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COUPLING REACTIONS OF VINYLKETENE SILYL ACETALS PROMOTED BY TITANIUM TETRACHLORIDE

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Summary: Homo- and cross-couplings of vinylketene silyl acetals were found to be effectively promoted by titanium tetrachloride to give the corresponding unsaturated diesters in good yields. The reactions between two different ketene silyl acetals afforded the corresponding cross-coupling products in unexpectedly good selectivities.

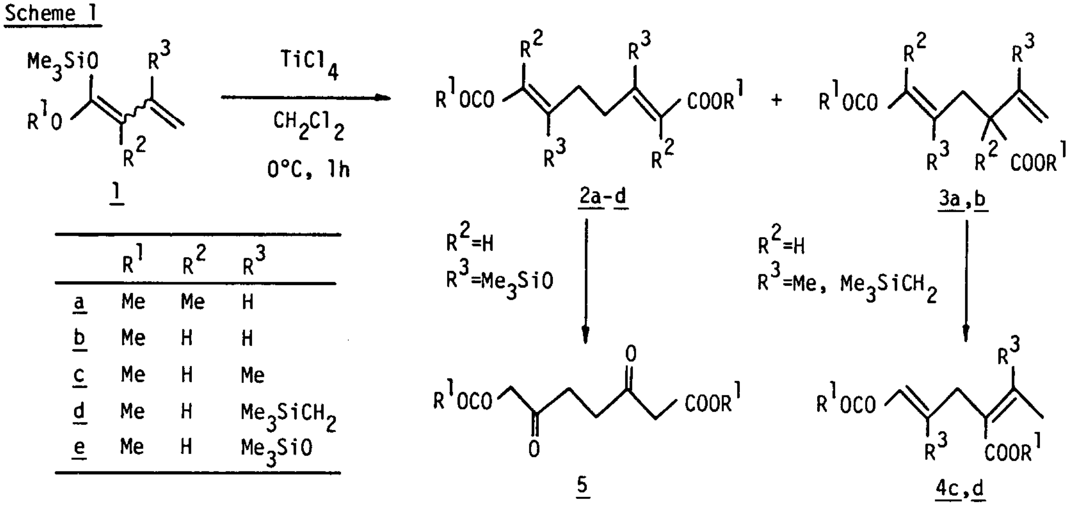
It has been shown that ketene silyl acetals serve as versatile reagents for a variety of carbon-carbon bond formations in organic syntheses.[1] Besides the extensively studied reactions with various carbonyl compounds and acetals in the presence of Lewis acids,[1] we reported previously a novel and effective homo-coupling of ketene silyl acetals promoted by titanium tetrachloride, which gave substituted succinates in good yields,[2] and a novel and convenient route to β-lactams by reacting ketene silyl acetals with Schiff bases in the presence of titanium tetrachloride.[3] In the course of our study along this line, we have studied the oxidative couplings of vinylketene silyl acetals promoted by titanium tetrachloride. Now, we describe here interesting features of homo- and cross-couplings of vinylketene silyl acetals which give the corresponding unsaturated diesters or diketo esters.

Vinylketene silyl acetals (1) were prepared from the corresponding unsaturated esters and keto esters following the literature methods.[4] These acetals were easily purified by distillation under the reduced pressure.[5] The homo-coupling of 1 was carried out simply by mixing 1 and an equimolar amount of titanium tetrachloride in dichloromethane.

In a typical run, the 1M solution of titanium tetrachloride in dichloromethane (10 ml, 10 mmol) was added to the dichloromethane solution (10 ml) of vinylketene silyl acetal, 1b, (1.72 g, 10 mmol) at 0°C with stirring. The color of the solution changed from colorless to dark brown immediately. After an hour, the reaction mixture was hydrolyzed by adding 10 ml of water and extracted several times with dichloromethane. The removal of solvent gave a pale yellow oil (1.49 g, 98% yield) containing two kinds of coupling products, 2b and 3b. The ratio of 2b/3b was determined to be 83/17 on the basis of GLC analysis. Identifications of these coupling products were made based on IR and NMR analyses after isolation by preparative GLC.[6] Typical results are summarized in Table 1.

It was found that the major product (2) was arising from terminal-terminal (γ-γ) coupling and the minor one (3) or (4) from terminal-internal (γ-α) coupling on the basis of NMR analyses. As Table 1 shows, the ratio of the (γ-γ) coupling product to the (γ-α) coupling product is affected by the substituent(s) of the starting vinylketene silyl acetal. For example, when methyl is attached to α-position (1a, R^2=Me), the (γ-γ) coupling product, 2a, is obtained in 96% selec-

Scheme 1



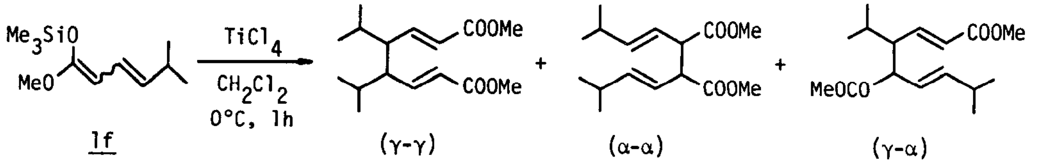
	R^1	R^2	R^3
a	Me	Me	H
b	Me	H	H
c	Me	H	Me
d	Me	H	Me$_3$SiCH$_2$
e	Me	H	Me$_3$SiO

Table 1. Homo-coupling of Vinylketene Silyl Acetals Promoted by Titanium Tetrachloride.

Vinyl Ketene Silyl Acetal				Conditions		Yield$^{a)}$	Ratio of Products$^{b)}$		
1	R^1	R^2	R^3	Temp(°C),	Time(h)	(%)	2	3	4
a	Me	Me	H	5	1	98	96	4	
b	Me	H	H	5	1	98	83	17	
c	Me	H	Me	5	1	76	64		36
d	Me	H	Me$_3$SiCH$_2$	5	1	81	58		42
e	Me	H	Me$_3$SiO	5	1	54$^{c)}$	100$^{c)}$		

a) Isolated yield. b) by glc. c) 1.4-Diketone 5

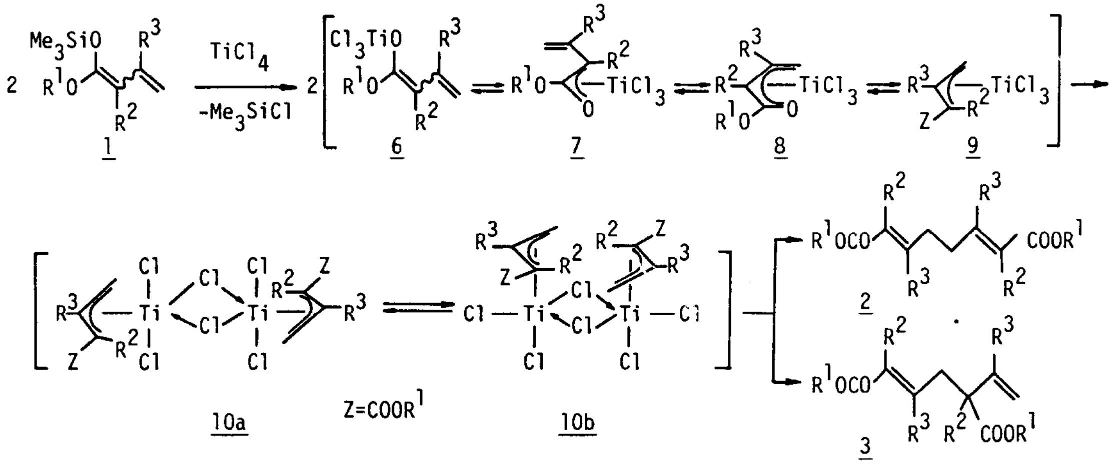
tivity, whereas the substituent at β-position decreases the selectivity of the (γ-γ) coupling. The diester, 4, should be formed by the isomerization of 3. It should be noted that no internal-internal (α-α) coupling products were obtained at all in the cases mentioned above (1a~1d). The vinylketene silyl acetal, 1e, reacted with two equivalents of titanium tetrachloride to give a 1,4-diketone, 5, in 54% yield after hydrolysis.[7] In this case, neither the (γ-α) nor the (α-α) coupling product was detected at all by GLC analysis. On the other hand, when a bulky group is attached to γ-position, i.e. in the case of 1f, the (α-α) coupling product is obtained together with the (γ-γ) and (γ-α) coupling products (eq. 1). The (α-α)/(γ-γ) ratio could not determined accurately because of an equilibrium between two products by facile Cope rearrangement in GLC columns: [(γ-γ)+ (α-α)]/(γ-α)=60/40.



(1)

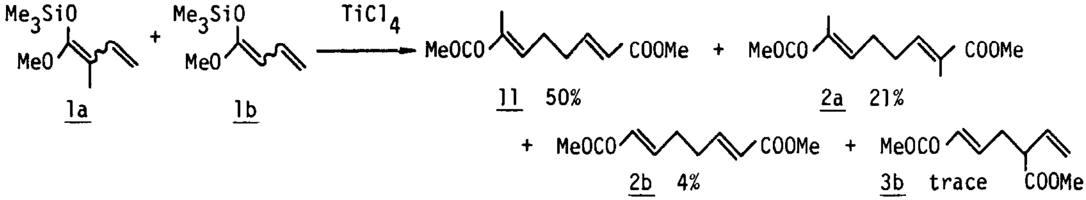
As for a possible mechanism of the present homo-coupling, we propose the one including bis-allylic dititanium complexes (10) as key intermediates, which would be formed via titanium di-enolate (6), oxo-pentadienyl titanium (8) and allylic titanium (9) species, as shown in Scheme 2.

Scheme 2

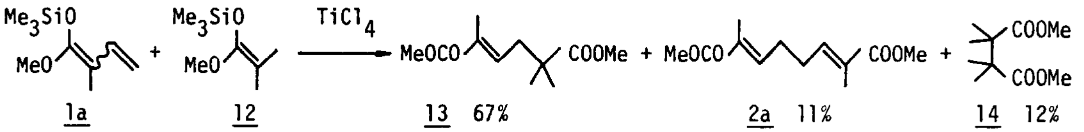


Cross-coupling of a vinylketene silyl acetal with another vinylketene silyl acetal or with a usual ketene silyl acetal was carried out by using titanium tetrachliride as the promoter in a similar manner to that of the homo-coupling.

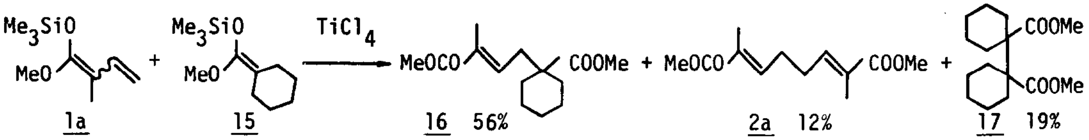
Typical procedure is as follows. To the equimolar mixture of 1a (2.00 g, 10.7 mmol) and 12 (1.87 g, 10.7 mmol) in dichloromethane (20 ml) was added the 1M solution of titanium tetrachloride in dichloromethane (21.4 ml) at 0°C with vigorous stirring. After an hour, the reaction mixture was treated in a similar procedure to that of the homo-coupling. A pale yellow oil (2.0 g, 85% yield) containing a cross-coupling product, 13, and homo-coupling products, 2a and 14, was obtained.[8] The ratio of 13/2a/14 was determined to be 75/12/13 by GLC analysis.



(2)



(3)



(4)

Typical results are exemplified in eqs. 2-4. It is noteworthy that these cross-coupling products were obtained in considerably higher selectivities than those anticipated for random coupling. For example, the reaction of 1a with 12 afforded the cross-coupling product (13) in 75% selectivity; 1b → 11, 67% selectivity; 15 → 16, 66% selectivity, respectively.

Further studies on the mechanism of the present homo- and cross-coupling reactions are actively underway.

References and Notes

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2. S. Inaba and I. Ojima, Tetrahedron Lett., 2081 (1977).
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5. The distillation of ketene silyl acetals should be carried out at temperatures below 70°C. Above that temperature, [1,5]-migration of trimethylsilyl group took place to give γ-silyl-α,β-unsaturated esters. cf. G. Anderson, D. W. Cameron, G. I. Feutrill, R. W. Read, Tetrahedron Lett., 22, 4347 (1981).
6. 2b: IR(neat); 2970, 1729, 1665, 1436, 1275, and 1208 cm^{-1}. NMR(CDCl$_3$, ppm); δ2.37(m, 4H), 3.72(s, 6H), 5.87(d, J=16.5Hz, 2H), 6.95(dt, J=16.5 and 6.0Hz, 1H).
   3b: IR(neat); 2940, 1725, 1655, 1430, 1264, 1190, and 1156 cm^{-1}. NMR(CDCl$_3$, ppm); δ2.55 (m, 2H), 3.18(dt, J=7.0 and 7.0Hz, 1H), 3.68(s, 3H), 3.71(s, 3H), 5.15(m, 1H), 5.18 (m, 1H), 5.82(m, 1H), 5.84(d, J=16.5Hz, 1H), 6.86(dt, J=16.5 and 7.0Hz, 1H).
   Satisfactory spectral data were also obtained for other coupling products.
7. Chan et al. reported in their communication that cyclopentenone derivative was obtained in 52% yield in the reaction of 1e: T. H. Chan and P. Brownbridge, J. C. S. Chem. Commun., 578 (1979). However, in our experiment, cyclopentenone was not obtained at all but 1,4-diketone, 5, was isolated in similar yield.
   5: IR(neat); 2970, 1745, 1720, 1435, 1410, 1325, and 1270 cm^{-1}. NMR(CDCl$_3$, ppm); δ2.83(s, 4H), 3.50(s, 4H), 3.72(s, 6H).
8. Identification of the cross-coupling products were made on the basis of IR and NMR analyses.
   11: IR(neat); 2960, 1724, 1655, 1434, 1268, 1200, 1165, and 1125 cm^{-1}. NMR(CDCl$_3$, ppm); δ1.82 (br s, 3H), 2.32(m, 4H), 3.70(s, 6H), 5.80(d, J=16.5Hz, 1H), 6.68(m, 1H), 6.90(dt, J=16.5 and 6.0Hz, 1H).
   13: IR(neat); 2970, 1735, 1725, 1653, 1435, 1265, 1205, and 1145 cm^{-1}. NMR(CDCl$_3$, ppm); δ1.23 (s, 6H), 1.86(br s, 3H), 2.45(d, J=8.0Hz, 2H), 3.17(s, 3H), 3.76(s, 3H), 6.73(m, 1H).
   16: IR(neat); 2925, 1720, 1650, 1430, 1256, 1190, and 1128 cm^{-1}. NMR(CDCl$_3$, ppm); δ1.08-1.68 (m, 8H), 1.80(s, 3H), 1.90-2.25(m, 2H), 2.35(d, J=6.0Hz, 2H), 3.65(s, 3H), 3.70(s, 3H), 6.65 (m, 1H).

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