedure, therefore, provides a convenient, practically useful, and stereoselective route to (*E*)-α,β-unsaturated carboxylic esters from acetylenes.

Although the mechanism has not yet been clarified, the reaction may proceed most probably via the carbon monoxide insertion into an alkenyl-palladium bond[9] resulting from the transfer of the alkenyl group from silicon to palladium(II). Mechanistic study and applications of this carbonylation reaction are now in progress.

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