Titanium Oxide-Supported Carbonylmolybdenum Catalyst in Liquid Phase: Application to Allylic Alkylation of Methyl *p*-Tolylsulfonylacetate

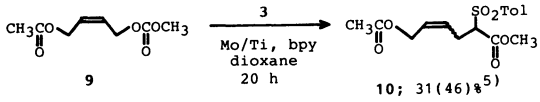
Yoshiro MASUYAMA,* Yutaka MITSUNAGA, Yasuhiko KURUSU, and Koh-ichi SEGAWA
Department of Chemistry, Faculty of Science and Technology, Sophia University,
7-1 Kioicho, Chiyoda-Ku, Tokyo 102
(Received March 26, 1987)

Synopsis Titanium oxide-supported carbonylmolybdenum catalyst was applied to selective monoallylation of methyl *p*-tolylsulfonylacetate using allylic acetates or carbonates in refluxing dioxane. This reaction required both 2,2′-bipyridyl as a ligand and sodium hydride as a base for preparation of the salt of methyl *p*-tolylsulfonylacetate.

We have applied metal oxide-supported carbonylmolybdenum [$Mo(CO)_3$–metal oxide] catalyst to allylic alkylation of carbon nucleophiles using allylic acetates.[1] The $Mo(CO)_3$–TiO_2 catalytic system is superior to others, and exhibits desirable characteristics as regards 1) long life and easy separation of the catalyst and 2) regio- and stereochemistry. Application of sulfones which stabilize an adjacent carbanion as carbon nucleophiles, instead of diethyl malonate or ethyl 2-oxocyclopentanecarboxylate, should further enhance the desirability of the $Mo(CO)_3$–TiO_2 catalyst in the allylic alkylation.[2] Homogeneous $Mo(CO)_6$ catalyst did not catalyze any reactions of allylic acetates with sulfones, whereas allylic carbonates did serve as allylating agents.[3] Here, we report the selective monoallylation of methyl *p*-tolylsulfonylacetate with several allylic acetates or carbonates by means of the $Mo(CO)_3$–TiO_2 catalytic system.

The reactions of 2-butenyl acetate (**1a**) or 2-butenyl methyl carbonate (**2b**) with the salt **3**, derived from methyl *p*-tolylsulfonylacetate and sodium hydride, were investigated under various conditions. The reaction proceeded in the presence of both the $Mo(CO)_3$–TiO_2 catalyst and 2,2′-bipyridyl (bpy) in refluxing dioxane. Some examples are shown in the Table 1. Neither **1a** nor **2b** reacted with **3** in refluxing toluene, which is a common solvent.[1,4] Allylic acetates could be utilized in this reaction, which was not the case with the homogeneous $Mo(CO)_6$ system (Entries 1—3).[3] However, the reactivity of the allylic acetates was less than that of the corresponding allylic carbonates. Monoallylation occurred selectively without diallylation. *p*-Tolylsulfonylacetonitrile, which was a good nucleophile in the homogeneous system, did not react under these conditions.[3]

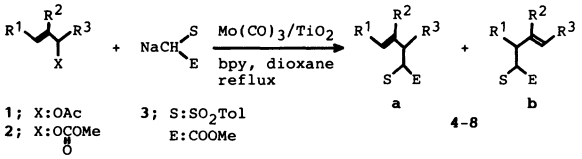
The reaction of **3** with **9**, containing both an allylic acetate moiety and an allylic carbonate moiety, occurred chemoselectively at the carbonate moiety and regioselectively at the less substituted end of the allyl unit (Eq. 1).

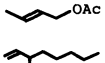
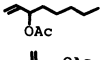
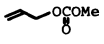
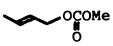
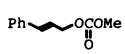


(1)

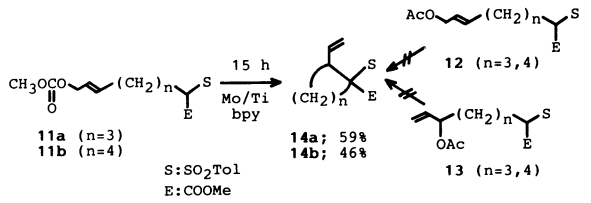
In order to extend this allylic alkylation to a cyclization, several intramolecular reactions were investigated under the same conditions.[6] The sodium salts of carbonates **11a** and **11b** reacted regioselectively to afford five- and six-membered ring compounds **14a** and **14b** respectively. No cyclizations occurred in the case of sodium salts of acetates **12** and **13** under the same conditions (Scheme 1).

Table 1. Allylic Alkylation of **3**



Entry	Allylic compd.		Time / h	Product R¹	R²	R³		Yield[a] / %	Ratio[b] a : b
1		**1a**	15	CH_3	H	H	**4**	33	42 : 58
2		**1b**	31	H	H	n-C_5H_{11}	**5**	36	11 : 89
3		**1c**	24	H	-$(CH_2)_4$-		**6**	40	81 : 19
4		**2a**	19	H	H	H	**7**	67	—
5		**2b**	17	CH_3	H	H	**4**	72	40 : 60
6		**2c**	15	Ph	H	H	**8**	76	33 : 67

a) Isolated yields. b) The ratio was determined by ^1H NMR. Diastereomer ratios: **4a** (60/40), **5a** (60/40), **6a** (71/29), and **8b** (58/42).



Scheme 1.

As mentioned above, the heterogeneous $Mo(CO)_3$–TiO_2 catalyst enabled us to use allylic acetates as allylating agents, and was found to show higher selectivity of monoallylation of **3** than that for homogeneous $Mo(CO)_6$ catalyst and higher chemoselectivity to allylic carbonates than acetates.

Experimental

Reaction of Allylic Acetates 1 or Carbonates 2 with Methyl *p*-Tolylsulfonylacetate. 4: To a solution of salt **3** derived from methyl *p*-tolylsulfonylacetate (0.23 g, 1.0 mmol) with sodium hydride (27 mg, 1.1 mmol) in dioxane (10 ml) were added 2-butenyl acetate (**1a**) (0.11 g, 1.0 mmol) and bpy (8.0 mg, 0.05 mmol) under argon atmosphere. The solution was added to a vessel, in which $Mo(CO)_3$–TiO_2 catalyst, prepared from TiO_2 (0.50 g) and $Mo(CO)_6$ (13 mg, 0.05 mmol),[1] had been placed. This mixture was refluxed for 15 h under argon atmosphere. The reaction mixture was diluted with ether (50 ml) and the catalyst was removed by filtration. Evaporation of solvents followed by purification of the residue by column chromatography (silica gel, hexane–ethyl acetate=3/1) gave the monoallylated product **4** as colorless oil in 33% yield (93 mg). The structure was confirmed by IR and ^1H NMR spectral comparison with an authentic sample.[3]

5: IR (neat) 1735 (C=O), 1320 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ=0.85 (t, J=7.0 Hz, 3H), 1.12—1.36 (m, 6.2H), 1.87—2.00 (m, 1.8H), 2.46 (s, 3H), 2.50—2.77 (m, 1.8H), 2.80—2.94 (m, 0.1H), 3.51 (s, 0.12H), 3.64 (s, 0.18H), 3.66 (s, 2.7H), 3.96 (dd, J=4.0, 11.4 Hz, 0.9H), 3.98, 4.01 (2d, J=2.6 Hz, 0.1H), 5.02—5.10 (m, 0.2H), 5.12—5.31 (m, 0.9H), 5.44—5.57 (m, 0.9H), 5.58—5.66 (m, 0.1H), 7.30—7.40 (m, 2H), and 7.71—7.81 (m, 2H); MS (70 ev) m/z (rel intensity) 338 (M^+, 1), 183 (100), 182 (39), 123 (34), 111 (30), 91 (46), 81 (39), and 67 (33). Found: m/z 338.1546. Calcd for $C_{18}H_{26}O_4S$: M, 338.1550.

6: IR (neat) 1735 (C=O), 1320 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ=1.34—1.97 (m, 5.6H), 2.02—2.17 (m, 1.8H), 2.23—2.35 (m, 0.6H), 2.44(s, 3H), 2.60 (br, 0.4H), 3.06—3.17 (m, 0.8H), 3.43 (s, 1.7H), 3.63 (s, 0.7H), 3.65 (s, 0.6H), 4.11 (dd, J=4.6, 10.8 Hz, 0.2H), 4.43 (d, J=11.7 Hz, 0.56H), 4.49 (d, J=9.8 Hz, 0.24H), 4.61 (s, 0.56H), 4.68 (s, 0.56H), 4.82 (s, 0.24H), 4.84 (s, 0.24H), 5.41 (br, 0.2H), 7.29—7.40 (m, 2H), and 7.72—7.82 (m, 2H); MS (70 ev) m/z (rel intensity) 322 (M^+, 0.7), 167 (82), 166 (100), 138 (26), 135 (50), 107 (46), 94 (40), 91 (58), and 79 (35). Found: m/z 322.1229. Calcd for $C_{17}H_{22}O_4S$: M, 322.1238.

7: The structure was confirmed by IR and ^1H NMR spectral comparison with an authentic sample.[3]

8: IR (neat) 1735 (C=O), 1320 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ=2.41 (s, 3H), 2.75—2.98 (m, 0.66H), 3.62 (s, 1H), 3.68 (s, 0.8H), 3.70 (s, 1.2H), 4.07 (dd, J=8.5, 12.1 Hz, 0.4H), 4.08 (dd, J=4.3, 10.7 Hz,0.33H), 4.18 (dd, J=8.5, 10.1 Hz, 0.27H), 4.50 (d, J=8.5 Hz, 0.4H), 4.54 (d, J=8.5 Hz, 0.27H), 4.99—5.20 (m, 1.34H), 5.80—6.04 (m, 0.67H), 6.23 (dt, J=6.9, 15.9 Hz, 0.33H), 6.47 (d, J=15.9 Hz, 0.33H), 7.02—7.36 (m, 7H), and 7.71—7.82 (m, 2H); MS (70 eV) m/z (rel intensity) 344 (M^+, 0.3), 189 (100), 188 (33), 157 (38), 130 (35), 129 (99), 128 (32), 117 (42), and 91 (41). Found: m/z 344.1080. Calcd for $C_{19}H_{20}O_4S$: M, 344.1081.

10: IR (neat) 1740 (C=O), 1320 and 1140 cm^{-1} (SO_2); ^1H NMR (CCl_4) δ=1.93 (s, 3H), 2.40 (s, 3H), 2.58—2.82 (m, 2H), 3.56 (s, 3H), 3, 88 (dd, J=7,9 Hz,1H), 4.38—4.60 (m, 2H), 5.22—5.71 (m, 2H), 7.29 (d, J=7.5 Hz, 2H), and 7.67 (d, J=7.5 Hz, 2H); MS (70 eV) m/z (rel intensity) 340 (M^+, 0.3), 185 (72), 184 (100), 141 (36), 125 (22), and 91 (23). Found: m/z 340.0976. Calcd for $C_{16}H_{20}O_6S$: M, 340.0979.

Intramolecular Cyclization of 11. 14a: A solution of **11a** (0.19 g, 0.5 mmol) in dioxane (5 ml) was added to the suspension of sodium hydride (17 mg, 0.7 mmol) in dioxane (5 ml) at room temperature under argon atmosphere. The solution followed by bpy (8.0 mg, 0.05 mmol) were added to a vessel, in which $Mo(CO)_3$–TiO_2 catalyst, prepared from TiO_2 (0.50 g) and Mo $(CO)_6$ (13 mg, 0.05 mmol),[1] had been placed. After refluxing for 15 h under argon atmosphere, the mixture was diluted with ether (50 ml) and the catalyst was removed by filtration. Evaporation of solvents followed by purification of the residue by column chromatography (silica gel, hexane–ethyl acetate=2:1) gave the cyclic product **14a** as colorless oil in 59% yield (91 mg). IR (neat) 1735 (C=O), 1310, and 1140 cm^{-1} (SO_2); ^1H NMR (CCl_4) δ=1.44—2.73 (m, 6H), 2.41 (s, 3H), 3.09—3.44 (m, 1H), 3.51 (s, >2.85H), 3.59 (s, <0.15H), 4.84 (d, J=10 Hz, 1H), 4.87 (d, J=16 Hz, 1H), 5.53 (ddd, J=7,10, 16 Hz, 1H), 7.21 (d, J=8 Hz, 2H), and 7.71 (d, J=8 Hz, 2H); MS (70 ev) m/z (rel intensity) 308 (M^+, 0.3), 153 (57), 152 (50), 121 (31), 93 (100), and 91 (39). Found: m/z 308.1082. Calcd for $C_{16}H_{20}O_4S$: M, 308.1081.

14b: IR (neat) 1735 (C=O), 1320, and 1140 cm^{-1} (SO_2); ^1H NMR (CCl_4) δ=0.91—2.36 (m, 8H), 2.40 (s, 3H), 2.60—2.93 (m, 0.6H), 3.04—3.31 (m, 0.4H), 3.51 (s, 1.2H), 3.62 (s, 1.8H), 4.84—5.20 (m, 2H), 6.02—6.51 (m, 1H), 7.07—7.28 (m, 2H), and 7.42—7.64 (m, 2H); MS (70 ev) m/z (rel intensity) 322 (M^+, 0.3), 167 (58), 121 (32), 119 (97), 117 (100), 107 (78), and 91 (23). Found: m/z 322.1236. Calcd for $C_{17}H_{22}O_4S$: M, 322.1237.

References

1) Y, Masuyama, Y. Kurusu, and K. Segawa, *J. Mol. Catal.*, **40**, 183 (1987).

2) B. M. Trost and T. R. Verhoeven, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, Pergamon Press, Oxford (1982), Vol. 8, p. 825; L. S. Hegedus, "Comprehensive Carbanion Chemistry," ed by E. Buncel and T. Durst, Elsevier, Amsterdam (1984), p. 30; R. F. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, London (1985), p. 130.

3) Y. Masuyama, H. Hirai, Y. Kurusu, and K. Segawa, *Bull. Chem. Soc. Jpn.*, **60**, 1525 (1987).

4) B. M. Trost and M. Lautens, *J. Am. Chem. Soc.*, **104**, 5543 (1982); **105**, 3343 (1983).

5) The figure in parentheses is the yield based on the consumed starting material **9**. The ratio of stereoisomers (E/Z) was not determined by ^1H NMR.

6) Preparation of **11** was carried out in the following manner: