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TRANSITION METAL PROMOTED REACTIONS

IV. THERMOLYSIS OF CYCLOPENTADIENONE DIMERS AND RELATED COMPOUNDS WITH GROUP VI METAL CARBONYL *

TIEN-YAU LUH

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T. (Hong Kong)

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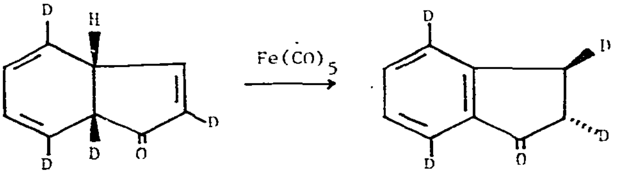
Summary

Thermal decomposition of dicyclopentadienone in the presence of $M(CO)_6$ (M = Cr, Mo, W) yields indanone. 2-Bromocyclopentadienone dimer, on the other hand, affords 4-bromoindanone under the same conditions. No corresponding organometallic complexes were isolated. The mechanism of this reaction is discussed.

Introduction

We recently reported iron carbonyl promoted regio- and stereospecific migration of double bonds in dihydroindenone and related systems, as outlined in eqn. 1 [1b]; this reaction is, to the best of our knowledge, the first example of an iron carbonyl catalyzed migration of a remote double bond to form an aromatic ring. The catalytic activity for olefin isomerization by the low spin d^6 $M(CO)_6$ (M = Cr, Mo, W) alone, however, should be low [2]. A few examples are reported on $M(CO)_6$ catalysis without [3—5] or with [6] photoassistance, but the yields are generally unsatisfactory. We now report our investigation on the $M(CO)_6$ promoted double bond shifts in dihydroindenones and related compounds, and the $M(CO)_6$ promoted reductive debrominations of α-bromoketones. These reactions may be synthetically useful.



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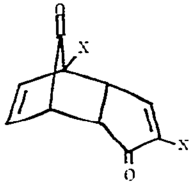
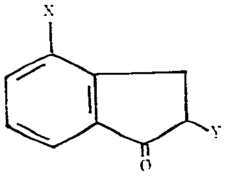
* Parts I to III see ref. 1.

Results and discussion

A mixture of cyclopentadienone dimer (Ia) and $M(CO)_6$ in diglyme or dioxane was refluxed for several hours. Indanone (IIa) was isolated in 32 to 51% yield as shown in Table 1. No significant amount of the corresponding organometallic π-arene complexes (IIIa) could ever be detected under the reaction conditions. In a similar fashion, treatment of 2-bromocyclopentadienone dimer (Ib) with $M(CO)_6$ afforded 4-bromoindanone (IIb) as the sole product in 28 to 46% yield (Table 1). No detectable amount of 2,4-dibromoindanone (IIc) or of the corresponding π-arene complexes (IIIb or IIIc) was observed.



(Ia X=H
b X=Br)



(IIa X=Y=H
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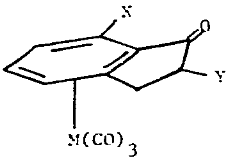
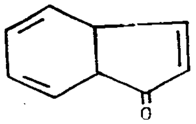


(IIIa X=Y=H
b X=Br, Y=H
c X=Y=Br)



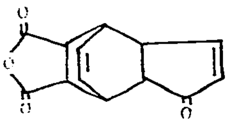
(IV)

The mechanism of this reaction obviously involves an initial decarbonylation step. There is no evidence that the metal carbonyl can promote this process. However, the corresponding dihydroindenone (IV) must be the intermediate in

TABLE 1

REACTION OF DICYCLOPENTADIENONES WITH $M(CO)_6$ (M = Cr, Mo, W)

Substrate	$M(CO)_6$	Product	Yield (%)
Ia	$Cr(CO)_6$	IIa	32
Ia	$Mo(CO)_6$	IIa	51
Ia	$W(CO)_6$	IIa	44
IV	$Cr(CO)_6$	IIa	40
IV	$Mo(CO)_6$	IIa	52
IV	$W(CO)_6$	IIa	49
Ib	$Cr(CO)_6$	IIb	28
Ib	$Mo(CO)_6$	IIb	46
Ib	$W(CO)_6$	IIb	42
Ia	$Mo(CO)_6$ and $C_4H_2O_3$	V	67



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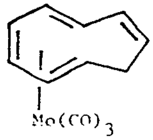

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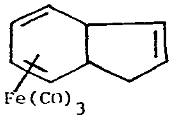
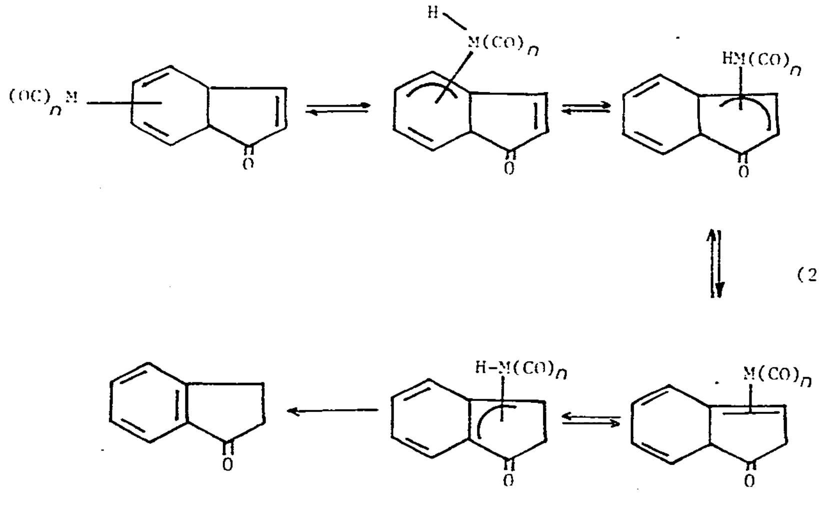


(VII)

this transformation and, indeed, has been trapped as the adduct V with maleic anhydride. Similar treatment of IV with $M(CO)_6$ also affords indanone in 40—52% yield. It is noteworthy that ring fission has been observed in the reaction of 3a,7a-dihydroindene with molybdenum hexacarbonyl yielding cyclononatetraenemolybdenum tricarbonyl (VI) [7]. However, this type of ring opened product has not been found under our conditions. The thermal equilibration between cyclononatetraene and 3a,7a-dihydroindene has been studied, and at high temperature the equilibrium favors the latter, ring closure product [8]. It is particularly relevant to note that the reactions of dihydroindene with $Fe(CO)_5$ and with $Mo(CO)_6$ give different products, namely VII and VI, respectively [7,8b]. However, the fact that both metal carbonyls react in the same manner with Ia or IV as observed in this study is striking. Had the reaction of $M(CO)_6$ with IV proceeded in a similar fashion as that with dihydroindene, ring cleavage would result in the formation of highly unstable, antiaromatic cyclononatetraenone as an intermediate. This pathway is therefore energetically unfavorable. Alternatively, the bridgehead hydrogens in IV may be activated by a neighboring carbonyl group. This may destabilize the complex and lead to subsequent double bond migration. A plausible mechanism is proposed in eqn. 2.



(2)

Similarly, Ib may also be transformed by this mechanism. The expected product IIc is obviously further reduced by $M(CO)_6$ to give IIb. Indeed, IIb was obtained by the reaction of IIc with $M(CO)_6$. The related reductive debromination reactions of activated halides with molybdenum carbonyls have recently been reported [9]. We found that all Group VI metal carbonyls are active catalysts for these reduction reactions.

In summary, we have established that Group VI metal carbonyls can function as catalysts for double bond migrations which may have synthetic applications.

Experimental

Materials

Cyclopentadienone dimer (Ia), 2-bromocyclopentadienone dimer (Ib), 3a,7a-dihydroindene (IV) were prepared according to literature methods [10]. Samples of chromium and tungsten hexacarbonyls were purchased from Research Organic/Inorganic Chemicals Corp., California. Molybdenum hexacarbonyl was obtained from Merck, Darmstadt. Melting points are uncorrected. Infrared spectra were measured on a Beckman IR-10 spectrophotometer. NMR spectra were taken on a JEOL C-60HL spectrometer. Mass spectra were recorded using a VG7070F mass spectrometer.

General procedure

A mixture of the substrate (10 mmol) and $M(CO)_6$ (10 mmol) in diglyme (10 ml) was refluxed under nitrogen for several hours until sublimation of $M(CO)_6$ subsided. The solution was cooled, diluted with ether and filtered through neutral alumina. Evaporation to dryness afforded indanone as the sole product.

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