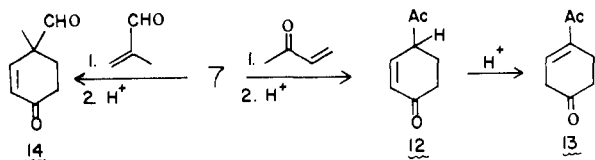


enediones, **12** and **13** (ca. 1:1), resulted. Neither was obtained in pure form but the presence of each component could be ascertained by nmr analysis. When this mixture was exposed to the action of 0.1 *N* HCl-THF for 1 hr at room temperature, an 86% overall yield of **13** ( $\nu_{\max}^{\text{CHCl}_3}$  1727, 1684, 1647  $\text{cm}^{-1}$ ; nmr  $\delta$  ( $\text{CDCl}_3$ ) 2.30 (s, 3 H), 2.10–2.80 (m, 4 H), 3.03 (d, xt,  $J = 4$  Hz,  $J = 2$  Hz, 2 H), 6.73 (t,  $J = 4$  Hz, 1 H)) contaminated by ca. 5% of **12** was isolated. The 2 H multiplet centered at  $\delta$  3.03 is assigned to the allylic methylene protons at C<sub>2</sub> adjacent to the cyclic ketone. Compound **13** was reduced (5% Pd-C-EtOH) to the known<sup>20</sup> 4-acetylcyclohexanone. Since the 2,4-DNP derivative produced from this material had a melting point (EtOAc) of 218–218.5°, while it has been reported from 200°<sup>20</sup> to 207°,<sup>21</sup> our compound was submitted to combustion analysis. *Anal.* Calcd for bis(2,4-DNP: C, 48.00; H, 4.02; N, 22.39. Found: C, 48.07; H, 3.95; N, 22.15. While we have not established the point with certainty, we believe **12** to be the principal kinetic product from unraveling of the Diels-Alder adduct. This would, of course, be the expected product if the enone is produced without involvement of an intermediate  $\beta$ -methoxy ketone. (cf. **3**  $\rightarrow$  **5** and ref 5).

The reaction of compound **7** with methacrolein (benzene, reflux, 20 hr) is indicative of its possibilities for the one-step synthesis of 4,4-disubstituted cyclohexenones.<sup>22</sup> The adduct, upon gentle acidic hydrolysis, gave a 72% yield of 4-methyl-4-formylcyclohex-2-ene-1-one (**14**).<sup>23</sup> Compound **14** ( $\nu_{\max}^{\text{CHCl}_3}$  2732, 1720, 1765, 1594, 874  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 1.31 (s, 3 H), 1.70–2.27 (m, 4 H); 5.94 (d,  $J = 10$  Hz), 6.62 (d,  $J = 10$  Hz, 1 H), 9.40 (s, 1 H)) was characterized as its bis(2,4-DNP), mp (EtOAc-EtOH) 136–136.5°. The AB pattern of the vinylic protons in the nmr spectrum rules out the alternative regioisomer 5-methyl-5-formylcyclohex-2-ene-1-one. The latter would be expected to exhibit a multiplet for the proton on the  $\beta$ -carbon.



Further applications of siloxydienes to organic synthesis are currently under investigation.

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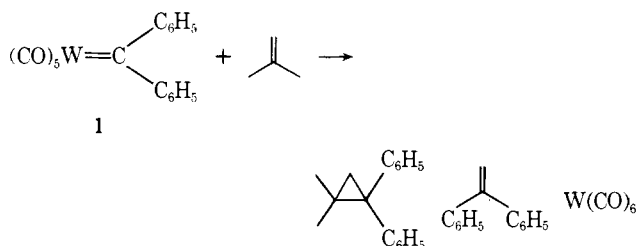
## Reactions of (Diphenylcarbene)pentacarbonyltungsten(0) with Alkenes. Role of Metal-Carbene Complexes in Cyclopropanation and Olefin Metathesis Reactions

Sir:

Stable transition metal-carbene complexes<sup>1</sup> are potentially useful model systems for the study of catalytic reactions such as cyclopropanation and olefin metathesis<sup>2</sup> which are postulated to involve metal-carbene complexes as transition intermediates.<sup>3</sup> Heteroatom-substituted carbene complexes have proven to be somewhat too thermally stable and unreactive as methylene transfer agents toward simple alk-

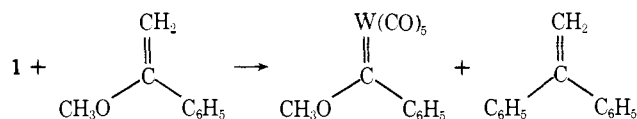
enes to serve as model systems for cyclopropanation.<sup>4</sup> In an effort to find a less stable and more reactive metal-carbene complex, we recently synthesized (diphenylcarbene)penta-carbonyl tungsten(0)<sup>5</sup> (**1**) a carbene complex not stabilized by electron donating heteroatoms attached directly to the carbene carbon atom.<sup>6</sup> Here we report several interesting reactions of **1** with alkenes that may bear upon the mechanism of cyclopropanation and olefin metathesis reactions.

Since even relatively stable metal-carbene complexes such as  $(\text{CO})_5\text{WC}(\text{OCH}_3)\text{C}_6\text{H}_5$  react with vinyl ethers,<sup>4</sup> we first studied the reaction of **1** with ethyl vinyl ether. Heating a solution of **1** in ethyl vinyl ether at 37° for 3 hr gave 65% 1-ethoxy-2,2-diphenylcyclopropane, 11% 1,1-diphenylethylene, ~45%  $\text{W}(\text{CO})_6$ , and no **1**. When **1** was heated to 100° for 2.5 hr with the unactivated alkene isobutylene, a 76% yield of 1,1-diphenylethylene was obtained in addition to 45%  $\text{W}(\text{CO})_6$  and approximately 10% 1,1-dimethyl-2,2-diphenylcyclopropane.



To determine the source of the methylene fragment in 1,1-diphenylethylene in these unusual reactions, we studied the reaction of *trans*-2-butene with **1**. When **1** was heated to 50° for 4 hr in *trans*-2-butene, a 54% yield of 1,1-diphenyl-1-propene was obtained in addition to 41%  $\text{W}(\text{CO})_6$  and a trace of 1,2-dimethyl-3,3-diphenylcyclopropane. These experiments demonstrate the scission of the carbon-carbon double bond of the alkene and the combination of a methylene fragment with the diphenylcarbene group of **1**.

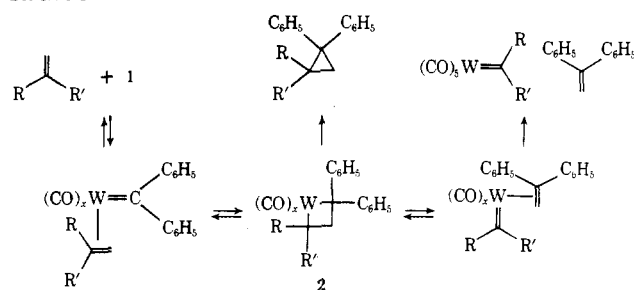
We considered the possibility that the second fragment from the alkene scission reaction might be incorporated as the carbene ligand in a new metal carbene complex. The reaction of **1** with 1-methoxy-1-phenylethylene was studied since the expected new carbene complex  $(\text{CO})_5\text{WC}(\text{OCH}_3)\text{C}_6\text{H}_5$  is stable under the reaction conditions. When **1** was heated to 32° for 6 hr with 1-methoxy-1-phenylethylene, a 24% yield of  $(\text{CO})_5\text{WC}(\text{OCH}_3)\text{C}_6\text{H}_5$  was obtained in addition to 26% 1,1-diphenylethylene, 13% **1**,  $\text{W}(\text{CO})_6$ , and a trace of 1-methoxy-1,2,2-triphenylcyclopropane. Thus in the alkene scission reaction, one fragment of the alkene is incorporated into 1,1-diphenylethylene while the other fragment is incorporated into a new metal-carbene complex.<sup>7</sup>



Both the cyclopropanation and alkene scission reactions of **1** can be explained in terms of the mechanistic scheme (Scheme I) shown below. The metalcyclobutane **2** formed by rearrangement of a metal complex containing both a carbene and an alkene ligand is the key intermediate in these reactions. **2** can undergo a reductive elimination to give a cyclopropane or can undergo cleavage to give a metal complex containing both a coordinated 1,1-diphenylethylene and a new carbene ligand.

The mechanistic scheme proposed here explains Fischer's observation of 1-methoxy-1-phenylethylene in the reaction of  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$  with ethyl vinyl ether<sup>4</sup> and with

Scheme I



1-vinyl-2-pyrrolidone.<sup>8</sup> Previously, Lappert has observed related exchange reactions of tetraaminoethylenes and bisnitrogen substituted carbene-metal complexes.<sup>9</sup> A metalcyclobutane intermediate similar to **2** was recently proposed by Noyori in the bis(1,5-cyclooctadiene)nickel(0) catalyzed reaction of bicyclobutanes with electron deficient olefins.<sup>10</sup>

It should be noted that the equilibrium between a metalcyclobutane and a metal complex containing both an alkene and a carbene ligand provides a sufficient mechanism for olefin metathesis. Such a scheme has previously been proposed by Chauvin.<sup>11</sup> A related equilibrium between a metalcyclopentane and a metalcyclobutane containing a carbene ligand has been proposed by Grubbs to explain olefin metathesis.<sup>12</sup>

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## Baluchistanamine. A Novel Type Dimeric Isoquinoline Alkaloid<sup>1</sup>

Sir:

It has been adumbrated that the isoquinolone alkaloids (**1**)<sup>2</sup> originate in plants from the oxidation of simple benzyl-isoquinolines. A parallel assumption is that the alkaloid her-