Table III. Product–Time Study for the Reaction of CH_3MgBr (0.50 *M*) with 2-Methylbenzophenone (0.00125 *M*)[a] in Ether

Reaction time	% unreacted ketone	% yield 1,2-Addition[b]	% yield 2-Methylbenzhydrol	% yield Pinacol[c]	By-product/addition
10 sec	68	2.7	28	1.7	10.8
1 hr	46	18	34	2	2.0
4 hr	11	48	39	2.3	0.85
12 hr	0	56	41	2.5	0.77

[a] At −30°. [b] 1-Phenyl-1-(2-methylphenyl)ethanol. [c] 2,2'-Dimethylbenzopinacol.

Reaction of CH_3MgBr with 2-methylbenzophenone (in stoichiometric amounts or in excess CH_3MgBr) produced almost immediately a pink solution whose visible absorption band (λ_{max} 512 nm) was identical with that of II. However, rather than slowly increasing throughout the reaction, the absorbance at 512 nm quickly reached a maximum and then decreased. The rate of decrease increased with larger excesses of CH_3MgBr. The same behavior was observed when excess CH_3MgBr was added to a solution of II, prepared according to eq 2 and 3. Thus, when the amount of expected by-product was calculated from the absorbance of ketyl at 512 nm, the result agreed with the amount of by-product found experimentally only in the early stages of the reaction, due to the disappearance of ketyl in the presence of excess CH_3MgBr (7% reaction, pinacol calculated from ketyl absorbance, 2.2%; pinacol found on hydrolysis, 2.1%). However, in all cases it was observed that when conditions were such that increased amounts of by-products were observed (increased amounts of excess CH_3MgBr or added $FeCl_3$), a corresponding increase in the amount of ketyl was observed. Thus, while the system is too complicated to establish a precise quantitative relationship between ketyl and by-products, the evidence is clear that the observed by-products do indeed result from the bromomagnesium ketyl intermediate (II).

Evidence for two competing mechanisms (i.e., "polar" vs. SET) was obtained by following the formation of products with time in the reaction of 0.50 *M* CH_3MgBr with 0.00125 *M* 2-methylbenzophenone (Table III, Figure 1). In the early stages of the reaction, 2-methylbenzhydrol is the major product being formed, while in the latter stages (presumably after most of the "catalysts" have been consumed) formation of 1,2-addition product is predominant. Clearly, more than one mechanism is operating. However, when $FeCl_3$ (0.05 mol %) was added to the reaction of 0.20 *M* CH_3MgBr with 0.020 *M* 2-methylbenzophenone, the results were strikingly different. The ratio of by-products to 1,2-addition product was constant throughout the reaction. In this case, there is sufficient "catalyst" present to allow the SET process to compete with the normal polar addition throughout the reaction, thus giving rise to a constant by-product to addition ratio. Although the ratio of the two mechanisms taking place is unknown at present, the $FeCl_3$ catalyzed reaction was found to be definitely faster, and, therefore, the SET mechanism must account for the majority of the products.

Thus, it appears that the addition of CH_3MgBr to 2-methylbenzophenone in ether proceeds via a normal polar mechanism, whereas in the presence of small amounts of transition metal catalysts (e.g., 0.05 mol % of $FeCl_3$) the reaction proceeds via a single electron transfer pathway.[5] The detailed nature of the SET mechanism, including the role of the iron, is presently being studied.

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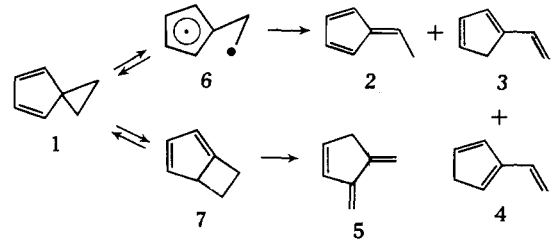
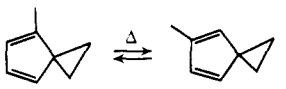
A Skeletally Degenerate Thermal Reorganization of the Spiro[2.4]hepta-4,6-diene Ring System

Sir:

As a part of our continuing interest in the electronic structure and chemical reactivity of the spiro[2.4]hepta-4,6-diene ring system,[1] we now report the observation of a thermal reorganization of this system in which the spiro[2.4]hepta-4,6-diene ring skeleton remains intact. The thermal reorganization of spiro[2.4]hepta-4,6-diene (**1**) has been reported to yield 6-methylfulvene (**2**), a mixture of the isomeric vinylcyclopentadienes (**3** and **4**), and 3,4-dimethylenecyclopentene (**5**).[2] The overall activation energy of 43.6 kcal/mol is close to that reported for thermal [1,5]-methyl migrations in cyclopentadienes.[3] The results have been interpreted[2] in terms of a rather delicate energy balance between homolytic rupture of the C-1–C-3 bond to provide the cyclopentadienyl–methylene diradical (**6**) and concerted [1,5]-sigmatropic migration of cyclopropyl methylene to afford the intermediate bicyclo[3.2.0]heptadiene (**7**). The pyrolytic interconversion of *cis*- and *trans*-1,2-dimethylspiro[2.4]hepta-4,6-diene at an activation energy of 42.7 kcal/mol[4] is consistent with the intervention of the diradical,[5] and evidence for the facile reverse of the **1** → **7** conversion has recently been reported.[6]



The synthesis of 4- and 5-methylspiro[2.4]hepta-4,6-diene (**8** and **9**) in a 3:2 product ratio (35% overall yield) was readily accomplished by the reaction of methylcyclopentadiene (as a mixture of positional isomers) with 1,2-dibromoethane,[7] and clean separation of the isomeric products was effected by preparative scale GLPC. The assignment of the structures of **8** and **9** is clear from the respective 60-MHz ^1H NMR spectra:[8] **8** ^1H NMR ($CDCl_3$) δ 1.36 (m, 2 H), 1.55 (m, 2 H), 1.70 (d, J = 1.5 Hz, 3 H), 6.18 (m, 1 H), 6.01, 6.46 (AB, 2 H); **9** ^1H NMR ($CDCl_3$) δ 1.51 (s, 4 H), 2.05 (d, J = 1.5 Hz, 3 H), 5.69 (q, J = 1.5 Hz, 1 H), 6.04, 6.35 (AB, 2 H), in which the most significant factor is the chemical shift nonequivalence of the syn and anti cyclopropyl protons induced by the proximity of the C-4 methyl group in **8.**



8 9

Vapor state pyrolysis of either **8** or **9** in a static system at 513–543°K provides an equilibrium mixture of **8** (~60%) and **9** (~40%). The pyrolyses are remarkably clean; no volatile products other than **8** or **9** are detectable by GLPC analysis, and >98% of the starting material is recovered as the spiroheptadienes **8** and **9.** Kinetic analysis provides E_a = 44 kcal/mol, $\Delta S^{\ddagger}$ = +2 ± 1.5 eu. The greater stability of **8** (approximately 0.4 kcal/mol under these conditions) may originate, at least in part, from the unusual electronic structure proposed for this spirodiene ring system.[1] Calculations by the MINDO/1 method[9] predict the standard heat of formation of **8** to be approximately 0.9 kcal/mol lower than that of **9** in qualitative agreement with the observed result.

The mechanisms of thermal [1,5]-alkyl shifts in cyclopentadienes have been extensively investigated for a number of systems,[2,10-15] and a rather delicate energy balance between the concerted and radical pathways is frequently apparent. The activation energy of 44 kcal/mol for the interconversion of **8** and **9** is in good agreement with that reported for pyrolysis of **1**,[2] and the positive activation entropy is suggestive of the intervention of the diradical. The estimated activation energy of 50–56 kcal/mol for homolysis of the 1,5,5-trimethylcyclopentadienes[15] corrected for the difference in cleavage of a secondary C–C bond (compare: D_{C-C} (C_2H_6) = 88 kcal/mol and D_{C-C} (C_3H_8) = 85 kcal/mol)[16] provides an estimate of 47–53 kcal/mol for the activation energy for homolysis of an "unstrained" **8** or **9.** Thus, if the **8** ⇆ **9** rearrangement proceeds exclusively via the diradical pathway, only 15–50% of the 18–20 kcal/mol[17] of the cyclopropane strain energy usually released in the transition state for cyclopropane rupture is realized in this process. Although the positive activation entropy ($\Delta S^{\ddagger}$ = +2 eu) is suggestive of the diradical process,[2] this value is somewhat lower than that normally observed in the geometric isomerization of cyclopropanes (*cis*-1,2-dideuteriocyclopropane, +13 eu;[18] 1-methyl-*cis*-2,3-dideuteriocyclopropane, +10 eu,[19] and *cis*-1,2-dimethylspiro[2.4]hepta-4,6-diene, +8 eu[4]). Thus, it appears reasonable to conclude that both the stepwise and concerted processes may be involved in this rearrangement. The apparently exclusive preference for the concerted rearrangement in the pyrolysis of *cis*- and *trans*-6,9-dimethylspiro[4.4]nona-1,3-diene,[14] as evidenced by the high degree of stereospecificity of the rearrangement, is understandable in terms of the strained character of the bicyclo[3.2.0]heptadiene intermediate derived from the spiroheptadienes, an appreciable degree of which must be experienced in the transition state for concerted cyclopropyl methylene migration.

The present observations appear most adequately accommodated by a stepwise perambulation of the C_2H_4 fragment and a hydrogen atom about the periphery of the cyclopentadiene ring. Although the stepwise process appears operative, *competitive concerted [1,5]-sigmatropic methylene migration may obtain.*[20] The results of detailed stereochemical experiments currently in progress should provide the basis for clarification of the mechanism of [1,5]-carbon shifts in this spiroheptadiene system.

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$Rh_6(CO)_{16}$. A Homogeneous Catalyst for the Oxidation of Carbon Monoxide to Carbon Dioxide and for the Oxidative Cleavage of Carbon–Carbon Bonds in Ketones to Carboxylic Acids

Sir:

We wish to report the first example of a homogeneously catalyzed oxidation reaction with molecular oxygen and a transition metal cluster compound. We have found that the compound $Rh_6(CO)_{16}$ will catalyze both the oxidation of CO to CO_2 and the oxidation of ketones to carboxylic acids, by molecular oxygen. The CO is completely oxidized and the catalyst retains its initial activity even after 12,500 mmol of CO_2 have been produced.[1]

Previous work with mononuclear complexes of Rh(I),[2] or the compound $Pt(PPh_3)_4$,[3] has shown that CO can be oxidized with molecular oxygen in a homogeneously catalyzed system, but in both of these cases there is a concomitant oxidation of the ligand. In our case since the compound used is an unsubstituted carbonyl complex the catalyst is recovered unchanged from the reaction. An alternative procedure has been used by Halpern et al., who effected oxidation of a coordinated carbonyl by attack with hydroxide ion.[4] The oxidation of CO to CO_2 in the presence of $Rh_6(CO)_{16}$ can be carried out in acetone as solvent. The cluster compound is insoluble in this solvent at 25° and is recovered in crystalline form at the end of a reaction run. Nevertheless, the catalytic reaction takes place in solution since the compound is catalytically inactive in the absence of solvent or as a suspension in hexane. Final verification of the homogeneity of the active species was obtained by cooling the reaction vessel, filtering the solution, returning the filtrate to the reac-