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Reductive Deacetoxylation of Allylic Acetates Using Hexacarbonylmolybdenum(0)

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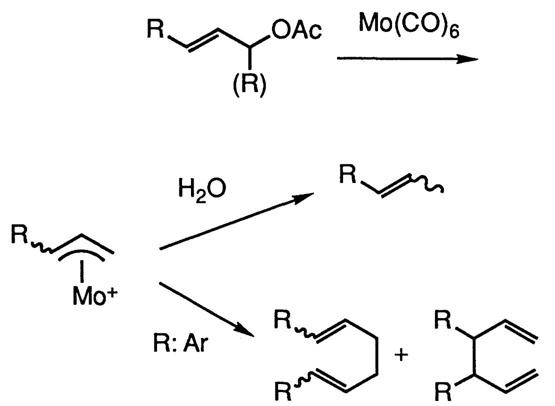
Synopsis. Aliphatic allylic acetates were reduced to alkenes with hexacarbonylmolybdenum(0) in refluxing dioxane under nitrogen atmosphere. These reactions were accelerated by the addition of H_2O. 1-Aryl- or 3-arylallyl acetates caused deacetoxylative allylic homocoupling under the same conditions.

Hexacarbonylmolybdenum [$Mo(CO)_6$] seems to have both oxidizing and reducing ability, since molybdenum has a variety of oxidation states between -2 and $+6$. In particular, the reducing ability can be presumably applied to organic synthesis. We have recently reported that hexacarbonylmolybdenum is a useful reducing agent for reductive chalcogenization of allylic sulfides, sulfones, and selenides.[1—3] The reductive desulfonylation of allylic sulfones with $Mo(CO)_6$ should proceed via the formation of π-allylmolybdenum complexes.[2—4] Allylic acetates have also reacted with $Mo(CO)_6$ to form π-allylmolybdenum complexes, which have been utilized to nucleophilic substitution by carbon nucleophiles.[5] If carbon nucleophiles were absence in the reaction system, allylic acetates would be reduced to alkenes by electron transfer from molybdenum atom to η^3-allyl ligand π-allylmolybdenum intermediates,[6] similarly to reductive desulfonylation of allylic sulfones.[2,3]Here we report a reductive deacetoxylation of various allylic acetates with $Mo(CO)_6$ under the same conditions as π-allylmolybdenum complex has been formed.

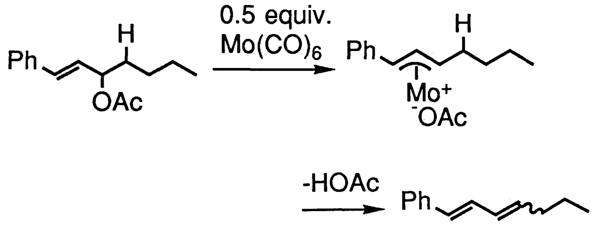
The reaction of methyl 9-acetoxy-10-undecenoate with $Mo(CO)_6$ was investigated under various conditions. Reductive deacetoxylation proceeded in refluxing THF or dioxane (Entries 1—4 in Table 1). Addition of H_2O accelerated the reductive deacetoxylation similarly to reductive dechalcogenization of allylic sulfides, sulfones, and selenides with $Mo(CO)_6$ (Entries 2 and 3). In refluxing THF (Entry 3), an elimination of acetic acid occurred to give a diene, in contrast with the reaction in refluxing dioxane (Entry 2). The reaction of various allylic acetates with $Mo(CO)_6$ was carried out in the presence of H_2O (5 equiv) in refluxing dioxane (Table 1). Aliphatic allylic acetates caused only the reductive deacetoxylation to produce the corresponding alkene isomers (Entries 1—11, and 16, Scheme 1). Allylic acetates bearing an aryl substituent on an allylic position of the π-allylmolybdenum intermediates, caused reductive allylic homocoupling with the reductive deacetoxylation without adding a reducing agent such as zinc powder (Entries 13, 14, and 17, Scheme 1).[7] In the case having a proton on an α-position of 1-aryl-π-allylmolybdenum intermediate, a diene was obtained as a single product without base, as shown in Scheme 2 (Entries 18 and 19).[8] The reductive deacetoxylation smoothly proceeded with even a half equimolar amount of $Mo(CO)_6$ (Entries 15 and 16).[9] Hexacarbonylmolybdenum(0) proved to have such a reducing ability that more than two electrons apparently transfered from molybdenum(0) to allylic acetates. Addition of D_2O instead of H_2O produced a quantitatively deuterated product, and use of dioxane-d_8 as a solvent did not cause the deuteration (Entries 7 and 8). Hence, a proton or radical hydrogen source is presumably H_2O.[10]



Scheme 1.

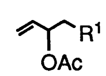
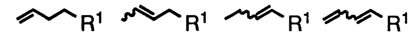
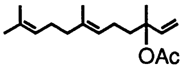
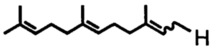
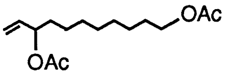
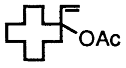
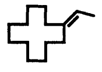
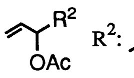
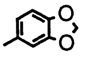
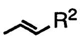
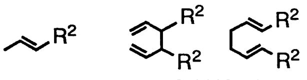
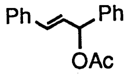
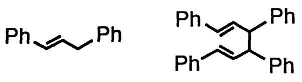
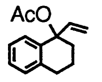
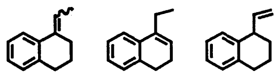
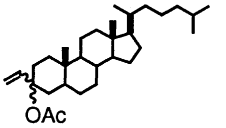
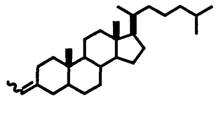
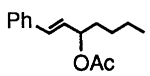
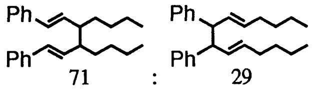
Experimental

General Procedure of Reductive Deacetoxylation of Allylic Acetates with $Mo(CO)_6$. To a solution of allylic acetate (1 mmol) and H_2O (5 mmol) in dioxane (3—5 ml) was added hexacarbonylmolybdenum(0) (0.5—1 mmol). The mixture was refluxed for 14—25 h under nitrogen atmosphere. The reaction mixture was diluted with ether (50 ml), washed with water (20×3 ml), and dried over $MgSO_4$. Evaporation of ether followed by purification of a residue by column chromatography on silica gel (Merck 60) using hexane or hexane/ethyl acetate as an eluent gave reductively deacetoxylated products and/or allylic homocoupling products. The structures were determined by IR (Hitachi 260-50), ^{1}H NMR (JEOLCO GX-270), and mass spectra (JEOLCO JMS-D300). The isomer ratios were determined by ^{1}H NMR.



Scheme 2.

Table 1. Reductive Deacetoxylation of Allylic Acetates with $Mo(CO)_6$

Entry	Allylic acetate	H^+ (or H·) source	Time/h	Product	Yield$^{a)}$/%
1		—	20	 13 : 70 : 17	40
2	R^1: $(CH_2)_6COOMe$	H_2O	15	15 : 54 : 31	58
3		H_2O	19	16 : 39 : 18 : 27	31$^{b)}$
4		CH_3COOH	18	15 : 63 : 15 : 7	64$^{b)}$
5		—	15		47
6		H_2O	15	H	55
7		D_2O	15	D	49$^{c)}$
8		—	19	H	49$^{c,d)}$
9		—	24	 20 : 80	39
10		H_2O	20		50
11		H_2O	22		60
12	 R^2: 	H_2O	17		35
13		H_2O	23	 31% 19%(56:44)	50$^{e)}$
14		H_2O	21	 19% 37%	56$^{e)}$
15		H_2O	25	67 : 20 : 13	70$^{e)}$
16		H_2O	19		82$^{e)}$
17		—	14	 71 : 29	48
18		H_2O	20		50$^{e)}$
19		—	22	cis:trans=50:50	50$^{e)}$

a) Yields of mixtures of regio- and/or stereoisomers. The ratio was determined by ^{1}H NMR (JEOLCO GX-270). b) THF as a solvent was used. c) The deuteration was confirmed by ^{1}H NMR and GC-MS (JEOLCO JMS-D300). d) Dioxane-d_8 as a solvent was used. e) A half equimolar amount of $Mo(CO)_6$ was used.

A Mixture of Methyl 8-Undecenoate, Methyl 9-Undecenoate, and Methyl 10-Undecenoate (Entry 1 in Table 1): IR (neat) 3000, 2920, 2845, 1735, 1430, 1160 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.95, 0.96 (2t, J=7.33 Hz, 0.5H), 1.22—1.42 (br, 8H), 1.54—1.70 (m, 4.1H), 1.90 (m, 2.3H), 2.30 (t, J=7.36 Hz, 2H), 3.66 (s, 3H), 4.89—5.03 (m, 0.25H), 5.30—5.50 (m, 1.7H), 5.80 (ddt, J=17.1, 10.3, 6.65 Hz, 0.13H). MS (70 eV) m/z (rel intensity) 198 (M$^+$, 6), 166 (21), 124 (28), 97 (21), 96 (27), 87 (46), 84 (34), 83 (37), 82 (25), 81 (23), 74 (83), 69 (55), 68 (24), 67 (25), 59 (23), 55 (100). Found: m/z 198.1622. Calcd for $C_{12}H_{22}O_2$: M, 198.1619.

2,6,10-Trimethyl-2,6,10-dodecatriene (Entry 5 in Table 1): IR (neat) 2950, 2900, 2850, 1435, 1370 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.56 (d, J=6.72 Hz, 3H), 1.59 (br.s, 6H), 1.62 (br.s, 2H), 1.67 (br.s, 4H), 1.93—2.13 (m, 8H), 5.05—5.16 (m, 2H), 5.20 (q, J=6.68 Hz, 1H). MS (70 eV) m/z (rel intensity) 206 (M$^+$, 3.7), 137 (12), 136 (11), 123 (12), 95 (27), 82 (11), 81 (40), 69 (100), 67 (13), 55 (14). Found: m/z 206.2027. Calcd for $C_{15}H_{26}$: M, 206.2033.

11-Acetoxy-2-undecene (Entry 9 in Table 1): IR (neat) 2920, 2860, 1730, 1440, 1365, 1235, 1035, 960 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.20—1.45 (br, 10H), 1.56—1.67 (m, 5H), 1.91—

2.01 (m, 2H), 2.04 (s, 3H), 4.06 (t, J=6.60 Hz, 2H), 5.37—5.44 (m, 2H). MS (70 eV) m/z (rel intensity) 212 (M$^+$, 1.2), 109 (20), 97 (28), 96 (31), 95 (34), 84 (32), 83 (22), 82 (51), 81 (66), 69 (63), 68 (90), 67 (66), 61 (21), 55 (100), 54 (40). Found: m/z 212.1773. Calcd for $C_{13}H_{24}O_2$: M, 212.1775.

Ethylidenecyclododecane (Entry 11 in Table 1): IR (neat) 2920, 2840, 1455 cm^{-1}. ^{1}H NMR (CCl$_4$) δ=1.00—1.70 (br, 18H), 1.57 (d, J=7.0 Hz, 3H), 1.80—2.23 (m, 4H), 4.93—5.37 (m, 1H). MS (70 eV) m/z (rel intensity) 194 (M$^+$, 44), 165 (24), 110 (23), 109 (46), 96 (62), 95 (61), 83 (56), 82 (70), 81 (69), 71 (32), 70 (88), 69 (55), 68 (50), 67 (81), 55 (100), 54 (32). Found: m/z 194.2034. Calcd for $C_{14}H_{26}$: M, 194.2033.

1-(3,4-Methylenedioxyphenyl)propene (Entry 12 in Table 1): IR (neat) 2900, 2850, 1485, 1440, 1245, 1120, 1035 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=1.84 (dd, J=6.52, 1.49 Hz, 3H). 5.93 (s, 2H), 6.06 (dq, J=15.6, 6.44 Hz, 1H), 6.31 (dq, J=15.6, 1.45 Hz, 1H), 6.73 (s, 2H), 6.87 (s, 1H). MS (70 eV) m/z (rel intensity) 162 (M$^+$, 100), 161 (31), 135 (46), 131 (40), 104 (42), 103 (33), 97 (36), 85 (30), 83 (37), 81 (32), 77 (34), 71 (46), 69 (46), 57 (77), 55 (59). Found: m/z 162.0678. Calcd for $C_{10}H_{10}O_2$: M, 162.0680.

1,3-Diphenylpropene (Entry 14 in Table 1): IR (neat) 3010, 2910, 2850, 1595, 1485, 1445, 960, 735, 690 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=3.54 (d, J=6.30 Hz, 2H), 6.34 (dt, J=15.7, 6.30 Hz, 1H), 6.45 (d, J=15.7 Hz, 1H), 7.14—7.37 (m, 10H). MS (70 eV) m/z (rel intensity) 194 (M$^+$, 100), 193 (54), 179 (37), 116 (36), 115 (58), 91 (35). Found: m/z 194.1096. Calcd for $C_{15}H_{14}$: M, 194.1095.

1,3,4,6-Tetraphenyl-1,5-hexadiene (Entry 14 in Table 1): IR (neat) 3030, 2930, 1600, 1490, 1450, 965, 745, 705 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=3.84—3.93 (m, 2H), 6.16—6.58 (m, 4H), 7.03—7.33 (m, 20H). MS (70 eV) m/z (rel intensity) 194 (21), 193 (100), 178 (12), 115 (51), 91 (17). Found: C, 92.93; H, 6.64%. Calcd for $C_{30}H_{26}$: C, 93.21; H, 6.78%.

A Mixture of 1-Ethylidenetetralin, 1-Ethyl-3,4-dihydronaphthalene, and 1-Vinyltetralin (Entry 15 in Table 1): IR (neat) 3010, 2920, 2850, 1475, 1445, 745 cm^{-1}. ^{1}H NMR (CCl$_4$) δ=1.14 (t, J=7.36 Hz, 0.60H), 1.76 (d, J=6.92 Hz, 2.0H), 1.64—1.97 (m, 1.9H), 2.17—2.54 (m, 2.1H), 2.64—2.82 (m, 2.1), 4.96—5.09 (m, 0.3H), 5.78—5.96 (m, 0.30H), 5.99—6.16 (m, 0.70H), 7.00—7.15 (m, 4H). MS (70 eV) m/z (rel, intensity) 158 (M$^+$, 48), 141 (23), 131 (49), 130 (69), 129 (100), 128 (49), 127 (20), 118 (20), 115 (41), 91 (25). Found: m/z 158.1095. Calcd for $C_{12}H_{14}$: M, 158.1095.

3-Ethylidenecholestane (Entry 16 in Table 1): IR (neat) 2930, 2860, 1455, 1380, 910 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=0.65 (s, 3H), 0.87 (d, J=6.89 Hz, 9H), 0.92 (s, 3H), 0.95—2.20 (m, 31H), 1.55 (d, J=6.61 Hz, 3H), 4.96—5.15 (m, 1H). MS (70 eV) m/z (rel intensity) 398 (M$^+$, 30), 396 (33), 243 (30), 161 (38), 149 (34), 147 (41), 135 (52), 134 (45), 133 (41), 123 (43), 122 (55), 121 (62), 120 (31), 119 (44), 109 (66), 108 (36), 107 (71), 105 (51), 97 (31), 95 (96), 93 (65), 91 (36), 83 (42), 81 (100), 79 (46), 71 (38), 69 (66), 67 (53), 57 (80), 55 (94). Found: m/z 398.3898. Calcd for $C_{29}H_{50}$: M, 398.3910.

A Mixture of 3,4-Dibutyl-1,6-diphenyl-1,5-hexadiene and 7,8-Diphenyl-5,9-tetradecadiene (Entry 17 in Table 1): IR (neat) 3020, 2940, 2920, 2850, 1485, 1445, 960, 735, 690 cm^{-1}. ^{1}H NMR (CCl$_4$) δ=0.93 (br, 6H), 1.10—2.80 (m, 13.4H), 3.17—3.43 (0.60H), 5.17—5.57 (m, 1.2H), 5.96(dd, J=15.0, 5.6 Hz, 1.4H), 6.36 (d, J=15.0 Hz, 1.4H), 6.93—7.33 (m, 10H). MS (70 eV) m/z (rel intensity) 174 (35), 131 (15), 118 (15), 117 (100), 116 (10), 115 (29), 105 (28), 104 (89), 92 (13), 91 (63), 81 (13), 77 (19), 69 (26), 57 (11), 55 (23). Found: C, 89.75; H, 10.12%. Calcd for $C_{26}H_{34}$: C, 90.10; H, 9.90%.

1-Phenyl-1,3-heptadiene (Entry 18 and 19 in Table 1): IR (neat) 3020, 2960, 2870, 1490, 1460, 990, 745, 690 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=0.92 (t, J=7.04 Hz, 1.5H), 0.95 (t, J=7.04 Hz, 1.5H), 1.36—1.53 (m, 2H), 2.11 (br.q, J=7.23 Hz, 1H), 2.26 (br.q J=7.42 Hz, 1H), 5.52 (dt, J=9.89, 7.42 Hz, 0.5H), 5.80 (dt, J=15.0, 7.04 Hz, 0.5H), 6.10 (m, 1H), 6.42 (d, J=15.6 Hz, 0.5H), 6.50 (d, J=15.6 Hz, 0.5H), 6.74 (dd, J=15.6, 10.3 Hz, 0.5H), 7.06 (ddd, J=15.6, 10.8, 1.33 Hz, 0.5H), 7.12—7.42 (m, 5H). MS (70 eV) m/z (rel intensity) 172 (M$^+$, 42), 143 (63), 131 (22), 130 (24), 129 (100), 128 (69), 117 (42), 115 (56), 91 (60), 77 (23), 71 (27). Found: m/z 172.1252. Calcd for $C_{13}H_{16}$: M, 172.1251.

References

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2) Y. Masuyama, K. Yamada, and Y. Kurusu, *Chem. Express*, **2**, 687 (1987).

3) Y. Masuyama, K. Yamada, S. Shimizu, and Y. Kurusu, *Bull. Chem. Soc. Jpn.*, **62**, 2913 (1989).

4) B. M. Trost, *Bull. Chem. Soc. Jpn.*, **61**, 107 (1988).

5) B. M. Trost and M. Lautens, *J. Am. Chem. Soc.*, **104**, 5543 (1982); **105**, 3343 (1983); **109**, 1469 (1987).

6) For reductive deacetoxylation via π-allylmetal complexes using reducing agents, see: J. Tsuji and T. Yamakawa, *Tetrahedron Lett.*, **1979**, 613; R. O. Hatchins, K. Learn, and R. P. Fulton, *ibid.*, **21**, 27 (1980); H. Matsushita and E. Negishi, *J. Org. Chem.*, **47**, 4161 (1982); E. Keinan and N. Greenspoon, *ibid.*, **48**, 3545 (1983); J. Tsuji, I. Minami, and I. Shimizu, *Synthesis*, **1986**, 623.

7) Allylic homocoupling may occur via the formation of bis(η^1-γ-arylallyl)molybdenum intermediates; the transformation of initially prepared η^3-allyl complexes to η^1-allyl complexes may create a vacant coordination site on the molybdenum, and then second η^1-allylation may easily occur on the molybdenum, since olefins bearing an electron-withdrawing aryl group are hard to coordinate to the molybdenum. For reductive allylic homocoupling with Mo(CO)$_6$-Zn, see: Y. Masuyama, K. Otake, and Y. Kurusu, *Bull. Chem. Soc. Jpn.*, **60**, 1527 (1987).

8) B. M. Trost, M. Lautens, and B. Peterson, *Tetrahedron Lett.*, **24**, 4525 (1983).

9) The reductive deacetoxylation scarcely occurred in the use of a 0.1—0.2 equimolar amount of Mo(CO)$_6$ to allylic acetate.

10) The reductive deacetoxylation of allylic acetates may occur via the reductive elimination of hydrido(π-allyl)molybdenum intermediates derived from initially prepared π-allylmolybdenum complexes with H_2O. In order to detect the hydrido(π-allyl)molybdenum intermediate, ^{1}H NMR spectroscopic investigation was carried out in the reaction of allyl acetate with Mo(CO)$_6$ and H_2O in dioxane-d_8. The formation of the hydrido(π-allyl)molybdenum complex was not confirmed, since the reductive deacetoxylation probably occurred rapidly at high reaction temperature (100 °C), which needed in the formation of initial π-allylmolybdenum complex. For reductive elimination of hydrido(η^1-allyl)molybdenum complexes, see: T. Ito, T. Matsubara, and Y. Yamashita, *J. Chem. Soc., Dalton Trans.*, **1990**, 2407.