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A STEREOSELECTIVE SYNTHESIS OF SYMMETRICAL (*E*,*E*)-1,3-DIENES BY SILVER(I) PROMOTED HOMO COUPLING OF (*E*)-ALKENYLPENTAFLUOROSILICATES[1]

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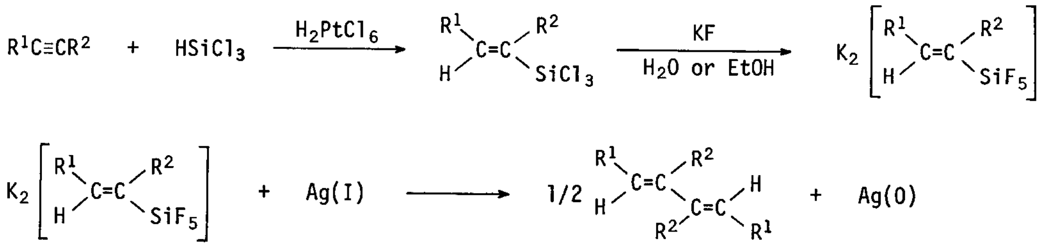
Summary: Symmetrical (*E*,*E*)-1,3-dienes can be prepared in high yields from (*E*)-alkenylpentafluorosilicates either by treating with silver fluoride in acetonitrile or by stirring with silver nitrate in water/ether.

There have been a number of methods for the preparation of 1,3-dienes, but most of them bring some limitations and difficulties into practice, because some require air-sensitive or sophisticated organometallic reagents, many of which are reactive enough toward common functional groups, and others require drastic reaction conditions, and/or suffer from rather low stereoselectivity.[2] We now find that the title procedure uses air-stable reagents with a rather wide functional group compatibility, requires mild reaction conditions, and gives (*E*,*E*)-1,3-dienes in a highly stereoselective fashion, and hence provides one of the most practically useful, general methods for the preparation of such compounds.

Mueller and his coworkers have previously reported,[3] as part of their excellent pioneering works on organopentafluorosilicates, that 1,3-butadiene and perfluorobutadiene can be prepared from the corresponding vinyl- and perfluorovinyl-silicate by the action of silver(I) nitrate or copper(II) sulfate in water in the presence of fluoride ions. In exploring new synthetic methods using organopentafluorosilicates,[1,4] we were interested in the stereoselectivity of such silver promoted coupling reaction of (*E*)-alkenylpentafluorosilicates, since they are readily obtainable by hydrosilylation of alkynes and silicate formation as mentioned previously,[1,4d] and have found that the reaction proceeds indeed highly stereoselectively with retention of configuration at the double bond.



Coupling reactions are greatly dependent upon the nature of silver salts and reaction media. Thus, the yields of (*E*,*E*)-5,7-dodecadiene from (*E*)-hexenylpentafluorosilicate by the action of various silver(I) salts in acetonitrile at room temperature for 1 day, varied as follows: AgF 86%, $AgNO_3$ 47%, $AgBF_4$ 41%, AgO_2CCH_3 and AgCl 0%. Yields in the reaction with AgF in various solvents were 68% in benzene, 57% in DMF, 16% in THF, and 14% in EtOH. It should also be noted that the reaction with $AgNO_3$ in water in the absence of fluoride ion gave 66% yield of the dodecadiene. These data showed that the following two reaction conditions may be most practically useful and convenient.

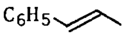
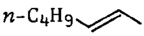
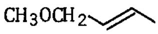
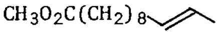
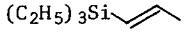
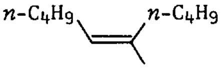
Condition A: Treatment with one equivalent of AgF in acetonitrile at room temperature for 1 day.

Condition B: Stirring with a two-phase mixture of an aqueous solution of $AgNO_3$ and ether at room temperature for less than 2 hours.

Representative results are summarized in Table I. As mentioned by Mueller as the color test for the organopentafluorosilicates,[5] characteristic color appeared immediately after silicates were mixed with silver salts. The color gradually disappeared during the course of the reaction, and at the end of the reaction the color changed to grey-black (condition A) or off-white (condition B), with the deposition of silver mirror or leaves occurring at the same time. Therefore the reaction could be monitored by color change, particularly in reactions under condition B, since the rather rapid reaction proceeds with a sharp change in color. The colors are also included in the table. In all cases the isomeric purity of the (*E*,*E*)-structure was higher than 99%, as confirmed by GLC (SE-30, 30% on Celite 545, 3m glass column), ^1H NMR, and IR spectra, and/or, if available, by comparison of spectral and physical properties with those reported in the literature.[2] There seems to be a tendency that condition A is suitable for the coupling of simple alkenylsilicates having no functional groups, while condition B is more widely useful for functional group substituted alkenylsilicates and also internal alkenylsilicates.

There is no significant difference in reactivity between a terminal alkenylsilicate and an

Table I. Homo Coupling of $K_2[RSiF_5]$ Promoted by Ag(I) Salts

R in $K_2[RSiF_5]$	Condition A (AgF/CH_3CN)[a]		Condition B ($AgNO_3/H_2O$)[a]	
	Color[b]	Yield (%)[c] of R-R	Color[b]	Yield (%)[c] of R-R
	Red purple	74	Blue	64
	Blue purple	63 (86)	Red purple	47 (66)
	Blue	(10)	Blue	51 (61)
	Red	36	Blue	65
	Red	43 (51)	Blue	58
	Orange	26	Orange	72
C_6H_5-	Orange	82 (93)	Orange	60 (69)
$C_6H_5CH_2$-	Yellow	46 (60)[d]	Colorless	0[d]
n-C_8H_{17}-	Colorless	0[d]	Colorless	0[d]

[a] See text for details. [b] Characteristic color of the initial reaction mixture (see text). [c] Isolated yield. GLC yields are given in parentheses. [d] Under N_2.

internal alkenylsilicate. Thus, a mixture of $K_2[(E)\text{-}C_4H_9CH{=}CHSiF_5]$ and $K_2[CH_2{=}C(C_4H_9)(SiF_5)]$, prepared from a 90/10 mixture of the corresponding trichlorosilyl precursors, gave, upon treatment with AgF in acetonitrile, an 80/20 mixture of $(E,E)\text{-}C_4H_9CH{=}CHCH{=}CHC_4H_9$ and $(E)\text{-}C_4H_9CH{=}CH\text{-}C(C_4H_9){=}CH_2$.[2c]

The present silver(I) promoted coupling can also be extended to the phenylsilicate giving biphenyl in high yields under both conditions. While the benzylsilicate gave bibenzyl under condition A, the octylsilicate formed no coupling product under both the conditions. Coupling of the octylsilicate was observed only by the reaction with $AgBF_4$ in CH_2Cl_2 at room temperature under nitrogen atmosphere, but yields were rather low (20 - 28%).

Typical procedures are given for conditions A and B.

Condition A: A mixture of $K_2[(E)\text{-}C_4H_9CH{=}CHSiF_5]$ (1.38 g; 4.88 mmol), silver fluoride (purity 84%, 0.739 g; 4.89 mmol), and dry acetonitrile (15 mL) was stirred at room temperature (not higher than about 20°C) for 1 day. The color changed from purple to grey-black. The mixture was diluted with ether and filtered. The filtrate was washed with a saturated aqueous solution of sodium chloride, dried over sodium sulfate and the solvents evaporated. The residue was column-chromatographed (silica-gel, hexane) to give pure (*E,E*)-5,7-dodecadiene (0.261 g; 64% yield); ^{1}H NMR (100 MHz, CCl_4, TMS) δ 0.89 (deformed t, *J*=6 Hz, 6H), 1.1-1.6 (m, 8H), 1.9-2.2 (m, 4H), 5.3-5.7 (m, 2H), 5.7-6.1 (m, 2H) ppm. IR (neat) 987 cm^{-1}.

Condition B: To an aqueous solution of silver nitrate (0.517 g; 3.42 mmol in 10 mL of water) were added successively $K_2[(E)\text{-}CH_3OCH_2CH{=}CHSiF_5]$ (0.814 g; 2.99 mmol) and 5 mL of ether. The resulting dark blue mixture was stirred at room temperature until the color disappeared (<2 h) and filtered. The organic layer separated from the filtrate was washed with an aqueous solution of sodium chloride, dried over sodium sulfate, and concentrated. The residue was distilled (bulb-to-bulb) gave 1,6-dimethoxy-(*E,E*)-2,4-hexadiene (0.116 g; 55% yield); ^{1}H NMR (100 MHz, CCl_4, TMS) δ 3.23 (s, 6H), 3.87 (d, *J*=6 Hz, 4H), 5.4-5.8 (m, 2H), 6.0-6.3 (m, 2H) ppm. IR (neat) 1110, 992 cm^{-1}.

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