observed from water photolysis using (Chl a·$2H_2O)_n$ films on microscope slides in the absence of Pt, although the quantum efficiency of water photolysis in this case is nearly two orders of magnitude lower than that corresponding to the results shown in Figure 3c. In contrast, for comparable line intensities at masses 2 (H_2^+), 3 (HD^+), and 4 (D_2^+) obtained in the Pt-H_2O experiments, the intensity of lines at masses 34 ($^{16}O^{18}O^+$) and 36 ($^{18}O_2^+$) are significantly weaker than those observed in the photolysis and electrolysis runs (compare Figures 3b and 3c). The weak mass 34 ($^{16}O^{18}O^+$) line observed in Figures 3a and 3b is greater than that expected from the 0.2% natural abundance of ^{18}O, however, and may be a result of isotopic redistribution of ^{18}O in the water and O_2 present as contamination from the atmosphere. The possibility that this line may have resulted from water decomposition appears rather unlikely from thermodynamic considerations.[10,11]

We rule out H_2O_2 as a product in the Pt-H_2O reaction by mass spectrometric determinations and by the colorimetric triiodide method.[12] Among possible explanations for the experimental effects described above is the thermodynamically characterized reaction[13]

$$2H_2O + Pt \xrightarrow[\Delta]{} Pt(OH)_2 + H_2 \quad \Delta G^\circ = 49.7\ \text{kcal/mol} \qquad (2)$$

in which Pt is oxidized in the reduction of the water. Reaction 2 is uphill in free energy, having an equilibrium constant $K \sim 10^{-27}$ at 150 °C. The observation of H_2 may be rationalized in spite of this unfavorable equilibrium constant on account of the fact that $Pt(OH)_2$ is extremely insoluble in water, so that reaction 2 is expected to occur entirely at the Pt-H_2O interface. The displacement of H_2 from the relatively hot ($\gtrsim$150 °C) reaction zone to the cooler ($\sim$40 °C) gaseous space above the water would thus shift the equilibrium of reaction 2 to the right. This interpretation appears to be consistent with the observed temperature dependence of the H_2 evolution rate (see inset, Figure 1). From tables of H_2 solubility[14] we estimate that the enthalpy of H_2 solvation in water at the boiling point of water is 3.62 kcal mol^{-1}. This value is in fair agreement with the activation energy 3.48 kcal mol^{-1} obtained from the Arrhenius plot in Figure 1.

In conclusion we have described the generation of molecular hydrogen in the thermochemical decomposition of water by Pt. In addition we have also established the red-light photochemical origin of the Pt/Chl a water splitting reaction based on the mass spectrometric data in Figure 3.

Acknowledgment. The method of gaseous sample transfer in the GC analysis was suggested by Dr. R. H. Wentorf, Jr.

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(8) The discrepancy between the rate determination from the GC analysis and the determination in mass spectrometric and pyrolytic studies could have originated from variations in the quality of the platinum surface and the extent to which air had been excluded from the sample. More probably, however, the difficulty may be attributable to systematic errors arising from the sample transfer procedure in the GC analysis. The mass spectrometric and Hersch determinations, unlike the GC work, were on-line experiments.

(9) Preparation procedures for the Pt-Chl a sample have been previously described in ref 4.

(10) Patents issued to French workers (*Chem. Abstr.*, **86**, 157711f, 191950t (1977)) described the thermochemical cleavage of water in the temperature range 100-1200 °C using a finely divided Pt group metal, preferably Pd, as catalyst. The H_2 and O_2 were reportedly generated in a chamber, the walls of which were selectively permeable to H_2. According to the present observations it would appear that Pt, being consumed in the Pt-H_2O reaction, would not be a suitable catalyst for reaction under conditions specified by these French workers.

(11) The effect of heat on Pt immersed in water was examined by comparing the rate of the catalytic decomposition of H_2O_2 by a Pt black sample heated in water for 20 h at 180 °C with that by an identically prepared Pt black sample stored in water at room temperature for 20 h. Both electrodes were maintained under an Ar atmosphere during the heat treatments. The rate of H_2O_2 decomposition catalyzed by each sample was subsequently determined by the colorimetric triiodide method.[12] The unheated Pt sample decomposed H_2O_2 at a rate 7.24×10^{-4} mol cm^{-2} s^{-1}, approximately twice that, 4.20×10^{-4} mol cm^{-2} s^{-1}, using the heat treated platinum. The results indicate that the number of Pt active sites was decreased as a result of heating the platinum in water. Details of these results will be published elsewhere.

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Received September 5, 1978

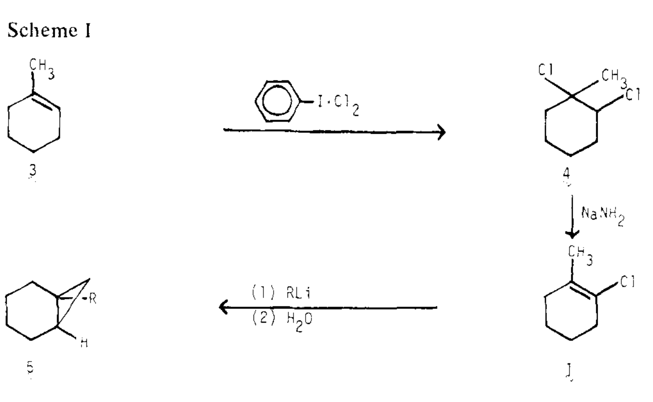
Reactions of 1-Chloro-2-alkylcyclohexenes with Organolithium Reagents. The Intermediacy of Cyclopropenes

Sir:

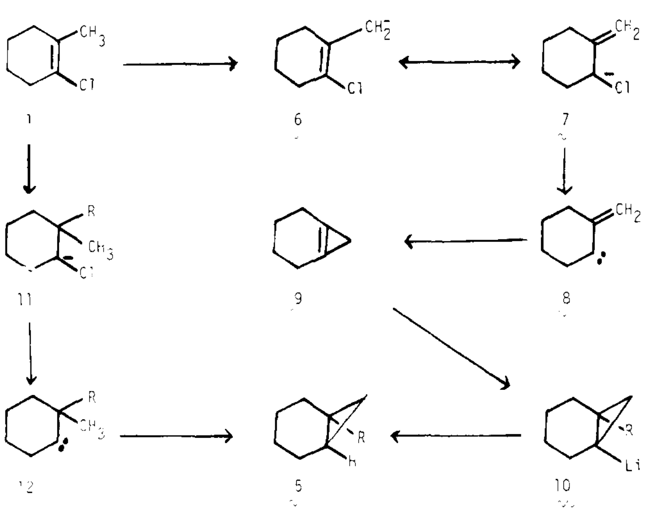
In 1967, it was reported that a mixture of 1-chloro-2-methylcyclohexene (**1**) and 1-chloro-6-methylcyclohexene (**2**) reacted with phenyllithium to yield 1-phenyl-3-methylcyclohexene, 1-phenyl-6-methylcyclohexene, and unreacted **1**.[1,2] In view of our recent findings on the reactions of vinyl halides with organolithium reagents,[3] the reported poor reactivity of **1** with phenyllithium seemed surprising. Thus, we set out to synthesize pure **1** and to investigate its behavior in the presence of organolithium reagents. We now report that **1** reacts with a variety of organolithium reagents to yield substituted bicyclo[4.1.0]heptanes. Mechanistic studies suggest the intermediacy of the highly strained cyclopropene, bicyclo[4.1.0]heptene-$\Delta^{1,6}$.

Pure **1** was prepared in 41% overall yield from 1-methylcyclohexene (**3**)[4] via the dichloride, **4**, which resulted from the reaction of **3** with iodobenzene dichloride (Scheme I). Dehydrochlorination of **4** with sodium amide in liquid ammonia gave

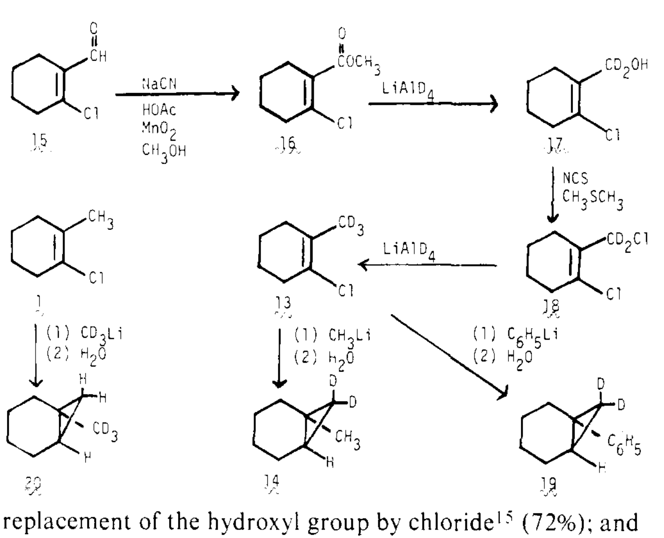
Scheme I



Scheme II



Scheme III



1.[5] In an unprecedented reaction, **1** (1–2 g) reacted with excess organolithium reagent (5 equiv) to produce **5**. Yields range from good to excellent (R = C_6H_5, 90%; R = $CH_3CH_2CH_2CH_2$, 52%;[6] R = CH_3, 47%). In each case, the structure of the product was based on spectral data and on comparison of the product with an authentic sample of the substituted bicyclo[4.1.0]heptane[7] prepared by an alternate route.[8]

Mechanistically, it appeared that the rather unprecedented organolithium reactions described above might be rationalized by either of two pathways (Scheme II). Both mechanisms involve a unique combination of reactions. However, each of the individual steps would appear to have some analogy in the literature. In one mechanism, the organolithium reagent would initially act as a base to pull off the allylic hydrogen which would generate the allylic anion, **6**. This anion could be considered in terms of the resonance structure **7**, which would yield **8** by α elimination.[9] Allyl carbene to cyclopropene conversion would give **9**.[9] The addition of organolithium reagents to cyclopropenes is well established.[10] In this manner, **9** could be converted into **10**, and subsequently into **5**. The alternate mechanistic rationale would involve the initial addition of the organolithium reagent to **1** to produce **11**; α elimination of chloride ion from **11** would produce the neopentyl-type carbene **12**. Selective insertion into the methyl group would then produce **5**. Such insertions have ample precedent.[11] Differentiating between these two mechanisms was of interest. The significant rate acceleration which occurred on the addition of tetramethylethylenediamine (TMEDA) indicated that the rate-determining step might be an acid–base reaction, but this was certainly not a definitive piece of evidence for the cyclopropene mechanism (**1** → **9** → **5**).

Careful examination of the two mechanisms indicated that a distinction might be made through the use of deuterium labeled starting materials. The unlabeled starting material **1** should react with trideuteriomethyllithium to yield **5** where R is trideuteriomethyl if **9** were involved as an intermediate. Similarly, 1-chloro-2-trideuteriomethylcyclohexene (**13**) should react with unlabeled methyllithium to produce **14**. In contrast, according to the alternate mechanism, the addition of trideuteriomethyllithium to **1** and of methyllithium to **13** should produce **12** via **11**. The same carbene (or carbenoid), **12**, should be generated from both sets of starting materials. Thus, the same products should be generated from both sets of starting materials if the reaction path involved **11** and **12**.

The synthesis of **13** could not be achieved by a route similar to that used for **1** (Scheme III).[12] However, it could be prepared by a sequence of reactions which involved (a) the oxidation[13] of **15**[14] to **16** (46%); (b) the reduction of **16** to **17** (97%); (c) the replacement of the hydroxyl group by chloride[15] (72%); and (d) lithium aluminum deuteride reduction of **18** to **13** (75%). Mass spectral analysis of **13** showed 97% d_3; the ^{1}H NMR indicated the complete absence of any signal due to the unlabeled methyl group.

Treatment of **13** with methyllithium gave **14** which was shown to have chromatographic behavior identical with that of 1-methylbicyclo[4.1.0]heptane. ^{1}H NMR showed **14** to be devoid of any signal in the δ 0.5–0.0 region where **5** has strong signals. However, mass spectral analysis showed 30% d_3, 66% d_2, and 4% d_1. In a similar manner, treatment of **13** with phenyllithium gave **19**, which lacked the geminal cyclopropyl protons, but analyzed for 44% d_3, 53% d_2, and 3% d_1 by mass spectroscopy. The presence of substantial amounts of d_3 material in both **14** and **19** could be interpreted to mean that both of the mechanisms discussed above were involved. However, this explanation would require that the portion of the reaction which occurred via **11** and **12** must have involved exclusive insertion[16] of the carbene into the deuterated methyl group for some obscure reason. Obviously, this could be tested by the addition of trideuteriomethyllithium to **1**. When this experiment was carried out, **20** was obtained which showed no ^{1}H NMR signal due to the methyl group in the 1 position, but did show a strong ^{1}H NMR signal due to the cyclopropyl methylene group. Mass spectral analysis of **20** showed 97% d_3. Clearly, no anomalous selectivity for insertion into a C–D bond existed.

The presence of some d_3 material in the product from the reaction of organolithiums can be rationalized in terms of the cyclopropene (**1** → **9** → **5**) mechanism. Addition of an organolithium reagent to **9**-d_2 would generate **10**-d_2. This might be expected to be a stronger base than either methyllithium or phenyllithium. If this were the case, **10**-d_2 could remove a deuteron from **13** to generate **6**-d_2 and **14**-d_3. This would be consistent with our observations.

Mechanistically, the results presented above are consistent with the intermediacy of bicyclo[4.1.0]heptene-$\Delta^{1,6}$. Although 1,2-bridged cyclopropenes have been described[17] and postulated[18] as highly reactive intermediates, those previously reported have originated from quite different precursors. In our case, the starting materials are readily available and the yields of cyclopropane derivatives are quite reasonable. The reaction is not restricted to **1** and its deuterated version. For instance, 1-chloro-2-ethylcyclohexene reacted slowly with *n*-butyllithium to give 34% 1-*n*-butyl-7-*endo*-methylbicyclo[4.1.0]heptane. It would appear that this should constitute a general procedure for the synthesis of fused-ring cyclopropyl derivatives.

We are continuing to explore the synthetic utility of this reaction.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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(19) National Science Foundation Fellow, 1976–1979.

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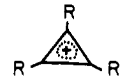
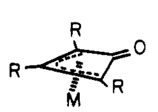
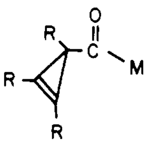
Received August 15, 1978

Interactions of Small Organic Rings with Transition Metals. Formation of η^3-Cyclobutenonyl Complexes by the Ring Expansion of 2-Cyclopropene-1-carbonyl Metal Species

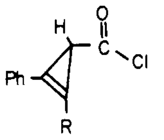
Sir:

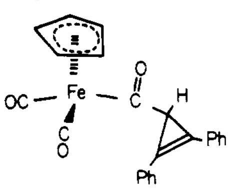
1a. R = Ph.
1b. R = Me.
1c. R = ᵗBu.

2a. M = Co(CO)$_3$; R = Ph.
2b. M = Fe(CO)$_2$ (NO); R = Ph.
2c. M = Co(CO)$_3$; R = Me.
2d. M = Fe(C$_5$H$_5$)(CO); R = ᵗBu.

3.



4a. R = Ph.
4b. R = p-MeOC$_6$H$_4$
4c. R = Me.

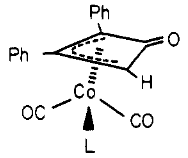


5.

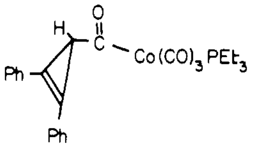
Reactions of cyclopropenium cations with transition metal complexes have been only moderately successful in the preparation of η^3-cyclopropenyl metal complexes.[1] Typical alternative reaction pathways have been shown to afford complexes derived from direct insertion of the metal into the three-membered ring,[2] or, in a more unusual reaction, the formation of four-membered-ring cyclobutenonyl complexes by a ring expansion with incorporation of carbon monoxide.[3] Thus, cations **1a–c** have been shown to afford the complexes **2a–d** on reaction with the appropriate metal carbonyl anion.[3] It has been suggested that the mechanism of this ring-expansion reaction involves attack on coordinated CO to afford an intermediate, coordinatively unsaturated, cyclopropenyl carbonyl metal species of general structure **3**, which then undergoes ring expansion.[3d,4] We here present direct evidence for such a mechanism and describe unusual spectroscopic and chemical properties of the cyclobutenonyl ligand.

Reaction of equimolar amounts of the 2-cyclopropene-1-carbonyl chloride **4a**[5] and $Fe(\eta^5\text{-}C_5H_5)(CO)_2^-Na^+$ [6] in tetrahydrofuran (THF) afforded, after dry column chromatography, the coordinatively saturated 2-cyclopropenyl-1-carbonyl-iron complex **5**, in which the cyclopropene ring remains intact.[7] Complex **5** can be recovered unchanged from refluxing hexane; ultraviolet irradiation of **5** in hexane led to decomposition, affording $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ as the only metal-containing product. No ring expansion to form a product analogous to **2d**[3d] was observed.

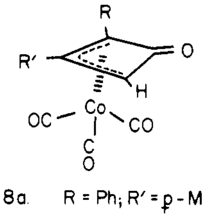
In contrast, reaction of **4a** with $Co(CO)_3L^-Na^+$ (L = CO, PPh$_3$, PPh$_2$Me, PMe$_2$Ph, PEt$_3$) in THF afforded the cyclobutenonyl complexes **6a–e** in excellent yields.[8] Complexes **6b–e** could also be prepared in essentially quantitative yield by reaction of **6a** with equimolar amounts of the appropriate tertiary phosphine (C_6H_6, 25 °C). Infrared monitoring of the reaction of $Co(CO)_3(PEt_3)^-Na^+$ with **4a** exhibited transient absorbances at 2075 (m), 2041 (s), 2017 (s), and 1651 (m) cm^{-1}, characteristic[9] of an acyl species **7**. These bands were rapidly



6a. L = CO.
6b. L = PPh$_3$
6c. L = PPh$_2$ Me.
6d. L = PPhMe$_2$.
6e. L = PEt$_3$.



7.



8a. R = Ph; R′ = p-MeOC$_6$H$_4$
8b. R = p-MeOC$_6$H$_4$; R = Ph.
8c. R = Ph; R′ = Me.
8d. R = Me; R′ = Ph.

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