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Preliminary communication

Reactions of 2,3-dicarbomethoxy-7-oxabicyclo[2.2.1]heptadiene with molybdenum carbonyls

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Abstract

Thermolysis with either $Mo(CO)_6$ or $Mo(CH_3CN)_3(CO)_3$ of 2,3-dicarbomethoxy-7-oxabicyclo[2.2.1]heptadiene (I) gave three major products, i.e. dimethyl phthalate (V), 3,4-dicarbomethoxyfuran (VI), and a dimeric ketone (IX) linked in an *exo-trans-exo* orientation. The formation of V and IX indicates two reaction pathways which start from a common organometallic intermediate. Compound VI is the major product in the thermal decomposition of IX.

In continuation of our study on the molybdenum-mediated dimerization of norbornadiene (NBD) derivatives, we found that the thermolysis of 2,3-dicarbomethoxy-7-oxabicyclo[2.2.1]heptadiene (I) with molybdenum carbonyls produced results which are unlike those of the NBD analogues. It has already been shown that derivatives of NBD with electron-withdrawing groups at C(2) and C(3), such as II–IV, do not dimerize to form a cage as does the unsubstituted NBD itself [1–4]. However, these derivatives yield stable metal complexes formulated as $MoL_2(CO)_2$, where L = II, III and IV (Scheme 1). The failure of these derivatives to dimerize was ascribed to the change in electronic configuration in the diene moieties *. In order to broaden our knowledge on this type of reaction, heterocycles with analogous structures were studied. The reaction of I with either $Mo(CH_3CN)_3(CO)_3$ or $Mo(CO)_6$ was tested and the results are described.

A n-hexane solution containing equimolar quantities of I [5,6] and $Mo(CO)_6$ was heated to reflux for 40 h to give two major products. They were isolated and identified as dimethyl phthalate (V, yield 45%) [7] and 3,4-dicarbomethoxyfuran (VI, yield 10%) [8] (Scheme 2) by comparison with spectroscopic data for authentic ones. Deoxygenation of I to V is novel and it presumably takes place via an

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* Dimerizations might be possible if some of the substituents are changed into electron-releasing groups, or if the metal complex in the catalytic system is changed.

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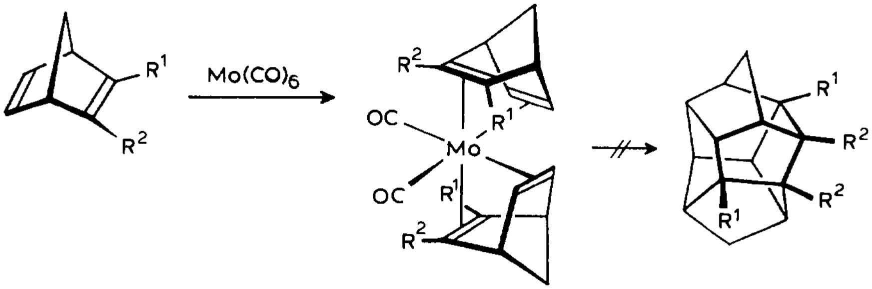
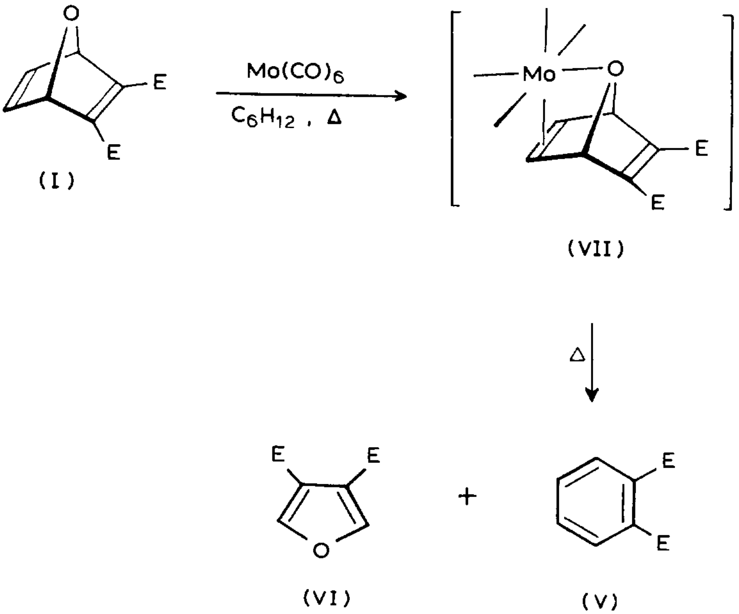


(II : $R^1 = H$, $R^2 = COOCH_3$;
III : $R^1 = H$, $R^2 = p\text{-}CH_3 \cdot C_6H_4 \cdot SO_2$;
VI : $R^1 = R^2 = COOCH_3$)

Scheme 1

intermediate (VII) in which the diene is coordinated to Mo from its *exo* side [7–10]. Oxygen extrusion from VII, aided partly by exothermic aromatization then occurs. The formation of furan VI could be a direct consequence of a thermal retrocyclization of I; however, a reference reaction carried out under the same reaction conditions showed that retrocyclization of I does not occur readily in absence of metal.

In order to understand more clearly the mechanism of the reaction, the temperature of the reaction was reduced so as to slow down the reaction in the hope of



(E = $COOCH_3$)

Scheme 2

trapping reactive intermediates. At room temperature tris(acetonitrile)tricarbonylmolybdenum, $Mo(CH_3CN)_3(CO)_3$ (VIII) [11], was used instead of $Mo(CO)_6$ as metal reactant. Equimolar amounts of I and VIII were stirred in an acetonitrile solution for 5 h, during which time the reaction was monitored by periodically examining the ^1H NMR spectra of the reaction mixture. A new product was observed along with the appearance of V and VI. It was isolated by column chromatography as white fiber-like needles and was recrystallized from methanol (m.p. 122–123° C, yield 15%). By examining its spectra, the structure was shown to be a dimeric ketone (IX) fused in an *exo-trans-exo* orientation [12].

The ^1H NMR spectrum for the cyclopentanone moiety of IX shows a pair of doublets (AB pattern) at δ 2.63 and 2.90 with J(H–H) 6.0 Hz. Such a pattern indicates a *transoid* junction between the two segments of I [13,14]. Other signals include two singlets at δ 3.78 and 3.84 (6H each) for the esters, and two other singlets at δ 5.29 and 5.36 (2H each) for the bridgeheads. The whole molecule shows C_2 symmetry. ^{13}C NMR spectra were recorded using the DEPT technique, and the ^{13}C–^1H 2D analyses are all consistent with the assigned structure *. IR spectrum shows strong absorptions at 1725 cm^{-1} (ketone), 1735 cm^{-1} (ester), and 1642 cm^{-1} (C=C).

The stability of IX is good at room temperature, but it decomposes upon heating to give VI. Owing to rapid fragmentation, the parent peak in the mass spectrum can not be observed. Low pressure hydrogenation (1 atm) of IX over 10% Pd/C produced X in nearly quantitative yield **. The pattern of ^1H couplings on the NMR time scale indicates that hydrogenation originates from the *exo* sides [6]. Mass spectroscopy of X (70 eV) shows a clear signal at $m/z = 452$ (parent peak) with a relative intensity of 5.1% (cf. base peak at 205), and thus provides unambiguous evidence for the molecular formula of IX.

The reaction of $Mo(CO)_6$ or $Mo(CH_3CN)_3(CO)_3$ with I is considered to be the same type so that the complete reaction sequence can be depicted as in Scheme 3. Coordination of I to Mo occurs first to form the transient intermediate VII, from there two major pathways for the subsequent reaction of VII are possible: one which gives V by deoxygenation of I and the other which gives the dimeric ketone IX. The isolation of IX is significant in the study of metal-mediated dimerization of NBD derivatives since it is the first dimeric ketone to be produced from a diene with electron-withdrawing substituents at the double bond.

The origin of VI can now be better explained in terms of a thermal retrocyclization of IX. Indeed a model test showed that heating a purified sample of IX gave VI in high yield. At elevated temperature (eq. in CH_3CN under reflux), the reaction of I with $Mo(CO)_3(CH_3CN)_3$ gave V and VI as expected but without IX. This information strongly indicates that IX was also produced as an intermediate in the

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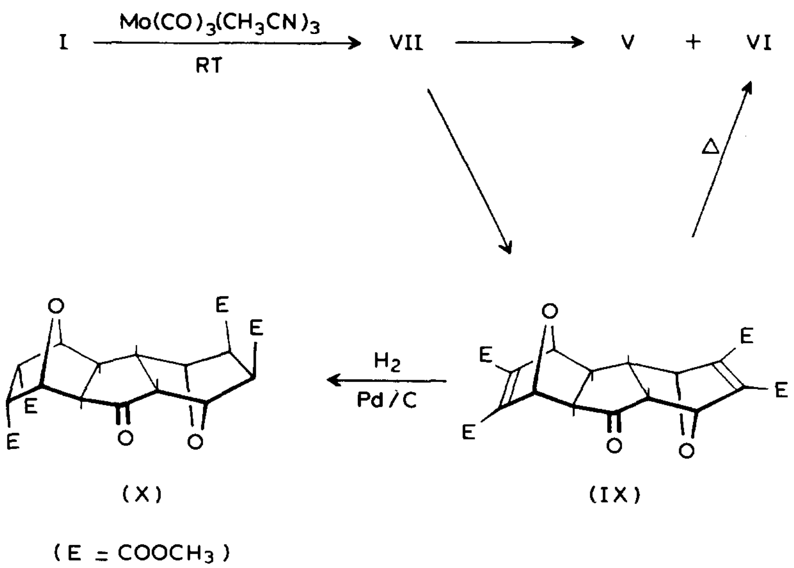
* The ^{13}C NMR spectrum of IX shows the following signals: δ ($CDCl_3$, TMS as internal standard) 47.27 (CH), 52.64 (2C for CH_3), 57.65 (CH), 85.50 (CH) 87.60 (CH), 143.91 (C=C), 144.89 (C=C), 161.87 (COO), 162.45 (COO), 213.12 (CO).

** Physical data of X: ^1H NMR ($CDCl_3$): δ 2.90, 3.10 (2d, AB pattern, 2H each, J 7 Hz), 3.20 (m, 4H), 3.67 (s, 12H), 4.76 (m, 4H). IR (KBr): ν(C=O) 1720–1760 cm^{-1} (br.). MS: m/z 452 (M^+), 421 ($M^+ - OCH_3$), 361, 315, 297, 248, 220, 205 (base peak), 145, 121, 113.



Scheme 3

reaction of I with $Mo(CO)_6$, but that it decomposed immediately after to form the more stable product, VI.

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