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MOLYBDENUM-PROMOTED REACTIONS OF 7-OXABICYCLO[2.2.1]HEPTADIENE AND DERIVATIVES

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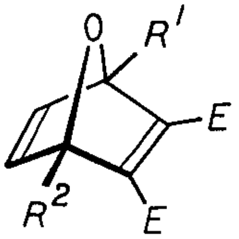
Abstract - The reactions of 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**1a**) and related compounds **1b**, **1c**, and **2** with molybdenum carbonyl complexes are examined at two different temperatures. In refluxed cyclohexane, reactions of **1a-c** with hexacarbonylmolybdenum produce mainly the corresponding derivatives of dimethyl phthalate (**3a-c**) and 3,4-bis(methoxycarbonyl)furan (**4a-c**), while the reaction of **2** produces naphthalene and 1-naphthol. At room temperature, reactions of **1a,b** with tris(acetonitrile)tricarbonylmolybdenum yield the dimer ketons **5a,b** in addition to **3a,b** and **4a,b**, while the reaction of **2** produces naphthalene as the only product. The mechanism for the generation of **3**, **4**, and **5** is rationalized as going through complex intermediate with structure of a molybdenum chelated by **1**.

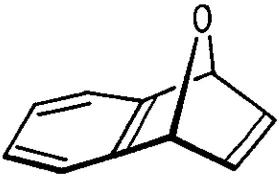
2,3-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (**1a**) and its derivatives are well-known Diels-Alder cycloaddition adducts of furans and the electron-deficient dimethyl acetylenedicarboxylate.[1] Utilities of these compounds are versatile in organic synthesis, e.g. in the preparation of polysubstituted phenols and cyclohexenols through ring-opening of the oxo-bridges.[2] Along with the progress of organometallic chemistry, new types of reaction have recently been observed upon treatment with transition metal complexes. The diene moiety as well as the lone pairs of oxygen may all act as effective ligands. Dimerization, deoxygenation, and carbonylation reactions become feasible, and even for conventional types of reactions their reactivities can be drastically altered. In this report we describe our observation of the reactions of several 7-oxanorbornadiene derivatives with molybdenum carbonyl complexes. Their reaction patterns are found to bear certain similarities to those of the norbornadiene homologues.[3]

RESULTS

The reactions of 1a–c with Mo(CO)$_6$. The reactions of Mo(CO)$_6$ with four derivatives of 7-oxabicyclo-[2.2.1]heptadiene (7-oxanorbornadiene, ONBD) have been analyzed, i.e. 2,3-bis(methoxycarbonyl)-ONBD (**1a**),[4] 1-acetoxymethyl-2,3-bis(methoxycarbonyl)-ONBD (**1b**),[5] 1,4-dimethyl-2,3-bis(methoxycarbonyl)-ONBD (**1c**),[6] and 1,4-dihydro-1,4-epoxynaphthalene (**2**).[7] Products and their distribution are summarized in Table 1. Heating a solution of **1a** and Mo(CO)$_6$ in cyclohexane to reflux for 2 days produced two major compounds, i.e. dimethyl phthalate (**3a**, yield 46%) and 3,4-bis(methoxycarbonyl)furan[8] (**4a**, yield 10%). Both **3a** and **4a** were isolated from column chromatography and were purified. Similar products were obtained for the reactions of Mo(CO)$_6$ with **1b** and **1c**. In the reaction of **1c**, **3c** and **4c** were isolated in yields of 34% and 10% respectively. The two compounds can also be quickly identified by gc-ms spectrometry, on which both of them produce clear signals corresponding to their molecular ions. In the reaction of **1b**, a combined yield of 40% for **3b** and **4b** was obtained. Relative quantity of **3b**/**4b** was determined by ^{1}H nmr signal integrations as 2/1. Isolation of the two was not readily



1 a $R^1 = R^2 = H$, $E = COOCH_3$
b $R^1 = H$, $R^2 = CH_2OC(O)CH_3$, $E = COOCH_3$
c $R^1 = R^2 = CH_3$, $E = COOCH_3$



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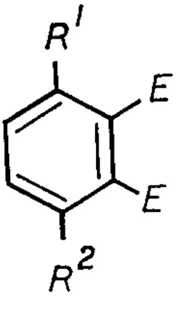
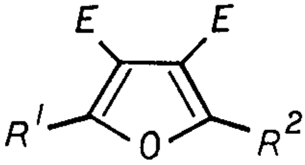


3 a $R^1 = R^2 = H$, $E = COOCH_3$
b $R^1 = H$, $R^2 = CH_2OC(O)CH_3$, $E = COOCH_3$
c $R^1 = R^2 = CH_3$, $E = COOCH_3$

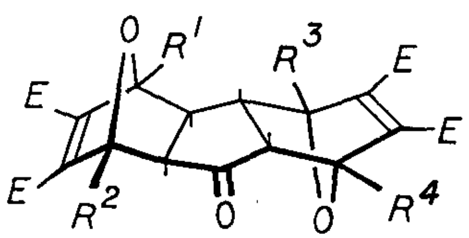


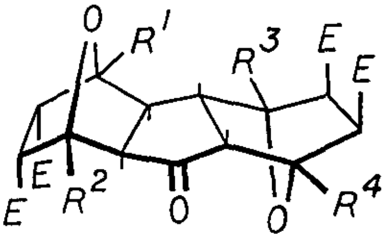
4 a $R^1 = R^2 = H$, $E = COOCH_3$
b $R^1 = H$, $R^2 = CH_2OC(O)CH_3$, $E = COOCH_3$
c $R^1 = R^2 = CH_3$, $E = COOCH_3$

achieved, however information received from gc-ms along with two-dimensional ^{1}H-^{13}C nmr COSY analysis confirmed their structures.

The reactions of **1a–c** seem to follow a general mechanism despite the changes of substituents on C(1) and C(4). Variation appears only in the reaction of **2** where major products found were 1-naphthol[9] (43%) and naphthalene[10] (17%). The absence of benzofuran among the products may be ascribed to its instability under the reaction conditions. The high yield of 1-naphthol from **2** was exceptional compared to **1a–c** since a similar rearrangement was not observed for the latter. From the above information it is clear that deoxygenation happens efficiently in these reactions. Such types of reactions have attracted considerable interest in recent years. It has been found that low-valent forms of iron, tungsten, and titanium[11] are all effective reagents.[12] However, deoxygenation induced by molybdenum complexes does not seem to have been well-recognized. The mechanism to account for formation of furan derivatives in these reactions is not so apparent. The furans could either be derived directly from metal-assisted cycloreversion of the starting materials, or derived indirectly from the fragmentation of certain primary adducts. Both possibilities were examined and the result will be discussed in later sections.

The Reactions of 1 with $Mo(CH_3CN)_3(CO)_3$. In order to acquire more information on the mechanism of the above reactions as well as in the hope of trapping some transient intermediates, reactions were reexamined at a lower temperature (ambient) with the more reactive complex $Mo(CH_3CN)_3(CO)_3$.[13] An equal molar solution of **1a** and $Mo(CH_3CN)_3(CO)_3$ in acetonitrile was stirred at room temperature for 5 h. Products were extracted with ether, isolated by column chromatography, and purified by repeated recrystallizations. Along with **3a** and **4a** a new product was identified to possess the structure of a dimer ketone (**5a**)[14] (Table 1). It forms stable needles at room temperature but slowly decomposes upon heating. It can not survive long in refluxed cyclohexane, that may explain its absence in the





5 a $R^1 = R^2 = R^3 = R^4 = H$, $E = COOCH_3$ **6 a**

b R^1 & $R^2 = R^3$ & $R^4 = H$ & $CH_2OC(O)CH_3$, $E = COOCH_3$ **b**

reaction of $Mo(CO)_6$. Its instability also gives rise to an irrational signal pattern in mass spectrum. Other spectroscopic evidences including ir, ^1H nmr, ^{13}C nmr with DEPT, and ^1H-^{13}C 2D COSY spectra are all consistent with the assigned structure. To solve the inconsistency of mass spectrum **5a** was reduced by catalytic hydrogenation to the more stable saturated derivative **6a**. All the spectroscopic information of **6a** including its mass spectrum can be unambiguously interpreted. The AB pattern of proton nmr signals for the cyclopentanone moieties of **5a** and **6a** suggests an exo-trans-exo junction between the two ONBD units.[15]

The reaction of **1b** with $Mo(CH_3CN)_3(CO)_3$ produced similar results. Diastereomers of **5b**, formed due to the asymmetrical geometry of **1b**, were not further purified. Catalytic hydrogenation of **5b** mixtures gave isomers of **6b**. The stability of **6b** is higher than that of **5b** and their molecular ions (M^+= 592, 4.2%) can be observed on mass spectrum. Heating either **5a** or **5b** in hexane afforded high yield of the corresponding furan **4a** or **4b**. Cycloreversion of 7-oxanorbornene is a well-known process, which must account for the instability of the dimer ketones. This process therefore should also have contributed partially to the overall yield of the furan products.

Reaction of **2** with $Mo(CH_3CN)_3(CO)_3$ did not produce either benzofuran or 1-naphthol. A trace amount of dimer ketone **5c** was detected in nmr analysis of crude products. The only major product was naphthalene resulting from deoxygenation.

Table 1. Product distribution for the reactions of **1a-c** and **2** with Molybdenum carbonyls

1^a	Mo complexes	3	4	5	rel. yield (3/4)
a	$Mo(CO)_6$	46%	10%	—	4.6
b	$Mo(CO)_6$	27%	13%	—	2.1
c	$Mo(CO)_6$	34%	10%	—	3.4
a	$Mo(CH_3CN)_3(CO)_3$	10%	9%	16%	1.1
b	$Mo(CH_3CN)_3(CO)_3$	12%	12%	<2%	1.0
c	$Mo(CH_3CN)_3(CO)_3$	20%	20%	—	1.0

	Mo complexes	naphthalene	1-naphthol	dimer ketone
2^b	$Mo(CO)_6$	17%	43%	—
2^b	$Mo(CH_3CN)_3(CO)_3$	68%	—	trace

[a] Mixtures of 3 and 4 were isolated together, relative yields were measured based on signal integrations in ^1H nmr spectra. [b] Isolated yields.

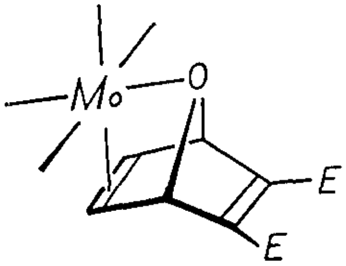
DISCUSSION

The formation of dimer ketones. The formation of dimer ketones **5a,b** may be correlated to the analogous reactions of metal-promoted dimerization of norbornadiene (NBD) and its derivatives. Iron carbonyls have been shown to be some of the most effective reagents for these types of reactions.[15,16] Other kinds of metals have also shown their effectiveness over a wide range of regio- and stereoselectivities.[3,17] Evidences have shown that the couplings proceed through intermediates of metal--olefin complexes such as the general structure shown in **7a.**[18] The oxo-bridge of ONBD is known to be capable of acting as a coordinating ligand.[3] Complexes with molybdenum chelated by the exo face of ONBD is therefore suggested as the intermediates of the reactions. The geometry of this structure correlates nicely with our experiments in the formation of dimer ketones, furans, and deoxygenated products. For the formation of the exo-trans-exo dimer ketone **5a**, intermediate with structure **7b** should be plausible, although it needs to be confirmed yet by experiments.

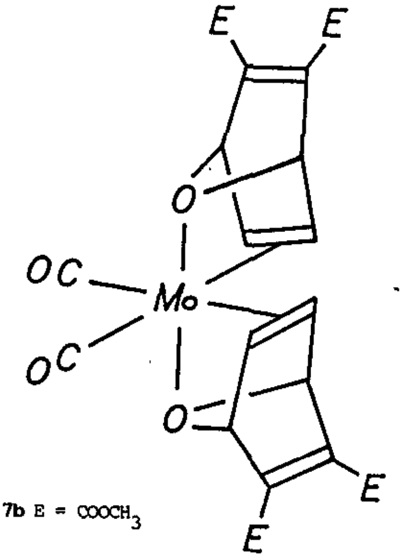
An nmr tracing experiment for the reaction of **1a** with $Mo(CH_3CN)_3(CO)_3$ has revealed advanced information on the structure of the metal-ONBD complex. A CD_3CN solution containing equal molar amounts of **1a** and $Mo(CH_3CN)_3(CO)_3$ was sealed in an nmr sample tube. ^1H nmr spectra were taken periodically to continuously monitor the transformation of signals. The formation of compounds **3a, 4a** and **5a** became apparent on nmr spectrum after 2 h, then their concentrations increased steadily for a further 8 h while nearly all the starting material **1a** was consumed. During this period a transient intermediate had been observed in addition to the signals corresponding to **3a, 4a** and **5a.** Its concentration accumulated to the optimum in the first 4 h, then diminished along with **1a.** On ^1H nmr a pair of doublets at δ 6.7 and 6.9 (J= 7 Hz), which are a little upfield from the parent signal of **1a** at δ 7.2, are clearly shown. Infrared spectrum of a crude sample shows two strong absorptions at 1940 and 2000 cm^{-1}. All the evidences indicate that it is a Mo-ONBD complex with a configuration similar to that of **7b.**[3] The exact structure of this intermediate cannot yet be solved due its instability.

The Origin of Furans. The furan **4a** may be produced from **1a** in one step via a cycloreversion that is believed to be thermochemically allowed.[19] However, in a reference study pure **1a** was heated to reflux in hexane for 2 days without the formation of **4a.** If cycloreversion indeed happened in the abovementioned reactions, it must have been catalyzed by the metal.

An alternative pathway may also have contributed to the formation of **4a**, that is via the thermodecomposition of the dimer ketone **5a.** Cycloreversion for 2,3-bis(methoxycarbonyl)-7-oxanorbornene is known to proceed readily upon heating, much more easily than that for the diene homologue **1a.** Controlled experiment showed that heating **5a** resulted in the production of **4a.** The easy fragmentation of **5a** explains its absence among the products in the reaction with $Mo(CO)_6$, where the reaction temperature is higher than in the reaction with $Mo(CH_3CN)_3(CO)_3$. Compound **5a** seems to be stable under the latter reaction condition.



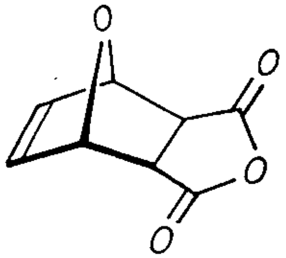
7a E = $COOCH_3$



7b E = $COOCH_3$

For the reactions of **1** with either $Mo(CO)_6$ or $Mo(CH_3CN)_3(CO)_3$, the mechanism is assumed to be similar. The formation of furans **4** in the reactions of $Mo(CH_3CN)_3(CO)_3$ indicates that metal-catalyzed cycloreversion happens with considerable efficiency. The absence of dimer ketones **5** in the reactions of $Mo(CO)_6$ also suggests that part of the yields of **4**'s came from secondary thermodecomposition of **5**'s.

Deoxygenation Reactions. The deoxygenation of **1** takes place usually in the presence of activated low-valent transition metals under strong reducing conditions.[10,11] Extrusion reactions were found to follow the approximate order of $N_2 > CO_2 > CO \geq SO > SO_2 > O_2 \geq S > O$ with increasing difficulty.[11] Only recently it was reported that deoxygenation may happen in the reactions of iron carbonyls.[14] In the cases of iron and molybdenum carbonyls, the energy of aromatization contributes as an important driving force for the extrusion. It was found that treatment of either one of the two 7-oxanorbornene homologues **8**[20] and **9**[21] with $Mo(CH_3CN)_3(CO)_3$ at room temperature did not yield the corresponding cyclohexadiene products. Another example was the reaction with **10**,[22] which was synthesized by condensing furan and two equivalents of dimethyl acetylenedicarboxylate upon the catalysis of $RuH_2(CO)(PPh_3)_3$.[23] No reaction was observed at room temperature while it was mixed with $Mo(CH_3CN)_3(CO)_3$ in acetonitrile. When the solution was heated to reflux, a messy mixture was produced after ca. 20 h, and the products from deoxygenation were not among the major components. The oxygen seemed to have been carried away through formation of metal complexes. In the case of iron carbonyls, the CO ligands act as the effective reducing agent and CO_2 evolution has been observed.[14] In the case of molybdenum carbonyls the mechanism is not yet clear. The formation of metal oxides is also plausible, where the metal itself is oxidized.



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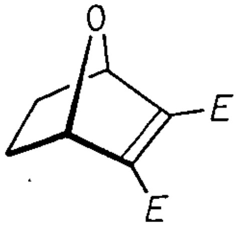
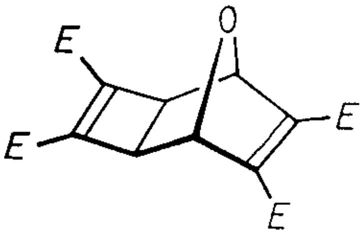


9 E = COOCH$_3$



10 E = COOCH$_3$

The Overall Reaction Mechanism. Summarized from the above information, the following mechanism is proposed for the diesters **1a–c**. The metal-olefin complexes **7a,b** forms first and acts as a common intermediate. Three independent pathways derived from **7a,b** are deoxygenation, cycloreversion, and dimerization with CO insertion. At elevated temperature the production of dimer ketones (**5**) is retarded due to its unstable nature. Part of the yields of 3,4-bis(methoxycarbonyl)furans (**4's**) come from the thermodecompositions of **5's**. The overall reaction pathway can be depicted in the following scheme.

$$\begin{tikzcd}
\mathbf{1} \arrow[r] & \mathbf{7a,b} \arrow[r] \arrow[d] \arrow[rd] & \mathbf{3} \\
 & \mathbf{5} \arrow[r] & \mathbf{4}
\end{tikzcd}$$

A small variation from this scheme is observed in the reaction of **2** at room temperature, for which only naphthalene is isolated (via dexoygenation) without benzofuran (via cycloreversion). At higher temperature 1-naphthol is produced as the major component. The difference is believed to derive from the change of substituents of the double bonds, which alters the electronic configuration of the diene moiety.[24]

EXPERIMENTAL

^{1}H and ^{13}C nmr spectra were obtained either on a Brucker AW 80 CW spectrometer or on a Brucker MSL-200 FT spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants in hertz (Hz). Results of DEPT experiments for ^{13}C nmr are indicated as multiplicities (s, d, t, q) in parentheses. Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer. Melting points were determined using a Yamato model MP-21 melting point apparatus and were uncorrected. Mass spectra were carried out on a Jeol JMS-D300 mass spectrometer.

Hexacarbonylmolybdenum, dimethyl acetylenedicarboxylate, and acetonitrile were purchased from MERCK. Furfuryl acetate and 2,5-dimethoxyfuran were purchased from Aldrich Chemical Co. Acetonitrile was dried over calcium hydride before use. Compounds **1a–c**,[4–6] **2**,[7] and $Mo(CH_3CN)_3(CO)_3$[13] were prepared according to the published procedures.

General Procedure for the Reactions of 1a-c and 2 with $Mo(CO)_6$.

An equal molar solution of **1a–d** and $Mo(CO)_6$ in cyclohexane was heated to reflux for 48 h under a nitrogen atmosphere. The black mixture was filtered and the filtrate was concentrated in rotary evaporator to obtain a pale yellow oil. The oil was applied onto a silica gel chromatographic column eluted with solvent combinations of ether/ethyl acetate/hexane. Yields of the products are listed in Table 1. Some of their spectroscopic data are shown as follows: **3a**, ^1H nmr ($CDCl_3$): δ 3.85 (s, 6H), 7.40-7.78 (m, 4H); ^{13}C nmr ($CDCl_3$): δ 52.13 (q), 128.39 (d), 130.69 (d), 131.47 (s), 167.53 (s); mass spectrum: m/z 194 (M^+), 163, 77. **4a**, ^1H nmr ($CDCl_3$): δ 3.79 (s, 6H), 7.92 (s, 2H); mass spectrum: m/z 184 (M^+), 153, 123. **3b**, ^{13}C nmr ($CDCl_3$): δ 20.48, 52.36, 52.45, 63.04, 128.60, 129.32, 129.57, 132.88, 133.75, 168.34, 169.91, 170.12; mass spectrum: m/z 235 ($M^+ - OCH_3$). **4b**, ^{13}C nmr ($CDCl_3$): δ 20.32, 51.78, 52.10, 56.24, 116.62, 118.72, 141.91, 147.20, 161.61, 162.18, 165.80; mass spectrum: m/z 256 (M^+). **3c**, ^1H nmr ($CDCl_3$): δ 2.40 (s, 6H), 3.79 (s, 6H), 7.15 (s, 2H); mass spectrum: m/z 222 (M^+), 191, 132. **4c**, ^1H nmr: δ 2.38 (s, 6H), 3.82 (s, 6H), 7.17 (s, 2H); mass spectrum: m/z 212 (M^+), 181, 122.

General Procedure for the Reactions of 1a-c with $Mo(CH_3CN)_3(CO)_3$. $Mo(CH_3CN)_3(CO)_3$ was prepared by heating $Mo(CO)_6$ (0.66 g, 2.5 mmol) in acetonitrile (30 mL) according to the published procedure.[13] To this solution was added an equal molar amount of the ONMD derivative (**1a**, **1b**, or **1c**) and the mixture was stirred at room temperature for 5 h while the color turned brown. It was concentrated on a rotary evaporator, and products were separated by silica gel column chromatography eluted with ether/n-hexane (v/v 1/1). Yields of the products are listed in Table 1. Ketone **5a** was recrystallized from methanol to form fiber-like crystals, mp 122-123° C. ^1H nmr ($CDCl_3$): δ 2.63, 2.90 (2d, J= 6.0 Hz, 2H each), 3.78, 3.84 (2s, 6H each), 5.29, 5,36 (2s, 2H each); ^{13}C nmr ($CDCl_3$): δ 47.27 (d), 52.64 (2C, q), 57.65 (d), 85.50 (d), 87.60 (d), 143.91 (s), 144.89 (s), 161.87 (CO), 162.45 (CO), 213.12 (CO); ir (KBr): 1735, 1725, 1642 cm^{-1}.

1,2,3,4,5,6,7,8-Hexahydro-2,3,6,7-tetramethoxycarbonyl-1,4:5,8-dioxo-9-fluorenone (6a). The ketone **5a** (0.100 g) was dissolved in THF (10 mL) containing catalytic amount of 10% Pd/C, and was hydrogenated under H_2 (1 atm) for 3 h at room temperature. A quantitive yield of **6a** was obtained, mp 168--169°C. ^1H nmr ($CDCl_3$): δ 2.90, 3.10 (2d, J=7 Hz, 2H), 3.20 (m, 4H), 3.67 (s, 12H), 4.76 (m, 4H); ir (KBr): ν(C=O) 1720-1760 cm^{-1} (br); mass spectrum: m/z 452 (M^+), 421 ($M^+ - OCH_3$), 361, 315, 297, 248, 220, 205 (base peak), 145, 121, 113.

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