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Iridium(I)-Catalyzed Rearrangements of *exo*- and *endo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene and *exo*- and *endo*-Tricyclo[3.2.1.0^{2,4}]octane

William H. Campbell and P. W. Jennings*

Department of Chemistry, Montana State University, Bozeman, Montana 59717

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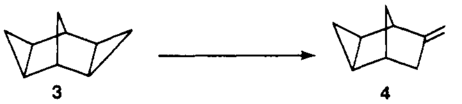
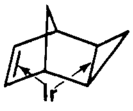
Cyclopropane moieties within the rigid hydrocarbon matrices of tricyclo[3.2.1.0^{2,4}]octane and tricyclo-[3.2.1.0^{2,4}]oct-6-ene systems are converted primarily to exocyclic methylene compounds by using an Ir(I) catalyst. O_2 is necessary for the reaction. In chloroform solvent, the reaction is more efficient but less selective than in benzene. A metallocarbene olefin intermediate is suggested for the reactions of hydrocarbons 7 and 8.

In 1969, Volger[1] reported on the interesting reactions shown as eq 1 and 2. Under the reaction conditions used, 130 °C and benzene, the endo isomer of 1 and the exo, endo isomer of 3 failed to react. Likewise the remaining cyclopropyl group of 4 was inactive. This led him to suggest that the reaction required an intermediate which had the metal atom situated on the endo side of the bicyclic ring system and coordinated to the olefin and the cyclopropane as shown in structure 5. As part of our program on transition metal catalyzed reactions of cyclopropanes in rigid hydrocarbon matrices, we were interested in the details of this reaction.[2]

(1)



(2)



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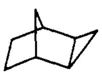
In this article we will show that O_2 is necessary in the reactions, that replacement of benzene with chloroform facilitates the reaction, and that a bidentate endo metal intermediate such as 5 is not warranted in $CHCl_3$. Further, under the revised reaction conditions ($CHCl_3$–O_2), not only is the endo isomer of 1 reactive but so are the exo and endo isomers of the saturated analogues (6–8).



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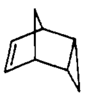

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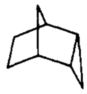

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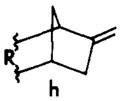
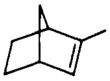
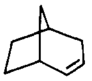
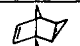
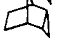
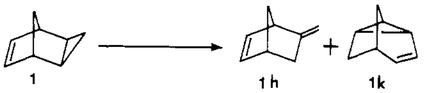
Table I. Products and Relative Yields for Hydrocarbons 1, 6, 7, and 8

	 h	 i	 j	 k
1 	54	0	0	45
6 	83	11	6	0
7 	72	0	0	28
8 	64	6	30	0

For 1 and 7 R is HC=CH; 6 and 8 R is H_2C-CH_2.

Oxygen Requirement. In attempting to repeat Volger's results, we placed the constituents in a glass vessel, removed the oxygen by evacuation and N_2 purge, sealed the vessel, and heated for 2–32 h. subsequent analysis (see Experimental Section) showed that the reaction had not progressed. We changed the solvent to chloroform and observed the same results. When the vessel was sealed without evacuation or N_2 purge, a good yield of rearranged hydrocarbon was obtained from tubes containing both benzene and chloroform. Presumably the O_2 is reacting with the iridium complex which subsequently facilitates the reaction. Triphenylphosphine oxide was identified among the reaction products. Further work is proceeding on the oxygen requirement.

Effect of Chloroform. As noted above chloroform was also investigated as a solvent for the reaction. When the reaction products were analyzed from hydrocarbon 1, using $CHCl_3$ as the solvent, two things were noted. First, there was less starting material remaining in this reaction (33%) compared to the same reaction in benzene (66%). Second, there were two products in the chloroform reaction (eq 3) whereas the benzene reaction produced only one, as previously reported. The overall product yield for eq 3 was 63%, and the ratio of products **1h** and **1k** was 1:1.



(3)

Since product **1k** had previously been reported[3] to result from the thermal reaction of 1, we considered the possibility that it arose from thermal processes. In addition, HCl might have been generated in the reaction and perhaps had catalyzed the reaction. Therefore three control experiments were run simultaneously. The first control tube contained all ingredients except the iridium complex. The second contained Na_2CO_3 in addition to all of the the reaction constituents. The third tube contained all of the reaction participants. There were no hydrocarbon products formed in tube 1 and the products from tubes 2 and

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(1) Volger, H. C.; Hogeveen H.; Gaasbeek, M. M. P. *J. Am. Chem. Soc.* **1969**, *91*, 218, 2137.

(2) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 385.

(3) Simmons, H. E., Quoted in ref 15 by: Prinzback, *Tetrahedron Lett.* **1966**, 1681.

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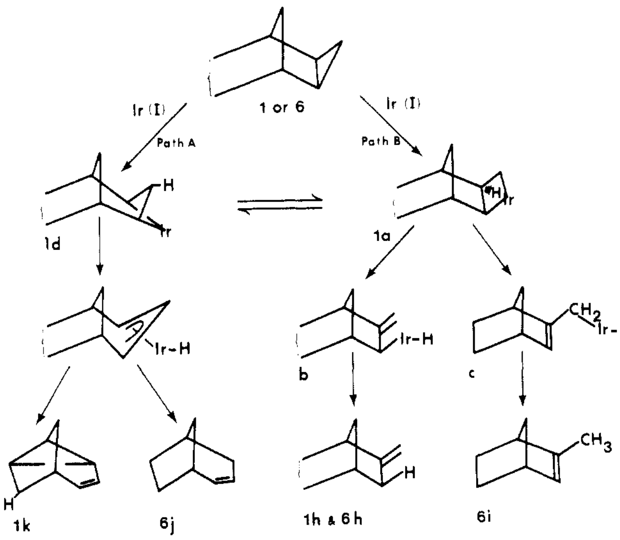
Scheme I



3 were identical in type and yield. Thus, it appears that product **1k** is indeed generated via the iridium catalyst.

Investigation of Other Cyclopropane Compounds. The enhanced activity found in using the solvent chloroform encourged us to reinvestigate some of the reactants (**6–8**) which were previously reported to fail in benzene solutions. The results are shown in Table I. Obviously these compounds do react in chloroform. Furthermore, a third product, **i**, was obtained from the saturated analogues **6** and **8**. The possibility that this third product is a reaction intermediate is being investigated.

The fact that compounds **6** and **8** react with high yields (see Experimental Section) suggests that the earlier proposed intermediate **5** has no merit at least in $CHCl_3$. We did not determine the relative reactivities of the substrates and thence the influence of the olefin on the relative rates.

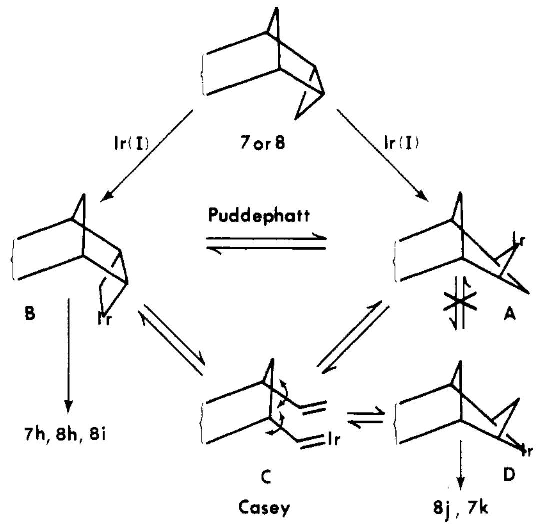
Discussion

The exocyclic methylene products, **1h** and **6h**, as well as product **6i** appear to be readily explained as arising from an *exo*-iridacyclobutane intermediate **1a** (path B) as shown in Scheme I. Likewise the formation of products **1k** and **6j** may be rationalized on the basis of the intermediate **1d** (path A) in Scheme I. The latter pathway has been well documented by the excellent work of Katz.[4]

The site of initial iridium insertion into these two substrates is uncertain. It could occur at two different cyclopropane edges to yield **1a** and **1d** or it could enter one of the edges and then equilibrate via a Puddephatt-type mechanism.[5] The low yield observed for the formation of product **6j** (Table I) suggests that the intermediate **1d** is not favored for substrate **6** either by the equilibrium connecting intermediates **1d** and **1a** or by the initial insertion of Ir into the more substituted cyclopropane bond.

While the mechanism for the formation of products from hydrocarbons 1 and 6 appears to have ample precedent in the literature, the products from 7 and 8 are proposed by us to involve a metallocarbene–olefin intermediate, Scheme II. In this discussion, we are assuming that substrates 7 and 8 follow similar paths. Products **7h**, **8h**, and **8i** can be rationalized by inserting the iridium into one of the least substituted cyclopropane bonds to form intermediate B. Subsequent β elimination and reductive elimination would yield the observed products **7h**, **8h**, an **8i**.

Scheme II



The unique feature in the formation of products **8j** and **7k** is that they require the inversion of at least one of the cyclopropyl ring juncture carbons. The Puddephatt rearrangement,[5] which nicely accommodates a 1,2 rearrangement of the metal atom in metallacyclobutane complexes would provide a path for the equilibrium between intermediates A and B. However, as presently viewed, it does not provide a path for the 1,3 rearrangement which is necessary for the formation of intermediate D which is the logical precursor for products **8j** and **7k**.

The Casey mechanism,[6] which is an alternative to the Puddephatt mechanism, appears to offer a reasonable pathway for the formation of these intermediates and subsequent products. In this case either intermediate A or intermediate B undergoes a 2 + 2 cycloreversion to form the metallocarbene–olefin intermediate C which may be free to rotate about the bonds indicated. Closure of this intermediate to D would accomplish the required inversion of the requisite carbons and subsequently lead to the formation of products **8j** and **7k**.

The Casey mechanism was proposed for a platinacyclobutane system which rearranged stereospecifically at 52 °C. In this rearrangement, Casey proposed that the reaction proceeded with the metal portion of the carbene coordinated to the olefin. We are now suggesting that intermediate C, if free, could rotate as required to form the iridacycle D which can generate products via the previously characterized paths. The reaction conditions of 130 °C in chloroform appear to be adequately rigorous to release the metal from coordination.

Conclusions

Cyclopropane moieties within rigid hydrocarbon matricies such as the tricyclo[$3.2.1.0^{2,4}$]octane and tricyclo[$3.2.1.0^{2,4}$]oct-6-ene systems are converted primarily to exocyclic methylene groups using $(Ph_3P)_2IrCOCl$. In benzene, the reaction is highly specific in that the exocyclic methylene compound is the only product formed. Further, in benzene the number of reactants may be limited. In chloroform, the specificity is somewhat reduced but the reaction proceeds further toward completion. Oxygen is required for the reaction in either solvent.

The fact that the saturated compounds react abrogates the need for the endo bidentate intermediate which had

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(4) Katz, T. J.; Cerefice, A. A. *J. Am. Chem. Soc.* **1969**, *91*, 2405; **1971**, *93*, 1049.

(5) Al-Essa, R. J.; Puddephatt, R. J.; Thompson, P. J.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1980**, *102*, 7546.

(6) Casey, C. P.; Scheck, M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233.

been previously suggested for this reaction. All of the products can be rationalized via mechanistic schemes involving iridacyclobutane intermediates followed by β elimination and reductive elimination. Another interesting development occurs with the two substrates which have the cyclopropane moieties in the endo configuration. For these two substrates a metallocarbene–olefin intermediate is proposed as the key intermediate which is responsible for the necessary inversion of one if not both of the ring juncture carbons.

Experimental Section

General Remarks. All NMR spectra were obtained with a Bruker WM 250 spectrometer using $CDCl_3$ as the solvent and Me_4Si as an internal standard. Mass spectra were recorded by using a Varian MAT CH5 spectrometer. GC data were measured in a Varian series 1400 chromatograph using a 10-ft. column of 5% SE30 on Chromosorb. W. Retention times and peak integrals were determined with a Spectra-Physics autolab minigrator.

Chloroform-d_1 was purchased from Stohler Isotope Chemicals and used as a reaction solvent without further purification. Benzene was purchased from J. T. Baker Chemical Co. and distilled over CaH_2 prior to use. Allyl chloride, cyclopentadiene, and norbornadiene were purchased from Aldrich and distilled prior to use. The following chemicals. were used as received: cyclooctane (Chem. Service), *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Aldrich), palladium acetate (Aldrich), chlorocarbonylbis(triphenylphosphine)iridium (Strem), and norbornene (Aldrich).

Synthesis of Substrates 1, 6, 7, and 8. *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene and its dihydro derivative, 6, were prepared by the method of Kottwitz.[7] *endo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene, 7, was obtained by using the procedure of Closs.[8] The dihydro derivative 8 was prepared by hydrogenating compound 7 with 10% Pd on carbon. The ^1H NMR data which were used to confirm the structures of all these substrates are listed at the end of the Experimental Section.

Attempted Reaction of 1 with $(Ph_3P)_2IrCOCl$ in an Oxygen-Free Environment. Two glass reaction vessels were charged with 75 mg of 1 (7×10^{-4} mol), 50 mg of iridium catalyst (6.4×10^{-5} mol), and 1.5 mL of benzene. They were then subjected to three freeze–thaw cycles under vacuum with N_2 used as the purging gas. After being sealed, the reaction vessel was heated in an oven at 130 °C. The first tube was opened after 2 h and th second after 32 h. Analysis of the reaction mixture by GC and ^1H NMR spectroscopy confirmed that >90% of the starting material remained and none of the expected product could be observed.

Reaction of Substrates 1, 6, 7, and 8 with $(Ph_3P)_2IrCOCl$ in an Oxygen Environment. All of the reactions were carried out in sealed glass tubes (13 mm × 120 mm) which were heated at 130 °C for 3 h. Each was charged with 0.45 M substrate, 8–10 mole % iridium complex, 20 μL of cyclooctane as a GC standard, and 2 mL of the solvent, benzene or chloroform. The product mixture was analyzed by GC and ^1H NMR spectroscopy immediately after opening the liquid N_2 cooled tubes by GC and ^1H NMR spectroscopy. Subsequently, the product mixture was distilled under vacuum at 25–60 °C, yielding the volatile components. The individual products were isolated by preparative GC. The NMR and MS data agree with the literature. The GC determined percent yield of products isolated for each of the substrates are as follows: 1 (benzene), 34%, ($CDCl_3$), 63%; 6 (benzene), 0%, ($CDCl_3$), 51%; 7 ($CDCl_3$), 83%; 8 ($CDCl_3$), 79%.

^1H NMR Data of Reactants and Products. These data are values (δ) obtained on our 250-MHz spectrometer. However, references are given of earlier data obtained on a lower field instrument.

Compound 1:[7] C_1, C_5, 2.75 (br s, 2 H); C_2, C_5, 1.01 (dd, 2 H, J = 6.4 and 3 Hz); C_3(anti), 0.80 (dt, 1 H, J = 6.4 and 6.4 Hz); C_3(syn), 1.47 (dt, 1 H, J = 6.4 and 3 Hz); C_6, C_7, 6.40 (br s, 2 H); C_8, 0.86 (d, 1 H, J_{gem} = 8.96 Hz); C_8, 1.13 (d, 1 H, J_{gem} = 8.96 Hz).

Compound 1h: C_1, 3.15 (br s, 1 H); $C_{3(exo)}$, 1.42 (br d, 1 H, J_{gem} = 8.5 Hz); $C_{3(endo)}$, 1.60 (br d, 1 H, J_{gem} = 8.5 Hz); C_4, 2.97 (br s, 1 H); C_5, C_6, 6.05–6.2 (m, 2 H); C_7, 1.76 (dd, 1 H, J = 14.5 and 2.6 Hz); C_7, 2.25 (dd, 1 H, J = 14.5 and 2.6 Hz); C_8, 4.71 (br s, 1 H); C_8, 4.99 (br s, 1 H).

Compound 1k:[9] C_1, 1.39 (d, 2 H, J = 7.7 Hz); C_2, 0.70 (d, 2 H, J = 11 Hz); C_2, 1.53 (dd, 2 H, J = 11 and 4.3 Hz); C_3, 2.50 (br s, 1 H); C_4, C_5, 5.82–5.90 (m, 2 H); C_6, 1.59 (br d, 1 H, J = 7.7 Hz).

Compound 6: C_1, C_5, 2.20 (br s, 2 H); C_2, C_4, 0.65 (dd, 2 H, J = 6.5 and 3.2 Hz); C_3(anti), –0.15 (dt, 1 H, J = 6.5 Hz); C_3(syn), 0.24 (dt, 1 H, J = 6.5 and 3.2 Hz); C_6, C_7, 1.15–1.45 (m, 4 H); C_8, 0.55 (d, 1 H, J_{gem} = 11 Hz); C_8, 0.90 (d, 1 H, J_{gem} = 11 Hz).

Compond 6h:[10] C_1, 2.79 (br s, 1 H); $C_{3(exo)}$, 2.01 (d, 1 H, J_{gem} = 15.4 Hz); $C_{3(endo)}$, 2.28 (br d, 1 H, J_{gem} = 15.4 Hz); C_4, 2.46 (br s, 1 H); C_5, C_6, C_7, 1.3–1.85 (m, 6 H); C_8, 4.62 (br s, 1 H); C_8, 4.85 (br s, 1 H).

Compound 6i:[10] C_1, 2.87 (br s, 1 H); C_3, 5.54 (br s, 1 H); C_5, C_6, C_7, 1.0–1.8 (m, 6 H); C_4, 2.72 (br s, 1 H); methyl, 1.8 (d, J = 1.7 Hz).

Compound 6i:[11] C_1, C_5, 2.3 (m, 2 H); C_2, 5.35 (m, 1 H); C_3, 5.80 (m, 1 H); C_4, C_6, C_7, C_8, 1.2–1.9 (m, 8 H).

Compound 7:[8] C_1, C_5, 2.79 (br s, 2 H); C_2, C_4, 1.35 (m, 2 H); C_3(anti), 0.49 (dtt, 1 H, J = 6.3, 6.3, and 2.6 Hz); C_3(syn), 0.38 (dt, 1 H, J = 6.3 and 3.0 Hz); C_6, C_7, 5.72 (br s, 2 H); C_8, 1.68 (br d, 1 H, J_{gem} = 8 Hz); C_8 1.82 (br d, 1 H, J_{gem} = 8 Hz).

Compound 8: C_1, C_5, 2.20 (br s, 2 H); C_2, C_4, 1.00 (dd, 2 H, J = 7.25 and 2.45 Hz); C_3(anti), 0.72 (dtt, 1 H, J = 7.4, 7.25, and 2.8 Hz); C_3 (syn), 0.88 (dt, 1 H, J = 7.4 and 2.45 Hz); C_6, C_7, 1.2–1.4 (m, 4 H), C_8, 1.44 (br d, 1 H, J = 8.9 Hz); C_8, 1.88 (dm, 1 H, J_{gem} = 8.9 Hz).

Acknowledgment. We express our gratitude for financial support of this research by Montana State University and the National Science Foundation, Grant CHE 7826160.

Registry No. **1**, 3635-94-7; **1h**, 694-91-7; **1k**, 3725-23-3; **6**, 22389-16-8; **6h**, 497-35-8; **6i**, 694-92-8; **6j**, 823-02-9; **7**, 3635-95-8; **8**, 13377-46-3; $(Ph_3P)_2Ir(CO)Cl$, 14871-41-1.

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(8) Closs, G. L.; Krantz, K. D. *J. Org. Chem.* **1966**, *31*, 638.

(9) Sauers, R. R.; Shurpik, A. *J. Org. Chem.* **1968**, *33*, 799.

(10) Banks, S.; Rowe, C., Jr.; Schriesheim, A.; Nasland, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 6897.

(11) Dixon, J. R.; James, G. J.; Moris, G. *J. Chem. Eng. Data.* **1976**, *21*, 389.