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Hexacarbonylmolybdenum(0)-Catalyzed Reaction of Allylic Carbonates with Arylsulfonyl-Stabilized Carbanions

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Synopsis. *p*-Tolylsulfonylacetonitrile reacted with allylic carbonates in the presence of a catalytic amount of hexacarbonylmolybdenum(0) to give monoallylated derivatives. Using sodium hydride as a base, methyl *p*-tolylsulfonylacetate reacted with those to give mixtures of mono- and di-allylated derivatives. No nucleophilic attack of bulky bis-(phenylsulfonyl)methane occurred, whether sodium hydride was present or absent.

Hexacarbonylmolybdenum(0), which is available and stable to oxygen and moisture, is a convenient catalyst for allylic alkylation of carbon nucleophiles with allylic acetates and carbonates.[1] However, sulfones, which stabilize an adjacent carbanion and are easily transformed into other functional groups,[2,3] can not be applied as a carbon nucleophile in this catalytic allylic alkylation yet. If sulfones could be used, the molybdenum-catalyzed allylic alkylation would increase significance as a synthetic tool for the formation of carbon framework in organic synthesis.[4] Here, we wish to report that sulfones, especially *p*-tolylsulfonylacetonitrile reacts with allylic carbonates in the presence of a catalytic amount of $Mo(CO)_6$ to give monoallylated products.

Using methyl *p*-tolylsulfonylacetate (**1**),[5] *p*-tolylsulfonylacetonitrile (**2**),[6] and bis(phenylsulfonyl)methane (**3**)[7] as carbon nucleophile, reactivity of allyl acetate and allyl carbonate for $Mo(CO)_6$-catalyzed reaction was investigated under various conditions. In the case of allyl acetate, neither of carbanions, derived from **1** and **2** with sodium hydride, reacted under the conditions similar to those in the reaction of dimethyl malonate.[1] In refluxing dioxane containing 2,2′-bipyridyl (bpy), a trace of likely product could be detected by thin-layer chromatography. Consequently, investigation of allyl carbonate was attempted using bpy in dioxane, as summarized in Table. **1** did not react under neutral conditions, namely without a base (Entry 1).[8] The use of sodium hydride for the abstraction of proton from **1** caused allylation. However, no selectivity of monoallylation was exhibited, and a mixture of mono- (**4**, 36%) and di-allylated product (40%) was found (Entry 2). On the other hand, the reaction of **2** under neutral conditions provided only monoallylated product in 64% yield (Entry 4). In refluxing THF, the yield was lowered to 16% (Entry 5). Unfortunately, even allyl carbonate did not react with **3**. It seems that steric hindrance of two bulky phenylsulfonyl groups disturbs nucleophilic attack of **3** to π-allylmolybdenum complex.[9] Addition of PPh_3 and *N,N,N′,N′*-tetramethylethylenediamine instead of bpy did not promote the reaction.

The reactions of several allylic carbonates were carried out under the same conditions as Entries 2 and 4 in Table. The results are also summarized in the Table. In the case of crotyl carbonate as well as allyl carbonate, selectivity of **1** to monoallylation was low, while **2** showed high selectivity (Entries 6—8). The reactivity of **2** to α,γ-disubstituted allyl carbonate (2-cyclohexenyl carbonate) was low (Entry 11). Further, geranyl carbonate did not react with **2**. This reaction should be limited by steric demand of both the α-sulfonyl carbanion and the allylic carbonate. At all events, it became possible to employ available *p*-tolylsulfonylacetonitrile (**2**) as the α-sulfonyl carbanion source in the chemistry of π-allylmolybdenum complex.

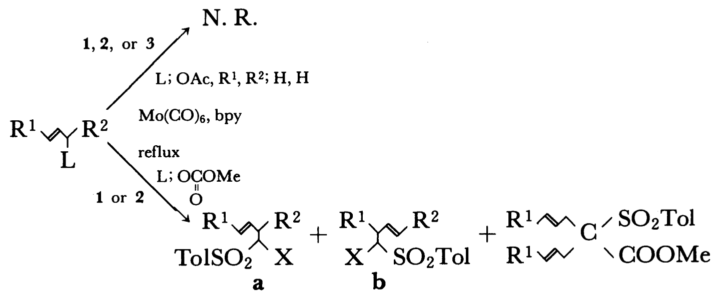
Experimental

Reaction of Allylic Carbonates with Carbon Nucleophiles. 5: To a solution of **2** (0.20 g, 1.0 mmol), allyl methyl carbonate (0.12 g, 1.0 mmol), and bpy (31 mg, 0.20 mmol) in dioxane (10 ml) was added $Mo(CO)_6$ (53 mg, 0.20 mmol) under argon atmosphere. The mixture was refluxed for 48 h. The reaction mixture was diluted with ether (50 ml), washed

Table. Reaction of Allylic Carbonates with **1** and **2**

Entry	Allylic carbonate		NuH	NaH /mmol	bpy /mol%	Solvent	Reaction time/h	Product	Yield[a)] /%	Ratio[b)] a:b
	R^1	R^2								
1	H	H	**1**	—	20	dioxane	48	—	0	—
2	H	H	**1**	1.1	20	dioxane	48	**4**	36(40)	—
3	H	H	**2**	—	—	dioxane	48	**5**	trace	—
4	H	H	**2**	—	20	dioxane	48	**5**	64	—
5	H	H	**2**	—	20	THF	48	**5**	16	—
6	CH_3	H	**1**	1.1	20	THF	70	**6**	19(53)	33 67
7	CH_3	H	**1**	1.1	20	dioxane	47	**6**	15(44)	40 60
8	CH_3	H	**2**	—	20	dioxane	30	**7**	69	22 78
9	Ph	H	**2**	—	20	dioxane	72	**8**	60	15 85
10	H	C_7H_{15}	**2**	—	20	dioxane	73	**9**	55	40 60
11	$-(CH_2)_3-$		**2**	—	20	dioxane	43	**10**	24	—

a) Isolated yields. Figures in parentheses are yields of diallylated products. b) The ratio was determined by ^{1}H NMR (Jeolco FX-200). Diastereomer ratios; **6b** (43/57), **7b** (45/55), **8b** (32/68), and **10** (50/50).



$\mathrm{TolSO_2CH_2COOMe}$ **1**
$\mathrm{TolSO_2CH_2CN}$ **2**
$\mathrm{PhSO_2CH_2SO_2Ph}$ **3**

4 and **6**; X = COOMe
5 and **7**—**10**; X = CN

with 10% aq HCl soln (20 ml) followed by water (2X20 ml), and dried over $\mathrm{MgSO_4}$. Evaporation of ether and column chromatography on silica gel using hexane/EtOAc (2/1) as eluent gave monoallylated product **5** as a colorless oil in 64% yield (0.15 g). IR (neat) 2240 ($\mathrm{C{\equiv}N}$) and 1320, 1140 $\mathrm{cm^{-1}}$ ($\mathrm{SO_2}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=2.48 (s, 3H), 2.41—3.03 (m, 2H), 3.82 (dd, *J*=11, 4 Hz, 1H), 5.20 (d, *J*=10 Hz, 1H), 5.26 (d, *J*=16 Hz, 1H), 5.51—6.05 (m, 1H), 7.38 (d, *J*=8 Hz, 2H), and 7.83 (d, *J*=8 Hz, 2H); MS (70 eV) *m/z* (rel intensity) 235 ($\mathrm{M^+}$, 8), 155 (71), and 91 (100). Found: *m/z* 235.0668. Calcd for $\mathrm{C_{12}H_{13}NO_2S}$: 235.0666.

4: The structure was confirmed by comparison with ^{1}H NMR of the reported one.[10]

6: An oil; IR(neat) 1735 (C=O) and 1320, 1140 $\mathrm{cm^{-1}}$ ($\mathrm{SO_2}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.10 (d, *J*=6.8 Hz, 0.9H), 1.35 (d, *J*=6.8 Hz, 1.2H), 1.61 (d, *J*=6.4 Hz, 0.9H), 2.45 (s, 3H), 2.50—2.88 (m, 0.6H), 2.92—3.15 (m, 0.7 H), 3.51 (s, 1.2H), 3.64 (s, 0.9H), 3.67 (s, 0.9H), 3.98 (d, *J*=9.1 Hz, 0.4H), 3.94 (d, *J*=8.4 Hz, 0.3H), 3.90—3.99 (m, 0.3H), 4.93—5.17 (m, 1.4H), 5.17—5.33 (m, 0.3H), 5.43—5.58 (m, 0.3H), 5.58—5.93 (m, 0.7H), 7.28—7.42 (m, 2H), and 7.69—7.83 (m, 2H); MS (70 eV) *m/z* (rel intensity) 282 ($\mathrm{M^+}$, 0.3), 155 (12), 127 (100), 95 (41), and 91 (44). Found: *m/z* 282.0930. Calcd for $\mathrm{C_{14}H_{18}O_4S}$: 282.0925.

7: An oil; IR (neat) 2240 ($\mathrm{C{\equiv}N}$) and 1320, 1140 $\mathrm{cm^{-1}}$ ($\mathrm{SO_2}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.29 (d, *J*=6.8 Hz, 1H), 1.38 (d, *J*=6.8 Hz, 1.4H), 1.68 (d, *J*=6.1 Hz, 0.6H), 2.47 (s, 3H), 2.76—2.92 (m, 0.4H), 3.13—3.33 (m, 0.8H), 3.91—4.02 (m, 1H), 5.13—5.32 (m, 1.6H), 5.32—5.47 (m, 0.2H), 5.60—6.00 (m, 1H), 7.36—7.48 (m, 2 H), and 7.82—7.93 (m, 2H); MS (70 eV) *m/z* (rel intensity) 249 ($\mathrm{M^+}$, 8), 155 (75), 94 (34), and 91 (100). Found: *m/z* 249.0824. Calcd for $\mathrm{C_{13}H_{15}NO_2S}$: 249.0823.

8: An oil; IR (neat) 2240 ($\mathrm{C{\equiv}N}$) and 1340, 1140 $\mathrm{cm^{-1}}$ ($\mathrm{SO_2}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=2.42 (s, 0.85H), 2.46 (s, 1.7H), 2.47 (s, 0.45H), 2.70—2.86 (m, 0.15 H), 3.00—3.16 (m, 0.15H), 4.01 (dd, *J*=10.4, 4.5 Hz,0.15H), 4.14 (d, *J*=3.2 Hz, 0.57H), 4.22 (br. t, *J*=6.6 Hz, 0.28H), 4.33 (d, *J*=6.6 Hz, 0.28H), 4.38 (dd, *J*=8.1, 3.2 Hz, 0.57H), 5.14—5.36 (m, 1.7H), 6.00—6.33 (m, 1H), 6.57 (d, *J*=15.4 Hz, 0.15H), 7.30 (s, 5 H), 7.24—7.46 (m, 2H), 7.70 (d, *J*=8.3 Hz, 0.57H), 7.85 (d, *J*=8.3 Hz, 1.14H), and 7.89 (d, *J*=8.3 Hz, 0.3 H); MS (70 eV) *m/z* (rel intensity) 311 ($\mathrm{M^+}$, 0.1), 155 (100), 154 (67), 128 (57), 127 (40), and 115 (54). Found: *m/z* 311.0985. Calcd for $\mathrm{C_{18}H_{17}NO_2S}$: 311.0979.

9: An oil; IR (neat) 2240 ($\mathrm{C{\equiv}N}$) and 1320, 1140 $\mathrm{cm^{-1}}$ ($\mathrm{SO_2}$) ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.87 (m, 3H), 1.25 (br, 10.8H), 1.92—2.08 (m, 1.2H), 2.48 (s, 3H), 2.40—2.58 (m, 0.6H), 2.76—2.93 (m, 0.6H), 2.93—3.07 (m, 0.4H), 3.91 (dd, *J*=11.1, 4.3 Hz, 0.6H), 3.84—3.95 (m, 0.4H), 5.15—5.43 (m, 1.4 H), 5.56—5.78 (m, 1H), 7.42 (d, *J*=8.2 Hz, 2H), and 7.86 (d, *J*=8.2 Hz, 2H); MS (70 eV) *m/z* (rel intensity) 333 ($\mathrm{M^+}$, 4), 178 (91), 155 (81), and 91 (100). Found: *m/z* 333.1760. Calcd for $\mathrm{C_{19}H_{27}NO_2S}$: 333.1761.

10: mp 92—94 °C; IR (KBr) 2240 ($\mathrm{C{\equiv}N}$) and 1320, 1140 $\mathrm{cm^{-1}}$ ($\mathrm{SO_2}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.41—2.24 (m, 6H), 2.47 (s, 3H), 2.91—3.22 (m, 1H), 3.67 (d, *J*=4.5 Hz, 0.5 H), 3.76 (d, *J*=5.0 Hz, 0.5 H), 5.27—6.02 (m, 2 H), 7.37 (d, *J*=8 Hz, 2H), and 7.81 (d, *J*=8 Hz, 2 H); MS (70 eV) *m/z* (rel intensity) 275 ($\mathrm{M^+}$, 0.5), 157 (44), 120 (100), and 91 (100). Found: C, 65.92; H, 6.31; N, 4.92%. Calcd for $\mathrm{C_{15}H_{17}NO_2S}$: C, 65.42; H, 6.22; N, 5.08%.

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