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Carbon-Carbon Bond Formation by Cross Coupling of Enol Phosphates or Enol Triflates with Organomanganese Compounds

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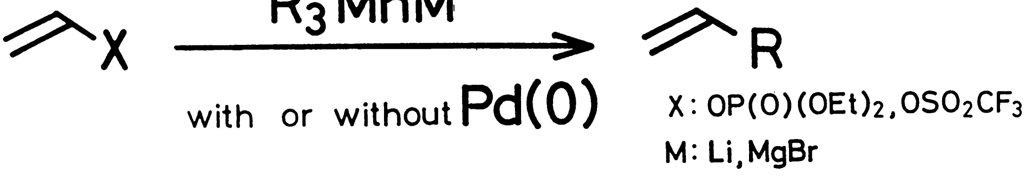
Trialkylmanganese-mediated alkylation of enol phosphates is performed in the presence of a catalytic amount of $Pd(PPh_3)_4$. The cross coupling reaction catalyzed by Li_2MnCl_4 between enol triflates and Grignard reagents is also described.

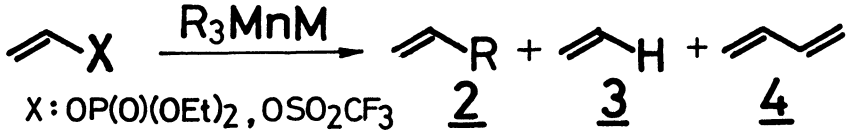
Organoaluminium compounds react with enol phosphates to give alkylative coupling products in the presence of a catalytic amount of Pd(0).[1)] The process provides a method of converting ketones into alkyl-substituted olefins regioselectively.[2)] Here we wish to report that trialkylmanganate, R_3MnM (M = Li or MgBr), is also effective for alkylation of enol phosphates or enol triflates.[3)]

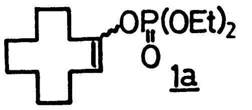
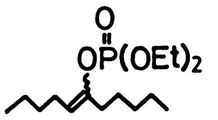
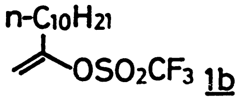
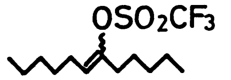
An ethereal solution of PhLi (1.5 M, 1 M = 1 mol dm^{-3}, 4.0 ml, 6.0 mmol) was added to a solution of Li_2MnCl_4 (2.0 mmol) in THF under an argon atmosphere at 0 °C. After stirring for 15 min, a solution of enol phosphate **1a** (0.32 g, 1.0 mmol) and $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol) were added to the solution of triphenylmanganese compound, Ph_3MnLi.[4,5)] The whole was heated at reflux for 2 h. The mixture was diluted with hexane and saturated aqueous NH_4Cl (0.5 ml) was added. The resulting precipitate was filtered and the filtrate was dried and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give 1-phenyl-1-cyclododecene (0.20 g, 82% yield).



The results of the reaction between enol phosphates or enol triflates with R_3MnM are summarized in Table 1. Several comments are worth noting. (1) The reaction of enol phosphates with R_3MnM required the coexistence of Pd(0) catalyst and heating of the reaction mixture was essential for the completion of the reaction. On the other hand, alkylation of enol triflates with R_3MnM proceeded smoothly at room temperature without any catalysts. (2) In general,

Table 1. Cross coupling reactions between enol phosphates or enol triflates with R_3MnM



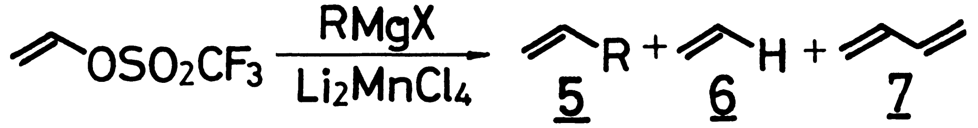
Entry	Enol phosphate (Enol triflate)	R_3MnM	Catalyst	Yield/%		
				2	3	4
1	 **1a**	Me_3MnLi	$Pd(PPh_3)_4$ a)	67	0	<8
2		$n\text{-}Bu_3MnLi$	$Pd(PPh_3)_4$	50	39	<8
3		Ph_3MnLi	$Pd(PPh_3)_4$	82	0	0
4		$n\text{-}Bu_3MnLi$	$Pd(PPh_3)_4$	34	29	0
5		Ph_3MnLi	$Pd(PPh_3)_4$	73	0	0
6		$Ph_3MnMgBr$	$Pd(PPh_3)_4$	48	0	0
7	 **1b**	Me_3MnLi	—— b)	86	0	0
8		$n\text{-}Bu_3MnLi$	——	93	1	6
9		Ph_3MnLi	——	100	0	0
10		$Ph_3MnMgBr$	——	93	0	<6
11		$n\text{-}Bu_3MnLi$	——	75	25	0
12		Ph_3MnLi	——	87	0	0

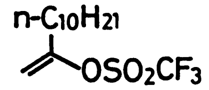
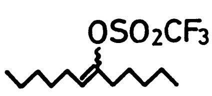
a) R_3MnM (2.0 mmol), enol phosphate (1.0 mmol), and $Pd(PPh_3)_4$ (0.1 mmol) were employed. The reaction mixture was heated at reflux for 2 h. b) A mixture of R_3MnM (3.0 mmol) and enol triflate (1.0 mmol) was stirred at 25 °C for 1 h.

the reagents R_3MnLi derived from Li_2MnCl_4 and alkyllithium were superior to the reagents R_3MnMgX generated from Grignard compounds. For instance, treatment of enol triflate, $CH_2=C(OSO_2CF_3)\text{-}n\text{-}C_{10}H_{21}$ (**1b**) with Me_3MnMgI gave the desired 2-methyl-1-dodecene in only 30% yield along with the recovered starting material (50%) under the same reaction conditions as entry 7 in Table 1. (3) Lithium tri-n-butylmanganate was considerably less effective as cross coupling reagents than the trimethyl analog. The formation of the byproducts such as reduced alkene **3** (replacement of $OP(O)(OEt)_2$ or OSO_2CF_3 by H) and symmetrical coupling product **4** was observed. The former byproduct might be derived from the reaction of enol phosphates or enol triflates with H_3MnM (or R_2HMnM, RH_2MnM) generated in situ by the decomposition of R_3MnM (R = n-Bu).

The amount of Li_2MnCl_4 could be reduced to a catalytic amount in the case of the reaction between enol triflates and Grignard reagents. The results are summarized in Table 2. The use of Grignard reagent was essential for the

Table 2. Li_2MnCl_4 catalyzed cross coupling reactions of enol triflates with Grignard reagents[a]



Entry	Enol triflate	RMgX	Reaction time/h	Product/% 5	6	7
1	 **1b**	MeMgI	15	35	0	0[b]
2		EtMgBr	42	24	5	30[c]
3			44	6	8	20
4		PhMgBr	5	80	0	15
5		$PhCH_2MgCl$	3	76	0	20
6			2	92	0	0
7			3	74[d]	0	0
8		$PhCH_2MgCl$	24	79	0	0
9			1	44[e]	0	0

a) Grignard reagent (3.0 mmol) was added to a solution of enol triflate (1.0 mmol) in the presence of Li_2MnCl_4 (0.1 mmol) at 0 °C and the resulting mixture was stirred at 25 °C. b) Starting material (63%) was recovered. c) Starting material (26%) was recovered. d) See Ref. 6. e) A mixture of (2E)-5-pentyl-2,5-undecadiene and 3-methyl-4-pentyl-1,4-decadiene (1:1) was obtained.

successful reaction. The reaction of enol triflate **1b** with methyllithium in the presence of Mn catalyst gave 2-dodecanone upon workup because the RLi caused nucleophilic attack on sulfur atom. The reaction proceeded well only with certain organomagnesium reagents such as PhMgBr, $PhCH_2MgCl$, and allylmagnesium bromide.[7]

References

1) K. Takai, M. Sato, K. Oshima, and H. Nozaki, Bull. Chem. Soc. Jpn., 57, 108 (1984).
2) Ni(0)-catalyzed coupling reactions of organomagnesium reagents under C-O bond fission have been reported. Enol ether: E. Wenkert, E. L. Michelotti, and C. S. Swindell, J. Am. Chem. Soc., 101, 2246 (1979). Enol silyl ether: T.

Hayashi, Y. Katsuro, and M. Kumada, Tetrahedron Lett., 21, 3915 (1980). Enol triflates with R_2CuLi: J. E. McMurry and W. J. Scott, Tetrahedron Lett., 21, 4313 (1980).

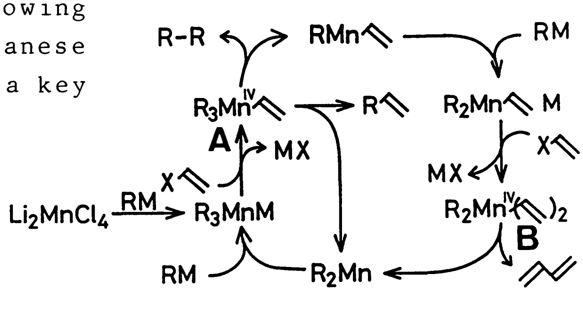
3) The reaction of enol phosphates with $(R_3Si)_3MnMgMe$ has been reported to give vinylsilanes. K. Fugami, K. Oshima, K. Utimoto, and H. Nozaki, Tetrahedron Lett., 27, 2161 (1986).

4) J. F. Normant, Organocopper and Organomanganous reagents in "Modern Synthetic Methods", Vol. 3, R. Scheffold ed., Otto Salle Verlag GmbH & Co., Frankfurt am Main, pp. 139-216 (1983). T. Kauffmann and M. Bisling, Tetrahedron Lett., 25, 293 (1984).

5) Cross coupling reaction between alkenyl halides and R_3MnLi has been reported. E. J. Corey and G. H. Posner, Tetrahedron Lett., 1970, 315; G. Cahiez, D. Bernard, and J. F. Normant, J. Organomet. Chem., 113, 107 (1976).

6) A mixture of 3-methyl-4-methylene-1-tetradecene (**8**) and (E)-5-methylene-2-pentadecene (**9**) (44:56) was obtained. IR (neat) 2922, 2852, 1719, 1655, 1466, 1459, 967, 910, 889 cm^{-1}. The analytical samples were prepared by preparative glpc (Silicone OV-1, 2% Uniport-HP, 130 °C, t_r = 5.7 min for **8** and 7.0 min for **9**). **8**: ^1H-NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.13 (d, J = 7.5 Hz, 3H), 1.27 (bs, 14H), 1.3-1.5 (m, 2H), 2.01 (t, J = 8.5 Hz, 2H), 2.79 (dq, J = 7.2, 7.5 Hz, 1H), 4.7-4.8 (m, 2H), 4.97 (ddd, J = 10.1, 1.8, 1.0 Hz, 1H), 5.01 (ddd, J = 17.3, 1.9, 1.0 Hz, 1H), 5.77 (ddd, J = 17.3, 10.1, 7.2 Hz, 1H). Found: C, 86.26; H, 13.85%. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60%. **9**: ^1H-NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.25 (bs, 14H), 1.2-1.5 (m, 2H), 1.6-1.7 (m, 3H), 1.98 (t, J = 7.5 Hz, 2H), 2.6-2.7 (m, 2H), 4.7-4.8 (m, 2H), 5.4-5.5 (m, 2H). Found: C, 86.37; H, 13.88%. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60%.

7) We are tempted to assume the following reaction mechanism. Trialkylmanganese reacts with enol triflate to give a key intermediate Mn(IV) species **A**.[8] The reductive elimination of alkyl and alkenyl groups provides the cross coupling product and dialkylmanganese R_2Mn. The addition of RM to R_2Mn regenerates R_3MnM. Meanwhile, the formation of the byproduct, diene **7** presumably is explained by the reductive elimination of R-R from **A** to give alkylalkenylmanganese(II) compound and subsequent generation of another Mn(IV) species **B** followed by the reductive elimination of two alkenyl groups.



8) The formation of Mn(IV) species has been proposed in the symmetrical coupling of iodoalkenes to dienes on treatment with organolithium in the presence of Mn(II) salt. G. Cahiez, D. Bernard, and J. F. Normant, J. Organomet. Chem., 113, 99 (1976).

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