

## Thermolysis of (2-Oxacyclopentylidene)pentacarbonylchromium(0): Evidence Against Free Carbenes in Thermal Decomposition of Metal-Carbene Complexes

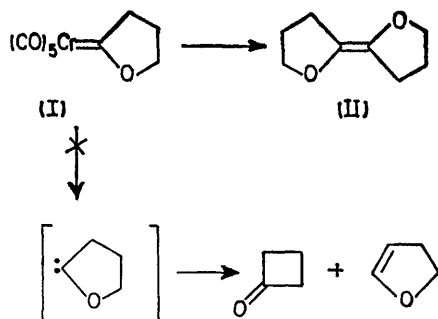
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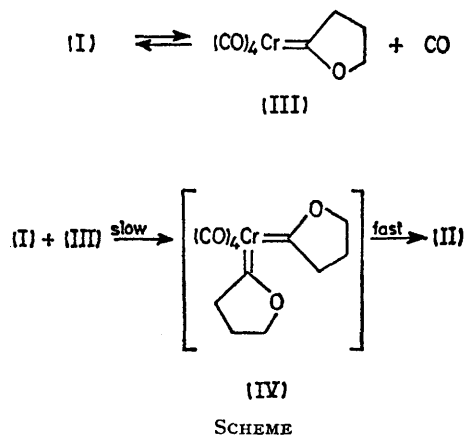
**Summary** Thermolysis of (2-oxacyclopentylidene)pentacarbonylchromium(0) (I) gives mainly the dimer and no cyclobutanone, a product characteristic of a free carbene; a bimolecular mechanism for decomposition of (I) is proposed based on kinetic studies.

WHILE stable transition metal-carbene complexes<sup>1</sup> have attracted much interest as potential sources of free carbenes, no reaction of these complexes has been shown to involve free carbenes. The synthesis of cyclopropanes from

been considered as possible intermediates in the thermolyses of  $[(CO)_5CrC(OMe)Ph]^3$  and  $[(CO)_5CrC(OMe)Me]^4$  which give formal carbene dimerization products, and in the pyridine-catalysed decomposition of the latter which gives  $CH_2=CHOMe$ ,<sup>4</sup> the formal product of the insertion of a carbene into an  $\alpha$  C-H bond.



carbene complexes and olefins has been demonstrated not to involve free carbenes.<sup>2</sup> However, free carbenes have



SCHEME

To provide a more definitive test for the intermediacy of free carbenes in the thermolysis of metal-carbene com-

plexes, we have studied the thermolysis of (2-oxacyclopentylidene)pentacarbonylchromium(0) (I).<sup>5</sup> 2-Oxacyclopentylidene, generated by thermolysis of the corresponding tosylhydrazone, has been shown to rearrange to dihydrofuran (25%) and to cyclobutanone (20%).<sup>6</sup> The thermolysis of (I) in decalin at 139 °C gave the dimer (II) (50%) and dihydrofuran (5%). Pyridine-induced decomposition of (I) gave a quantitative yield of dihydrofuran. The absence of cyclobutanone (<0.1%), the characteristic rearrangement product of 2-oxacyclopentylidene, rules out the intervention of free carbenes in the thermolysis and in the pyridine-catalysed decomposition of (I).

The mechanism of the thermal decomposition of (I) was investigated kinetically. The rate of disappearance of (I) at 139.4 °C was second order in (I) over the concentration range 0.62–0.08 M ( $k_2 = 3.5 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ ). Decomposition of (I) was inhibited by CO; under 1480 mmHg CO pressure, the disappearance of (I) was 27 times slower than in the absence of added CO. Exchange of <sup>13</sup>CO with (I) was found to be first order in (I) and to occur *ca.* 40 times more rapidly than thermal decomposition over the con-

centration range studied. In addition, (I) was found to react with  $[\text{W}(\text{CO})_6]$  to give  $[\text{Cr}(\text{CO})_6]$  and the corresponding tungsten-carbene complex. Previously, the transfer of a carbene ligand between metal complexes was shown to occur photochemically.<sup>7</sup>

A mechanism for the thermal decomposition of (I) consistent with our kinetic and exchange data is shown in the Scheme. The slow step involves the transfer of a carbene ligand from (I) to the co-ordinatively unsaturated intermediate (III) to give a biscarbene complex which leads eventually to the dimer (II).

Several examples of biscarbene complexes have been reported.<sup>8,9</sup> The conversion of tetra-aminoethylenes into metal-carbene complexes is known;<sup>9</sup> this is the microscopic reverse of the proposed decomposition of the biscarbene complex intermediate.

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