with a gas inlet tube containing a stopcock, and, in those experiments with benzalacetophenone, an addition funnel was charged with 500 mg (2.40 mmol) of 1 and a solution of 67.2 mg (0.500 mmol) of durene in 35 ml of ether. The flask was removed from the glove box but maintained under a nitrogen atmosphere, magnetic stirring was started, and the first 1.5-ml sample was withdrawn by syringe through the septum. The solution was heated to reflux, when the timing began. Other 1.5-ml samples were withdrawn from time to time. Each sample was injected into 2 ml of ice-cold D_2O, and the mixture was stirred for 15 min under nitrogen and extracted with four 6–8-ml portions of ether. The dried (magnesium sulfate) ether extract was stored in capped vials at −20 °C within a closed jar containing Drierite. The visually observed changes which occurred during the reaction are described in the Results. The same procedure was used for the decompositions in the presence of benzalacetophenone, except that an ethereal solution of 2.00 g (9.60 mmol) of the latter was added by the addition funnel; the total volume of ether was also 35 ml. The experiment was done in triplicate; in one run, DCl in D_2O was used for the quench and it was necessary to wash the ether extracts with aqueous sodium bicarbonate and saturated saline solution before drying.

Decomposition of 1 in Tetrahydrofuran. The large-scale run was performed in the same manner as that in ether except that 35 ml of THF was used instead of the ether. The zero hour sample contained 0.10 mmol of biaryl and 1.98 mmol of arene which contained 92% ArD. The following are the results of analyses of samples withdrawn at the stated times after refluxing commenced [time, mmol of biaryl, mmol of arene (% ArD)]: 0.5 h, 0.24, 1.57 (89%); 1.5 h, 0.49, 1.33 (85%); 3 h, 0.97, 0.35 (41%); 18.5 h, 1.01, 0.31 (0%); 45 h, 1.05, 0.34 (0%). The small-scale runs in THF and perdeuterio-THF were performed in similar fashion except that 27 mg (0.20 mmol) of durene, 100 mg (0.48 mmol) of arylcopper, and 2 g of THF were used. In the experiment with unlabeled solvent, D_2O quenches were used. In the experiment with labeled solvent, the zero hour sample (0.3 ml) was quenched with D_2O and subsequent samples with H_2O. Extractions of the quenched samples were performed in centrifuge tubes, with centrifugation being used to break the emulsions. The yields of products were somewhat erratic but, in general, the usual trends were observed. In the labeled case, the zero hour sample contained arene which was 76% monodeuterated and the 3-, 5.5-, and 18-h samples were 43, 46, and 46% monodeuterated, respectively.

Acknowledgments. We thank the National Science Foundation for partial support of this work (Research Grant GP 22955 and Science Development Grant GU 3184). We are very grateful to Dr. Allan Cairncross for providing the procedure for synthesizing *m*-trifluoromethylphenylcopper and some analytical data on this compound. We thank Drs. Ronald Berninger and John Wood and Mr. John Naworal for recording the mass spectra, Mr. James Boal for determining the exact molecular weight of the conjugate addition product, and Mr. Monroe Snider for recording the infrared spectrum of the organometallic.

Registry No.—1, 18206-44-5; 3, 580-82-5; 4, 58540-91-3; benzalacetophenone, 94-41-7; ether, 60-29-7.

References and Notes

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Methanolysis Products of Dichloro(1,5-cyclooctadiene)palladium(II) in the Presence of Bases and of Its Methoxy Adducts[1]

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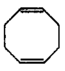
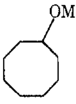
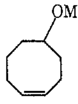
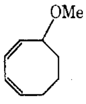
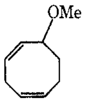
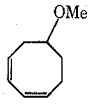
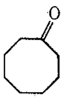
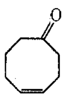
When di-μ-chloro- and di-μ-methoxidobis(2-methoxycyclooct-5-enyl)dipalladium(II) were refluxed in methanol with and without added bases and when dichloro(1,5-cyclooctadiene)palladium(II) was refluxed in methanol with added bases, complex mixtures of products were obtained comprising 4-cyclooctenyl methyl ether and 2,4-, 2,5-, 3,5-, and 1,5-cyclooctadienyl methyl ethers as well as 4-cyclooctenone. Products were identified, and mechanisms are discussed.

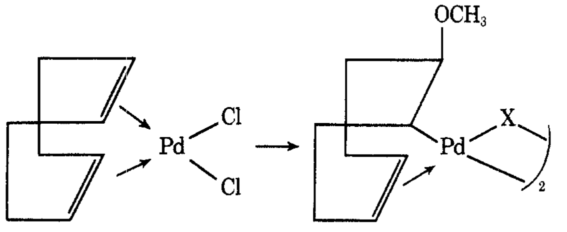
Dichloro(1,5-cyclooctadiene)palladium(II) (1) and the methoxy adduct derived from it, di-μ-chlorobis(2-methoxycyclooct-5-enyl)dipalladium(II) (2-Cl), were reported by Chatt and Vallarino in 1957.[2] Although many other adducts of 1,5-cyclooctadiene have been made and some of their reactions studied,[3] the nature of the organic oxidation products has been given only scant attention.[4] In this report the complex mixtures of organic oxidation products formed when dichloro(1,5-

Table I. Percentage Yield of Products from Methanolysis of (Cyclooctadiene)palladium chloride (1), Di-μ-chlorobis(2-methoxycyclooct-5-enyl)dipalladium(II) (2-Cl), and Di-μ-methoxidobis(2-methoxycyclooct-5-enyl)dipalladium(II) (2-OMe) in Refluxing Methanol (68 °C)[a]

Reaction conditions: compd (mmol), base (mmol), reaction duration, h									Total organic	Total Pd	COD–$PdCl_2$ recovered
2-Cl (0.94), none 5	12.4 (23.3)	<0.1	1.6 (3.0)	0.8 (1.5)	1.8 (3.4)	6.4 (11.8)	1.8 (3.4)	22.3 (51.2)	52.1 (97.6)	53.4 (98.5)	44.6
2-Cl (0.91), Na_2CO_3 (9.4) 5	4.1	0	39.2	14.7	27.3	11.2	0.1	5.1	96.6	99.0	0
2-OMe (0.81), none 1	6.9	<0.1	43.6	22.0	15.4	5.5	0	6.4	99.8	97.5	0
1 (2.44), Na_2CO_3 (3.05) 5	2.7 (4.2)	0.6 (0.9)	15.5 (23.3)	5.7 (8.6)	10.8 (16.3)	13.2 (20.3)	0.2 (0.3)	12.8[b] (19.4)	61.5	66.0	34.0
1 (2.03), Na_2CO_3 (9.4) 3	4.3	0	36.8	11.5	18.5	16.4	<0.1	12.0[b]	99.0	100.0	0
1 (3.36), NaOMe (3.5) 1	7.4	0.7	52.3[c]	18.7	9.5	4.7	0	6.4	99.7	99.0	0
1 (3.4), NaOMe (3.5) 2	<0.1	<0.1	40.0	56.0	<0.1	<0.1	<0.1	<0.1	96.0	100.0	0
1 (2.0), NaOMe (4.1) 1	1.1	1.2	55.8	27.3	8.4	2.8	0	3.2	99.8	98.5	0
1 (1.95), NaOMe (5.9) 1	0	1.6	60.4	36.3	1.6	<0.1	0	<0.1	99.9	97.5	0
1 (2.2), NaOMe (8.7) 1	0	0.2	58.0	41.0	0.3	0.3	0	<0.1	99.7	100.0	0

[a] All reaction solutions were in 15 ml of MeOH. Values in parentheses are based on the amount of complex which reacted where reaction was not complete. [b] In two early experiments, cyclooct-4-enone was not observed, but 1,5-cyclooctadienyl ether was (retention time, 67 min). In later experiments, only the cyclooctenone could be found. [c] In this experiment, the 2,4-dinitrophenylhydrazone of formaldehyde was obtained in 51% yield.

cyclooctadiene)palladium(II) (1) and its methoxy adduct, 2, are refluxed in methanol will be described.



1 2 (X = Cl, OMe)

The cyclooctadiene palladium chloride complex, 1, is prepared by precipitating it from a solution of sodium tetrachloropalladate(II) and 1,5-cyclooctadiene in methanol. The methoxy–palladium chloride adduct, 2-Cl, can be formed by stirring the diene complex in methanol with sodium carbonate. Reaction with 1 equiv of sodium methoxide might seem a reasonable alternate method,[5] but with this system we found that a di-μ-methoxido–methoxy adduct was formed, di-μ-methoxidobis(2-methoxycyclooct-5-enyl)dipalladium(II) (2-OMe).

Dichloro(1,5-cyclooctadiene)palladium(II) (1), which is only slightly soluble in methanol does not react when a suspension is stirred and refluxed (68 °C) for 10 h. Less than 0.1% decomposed. When this diene complex is refluxed in methanol with various added bases, palladium metal is precipitated quantitatively as a mirror and small particles within 1–3 h.

When the adduct 2-Cl is refluxed in methanol without added base, hydrogen chloride is formed as the reaction proceeds in addition to palladium metal and organic products. This hydrogen chloride reacts with the unreacted adduct 2-Cl converting it to diene complex 1 which is stable in refluxing methanol in the presence of hydrogen chloride. As can be seen in Table I, after 5 h, a 53% yield of palladium was found and a 45% yield of 1 was recovered. In the presence of sodium carbonate 2-Cl gives no 1 (Table I), but like the methoxido adduct 2-OMe gives palladium and oxidized products. In the rest of the experiments in Table I, 1 was stirred with base in methanol until the yellow color of 1 disappeared and then was refluxed for the times stated.

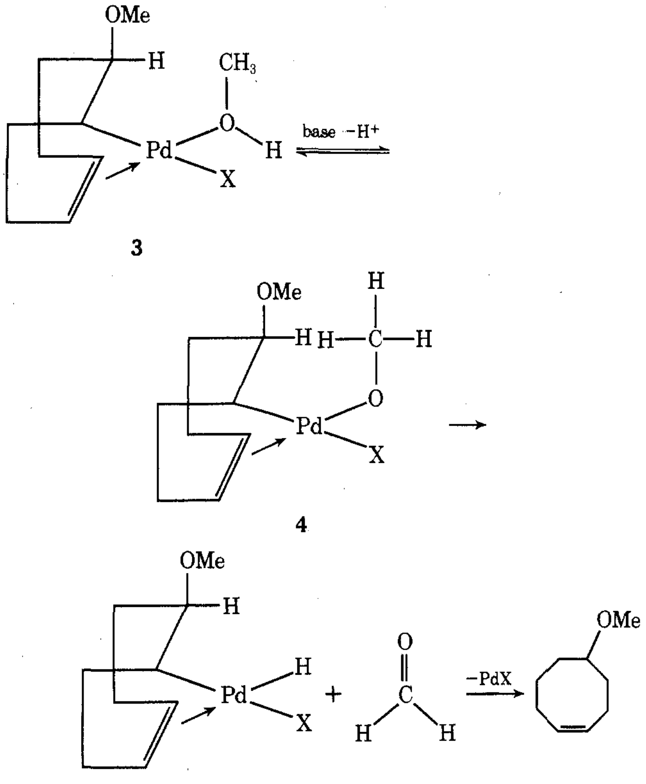
The organic product mixtures were analyzed by gas chromatography. The percentage yields of products from these reactions are listed in Table I. The organic products were identified by comparison of the gas chromatograph retention time and the NMR, ir, and uv spectra of collected peaks with those of samples synthesized in independent ways. The organic products from the methanolysis reactions were 1,5-cyclooctadiene, cyclooctyl methyl ether, 4-cyclooctenyl methyl ether, 2,4-cyclooctadienyl methyl ether, 2,5-cyclooctadienyl methyl ether, 3,5-cyclooctadienyl methyl ether, cyclooctanone, 4-cyclooctenone, and palladium metal. All of these products, except 1,5-cyclooctadienyl methyl ether, which is discussed later, were found to be stable in methanol in the presence of hydrogen chloride, sodium carbonate, sodium methoxide, and 1 for the reaction times. The syntheses of these compounds will be found in the Experimental Section. The organic product yields were calculated by adding a calibrated internal standard. Total palladium metal was measured by filtering the reaction solution and weighing.

The methanolysis products arise from two primary reactions of the methoxypalladium adduct: (1) the reductive cleavage of the carbon–palladium σ bond by complexed alcohol yielding a monoenyl ether and (2) the β-elimination of HPdX yielding a dienyl ether. The very minor amount of saturated compounds probably arise from the hydrogenation of the double bond by palladium hydride formed in situ. Formation of 1,5-cyclooctadiene may be explained by the deoxypalladation of the adduct which is minor in the solvolysis of the methoxy adduct.

The reductive cleavage product is 4-cyclooctenyl methyl ether. Tsuji[6] noted that degradation of the methoxy adduct, 2-Cl, with methoxide yielded 4-cyclooctenyl methyl ether and that a similar reductive cleavage of di-μ-chlorobis(8-diethoxycarbonylmethyl-4-cyclooctenyl)dipalladium(II) by ethoxide in ethanol yielded 4-cyclooctenyl malonate. The ethanol was presumed to be oxidized to acetaldehyde which was not isolated. Base and ethanol has been used as a reducing agent for producing hydridoplatinum complexes.[7]

When the diene complex, **1**, was solvolyzed in methanol with excess sodium carbonate, the 4-cyclooctenyl methyl ether isolated (36.8% yield, see Table I) by gas chromatography showed a parent peak in the mass spectrum at *m/e* 140. The methyl ether from the solvolysis in methanol-d_1 was collected and the mass spectrum showed the parent peak at *m/e* 140 which is the same as in the undeuterated methanol from above. The P:P + 1 ratio was within experimental error of the value calculated on the basis of the natural abundance of isotopes. The same reaction of the diene complex, **1**, in methanol-d_4 gave 4-cyclooctenyl methyl ether with the parent peak at *m/e* 144 demonstrating that this product contained four deuterium atoms. Three of the deuterium atoms must be on the methyl group as the methoxy adduct **2**-Cl was prepared in situ, and one was introduced at C-2 from the methanol-d_4 methyl group in the reductive cleavage reaction.

In another experiment, when the reaction product solution (after filtering off the palladium metal) was treated with 2,4-dinitrophenylhydrazine reagent, a yellow solid was formed. This turned out to be the 2,4-dinitrophenylhydrazone of formaldehyde by melting point and mixture melting point, and the yield of this 2,4-dinitrophenylhydrazone corresponded to the yield of 4-cyclooctenyl methyl ether. A mechanism for this reductive cleavage of the carbon–palladium σ bond by complexed alcohol can be formulated as shown, **3** → **4** → **5**.



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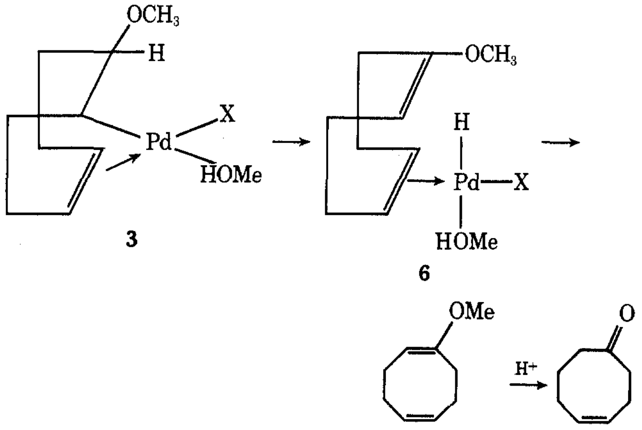
The reacting species in methanol is not the binuclear adduct di-μ-chlorobis(2-methoxycyclooct-5-enyl)dipalladium (**2**-Cl), because it is largely solvolyzed in methanol solution yielding a methanol coordinated palladium species, **3**.[8] Base removes a proton giving a methoxidopalladium intermediate, **4**. That this methoxidopalladium intermediate is the reactive species is suggested by the increasing yield of 4-cyclooctenyl methyl ether with increasing base strength. Compare data in Table I for reactions with no base (and hence in the presence of developing HCl) with those with added sodium carbonate and with added sodium methoxide. With no base present, the yield of 4-cyclooctenyl methyl ether is only 3%, but in the presence of base the yield increases to 37–60%. However, in sodium methoxide, the complex must be almost all the methoxidopalladium species **4** because increasing the sodium methoxide concentration makes only a small increase in the monoenyl ether.

The β-elimination of HPdX from **2** yields dienyl ethers (Table I). The 4-cyclooctenone obtained is formed from a β-elimination of the adduct yielding 1,5-cyclooctadienyl methyl ether (**7**) which in the presence of acid or palladium(II) converts to the 4-cyclooctenone. In early experiments with base present the vinyl ether **7** was observed instead of the ketone, but in later runs only the unsaturated ketone was found. The vinyl ether was identified by the ir and NMR spectra of the collected GC peak as well as by the observation that addition of aqueous acid converted it to 4-cyclooctenone. We were unsuccessful in preparing this compound by another route, no doubt because of the large strain energy of the cyclooctadiene system.[9] The reason that it could not be isolated in later experiments could be isomerization in the gas chromatograph despite efforts to prevent it. Thus, the total percentage of products to or through dienyl ethers (including 4-cyclooctenone) ranges from 71.3% of the oxidized organic product in acidic solution to 38% in basic solution (see Table I).

As pictured **3** → **6**, a cis β-elimination of HPd from the trans adduct leads to a 1,5-cyclooctadienyl ether **7** which in acidic solution would form 4-cyclooctenone. A trans β-elimination of the elements of HPdX could only result from a cis adduct, but also should be base catalyzed, since the base would be able to assist in pulling off the hydrogen trans to the palladium to give the dienyl product. However, the data do not support this because much more 4-cyclooctenone is formed in acidic solution with no added base (see Table I). The isomerization by β-elimination–addition (see below) will not lead to vinyl ether unless the adduct was originally trans (or unless the olefin moiety is free from the palladium at some stage). Thus, vinyl ether and hence 4-cyclooctenone arise via cis β-elimination of HPdX from a trans adduct.



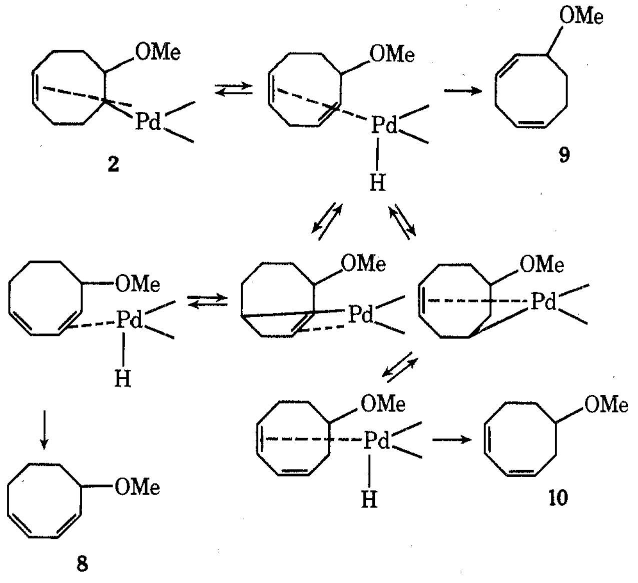
3

6

7

A cis β-elimination of HPd from **2** would also be expected to form the 2,5-cyclooctadienyl methyl ether. Although the 2,5-dienyl ether is stable in refluxing methanol in the presence of acid or bases or **1** for these reaction times, other dienyl ethers are found besides. Consequently it is proposed that intermediate olefin hydridopalladium species readd and undergo elimination leading to the other dienyl ethers as shown below (**2** → **8**, **9**, **10**). Such elimination–addition has been proposed before for olefin isomerization by Pd^{II}.[10]

Although the rearrangement of dienyl ethers is easily rationalized, the reason for the relative amounts of each isomer is not obvious. In the literature the 3,5-cyclooctadienyl derivatives appear to be more stable than the 2,4- inasmuch as



2,4- will thermally isomerize to 3,5-.[11] Probably the differences in the product yields can be attributed to the different reactivities of the various reactive intermediates which would be present under the different reaction conditions (**3**-Cl, **3**-OCH_3, and **4**-Cl) and of the hydrido intermediates **5**-Cl, **6**-Cl, and **6**-OMe.

Another anomaly is that the product composition of the reactions in the presence of sodium carbonate does not change when they are refluxed longer than needed to give a quantitative yield of palladium. This is not the case for the reactions with added sodium methoxide. Even though the yield of palladium is within experimental error of quantiative, the ether product distribution changed under continued reflux.

As pointed out earlier, if there is insufficient sodium carbonate to neutralize product hydrogen chloride, **1** will be formed. The hydrogen chloride arises as follows:

$$(COD)PdCl_2 + 2MeOH \rightarrow (CODOMe)PdCl(MeOH) + HCl$$

$$(CODOMe)PdCl(MeOH) \rightarrow products + Pd + HCl$$

In Table I where one might think 3.05 mmol of sodium carbonate should neutralize 2.44 mmol of **1**, it can be seen that 1 mol of sodium carbonate only neutralizes 1 mol of hydrogen chloride. Apparently sodium bicarbonate does not neutralize the hydrogen chloride so that it cannot react with the intermediates to form **1**. Furthermore, in Table I where the ratio of **1** to sodium methoxide is 1:1, the reaction goes quantitatively to palladium(0) and oxidized organic products instead of yielding a 50% yield of **1** back again. The only conclusion we can draw is that hydridopalladium species do not decompose to metal immediately, but are relatively long lived, more so in the sodium methoxide reactions than in those with carbonate. Perhaps related is the ease of reduction of carbonate phosphine platinum complexes.[12]

A final anomaly is the observation that although some cyclooctadiene is formed in some reactions, nevertheless the yield of palladium is essentially quantitative. Note that deoxymetalation of **2** would lead to cyclooctadiene and palladium(II) (no oxidation–reduction). The facts can, however, be explained as the result of deoxymetalation of a species like **5**, the hydridopalladium adduct, which would deoxypalladate to cyclooctadiene and palladium and hydrogen chloride ultimately.

Experimental Section

Chloro Complexes. Dichloro(1,5-cyclooctadiene)palladium(II) (**1**) was prepared by Chatt's method: mp 210 °C dec (lit.[2] 205–210 °C dec); NMR spectral resonances at 6.48 (multiplet, 4 protons) and 2.80 ppm (m, 8 protons); uv spectrum λ_{max} 347.5 nm (ϵ 1680) in chloroform. Di-μ-chlorobis(2-methoxycyclooct-5-enyl)dipalladium(II) (**2**-Cl): mp 150–155 °C dec (lit.[2] 136–140 °C dec); NMR (chloroform) 1.60 (m, 1), 2.00 (m, 4), 2.40 (m, 4), 3.21 (s, 3), 3.60 (m, 1), 5.70 ppm (m, 2); uv spectrum λ_{max} 325 nm (ϵ 3430) in chloroform.

Di-μ-methoxido(2-methoxycyclooct-5-enyl)dipalladium(II) (2-OMe). To a solution of 1.50 g (0.0268 mol) of sodium methoxide in 50 ml of methanol cooled to −20 °C was added 3.00 g (0.011 mol) of **1**. After a few minutes, a white solid formed which was filtered, washed with methanol, and dried to yield 2.60 g (90%) of **2**-OMe, mp 110–120 °C dec.

Anal. Calcd for $C_{20}H_{36}O_4Pd_2$: C, 43.42; H, 6.56; Pd, 38.46. Found: C, 43.17; H, 6.74; Pd, 38.22. NMR spectrum (chloroform) 1.5 (m, 1), 2.00 (m, 4), 2.60 (m, 4), 3.22 (s, 3), 3.28 (s, 3), 3.60 (m, 1), 5.20 ppm (m, 2); uv (chloroform) λ_{max} 315.0 nm (ϵ 3510).

Solvolysis Method. A weighed sample of the complex was added to a solution of sodium methoxide or a slurry of sodium carbonate in 15 ml of methanol. The mixtures were stirred at room temperature until the yellow color of the diene complex disappeared, and then the mixtures were heated at reflux for the times given in Table I. After cooling, the palladium black was filtered off on a sintered glass funnel, washed with methanol and water, and dried to constant weight. The organic products in Table I were analyzed by GC using a 3 m × 0.25 in. column of 20% Carbowax 4000 on non-acid-washed 60/80 mesh Chromosorb W operated at 100 °C and 13 psi. Under these conditions the retention times are as follows: 1,5-cyclooctadiene, 15 min; cyclooctyl methyl ether, 36 min; 4-cyclooctenyl methyl ether, 39 min; 2,4-cyclooctadienyl methyl ether, 40.5 min; 2,5-cyclooctadienyl methyl ether, 50.5 min; 3,5-cyclooctadienyl methyl ether, 52 min; cyclooctanone, 94 min; 4-cyclooctenone, 106 min. Percentages of products were obtained by using a calibrated internal standard, 1,5-cyclooctadiene. The GC peaks were cut out and weighed. Thermal response differences were taken into account in calculating yields.

In two early experiments, cyclooct-4-enone was not observed among the products of methanolysis in the presence of sodium carbonate (Table I). Instead, a peak was observed at a retention time of 67 min. Treatment of the product mixture with a drop of dilute sulfuric acid caused the 67-min peak to disappear and the appearance of the 4-cyclooctenone peak at 106 min. The 67-min peak is thought to be the 1-methoxy-1,5-cyclooctadiene. A weak, possibly impure NMR spectrum of the collected peak showed resonances at δ 5.9, 5.1, 3.7, and 2.4 ppm. The ir spectrum of the collected peak showed absorptions at 1702 (s), 1670 (m), besides 3010 (m), 2940 (vs), 2850 (s), 1475 (s), 1100 cm^{-1} (vs).

In experiments where the yield of formaldehyde was measured (Table I), the reaction solution after GC analysis was added to 2,4-dinitrophenylhydrazine solution prepared according to the instructions of Shriner, Fuson, and Curtin.[13] The solid 2,4-dinitrophenylhydrazone was chromatographed and recrystallized, 0.34 g (51%), mp 166–168 °C (lit.[13] mp 166 °C). A mixture melting point with an authentic sample was not depressed.

4-Cyclooctenyl Methyl Ether. 4-Cyclooctenol[14] (2 g, 0.016 mol) was added to sodium hydride (1 g, 0.22 mol) 54% in mineral oil suspended in dimethylformamide and stirred for 1 h. Methyl iodide (3 g, 0.021 mol) was added slowly, and the mixture was stirred for 1 h. Water was added dropwise with stirring. The mixture was extracted with ether. After drying and concentrating the ether solution, the product was distilled 1.7 g (76%), bp 45–47 °C (4 mm).

Anal. Calcd for $C_9H_{16}O$: C, 77.67; H, 11.50. Found: C, 77.67; H, 11.75. NMR spectrum δ 1.5–1.9 (m, 6), 1.9–2.4 centered at 2.1 (m, 4), 3.18 (s, 3), 3.2 (m, 1), 5.5 ppm (broad m, 2).

Cyclooctyl Methyl Ether. The saturated ether was prepared from commercially available cyclooctanol by the method as described above: bp 58–60 °C (5 mm) [lit.[15] bp 76–77 °C (18 mm)]; NMR spectrum δ 1.55 (m, 14), 3.12 (s, 3), 3.10 ppm (m, 1).

4-Cyclooctenone. A 10% solution of 4 g (0.032 mol) of 4-cyclooctenol[14] in pyridine was added to 4.5 g (0.045 mol) of chromium trioxide in 45 ml of pyridine and stirred for 24 h. Water was added, and the mixture was extracted with ether. The ether solution was washed with water and 10% hydrochloric acid, dried over K_2CO_3, and concentrated. Distillation gave 2 g (50%) of the ketone: bp 50–53 °C (2 mm); NMR spectrum δ 1.4 (broad m, 10), 2.2 ppm (m, 4); ir spectrum 3020 (m) 2940 (s), 2850 (m), 1710 (vs), 1475 (m), 1340 (m), 740 cm^{-1} (m). 2,4-Dinitrophenylhydrazone was made and purified by column chromatography, mp 187–189 °C (lit.[16] 194–196 °C).

2,4-Cyclooctadienyl Methyl Ether. 2,4-Cyclooctadienyl acetate was prepared by Cope's method,[17] bp 50–55 °C (0.3 mm) [lit.[17] 56–57 °C (0.6 mm)]. To a solution of 2 g (0.012 mol) of 2,4-cyclooctadienyl acetate dissolved in dry dimethylformamide was added 1.5 g (0.033

mol) of sodium hydride 54% in mineral oil. After stirring for 1 h, methyl iodide (9 g, 0.064 mol) was added slowly, and stirring was continued for 1 h. Water was added dropwise, and the mixture was extracted with ether. The ether solution was washed with water and dried over K_2CO_3. After evaporation of ether, the residue was distilled, bp 40–43 °C (2 mm), 0.7 g (42%).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.40; H, 10.31. NMR spectrum δ 1.1–1.9 (m, 4), 1.9–2.2 (m, 2), 3.21 (s, 3), 3.90 (m, 1), 5.3–6.0 ppm (m, 4).

2,5- and 2,6-Cyclooctadienyl Acetate. Method A. A suspension of 70 g (0.22 mol) of mercuric acetate, 30 g (0.28 mol) of 1,5-cyclooctadiene, and 50 ml of acetic acid was refluxed for 3 h, producing metallic mercury. The brown solution was decanted from the mercury, and 300 ml of ether added. The ether solution was extracted with water and saturated sodium bicarbonate solution, dried, and concentrated. The residue was distilled, bp 75–77 °C (2 mm), giving 21 g (58%) of a mixture of 7% 2,5- and 93% 2,6-cyclooctadienyl acetate by GC peak areas. The peaks were separated by GC.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found for the 2,5 isomer: C, 72.17; H, 8.66. For the 2,6-isomer: C, 72.43; H, 8.75.

Method B. A mixture of 30 g (0.28 mol) of 1,5-cyclooctadiene and 40 g (0.22 mol) of *N*-bromosuccinimide in 200 ml of carbon tetrachloride was refluxed with a catalytic amount of 2,2′-azobis-2-methylpropionitrile for about 5 h. The succinimide was filtered off, and the solution was washed with hot water and saturated sodium carbonate solution and dried over sodium carbonate. After the solvent was removed under reduced pressure, the residue was dissolved in 50 ml of acetic acid. Silver acetate (37 g, 0.22 mol) suspended in 200 ml of acetic acid was added slowly with cooling and stirring. The silver bromide was filtered off and 300 ml of ether was added to the solution which was then washed with water and aqueous sodium bicarbonate and dried. After the solvent was removed, the residue was distilled, bp 62–68 °C (1 mm), giving 24 g (65%) of a mixture of 30% 2,5- and 70% 2,6-cyclooctadienyl acetates.

2,5- and 2,6-Cyclooctadienol. A mixture of 20.0 g (0.12 mol) of 93% 2,6- and 7% 2,5-cyclooctadienyl acetate was added to 15 g of sodium hydroxide dissolved in 200 ml of methanol and refluxed for 1 h. The mixture was neutralized with dilute hydrochloric acid and extracted with ether. After drying and removal of the ether, the residue was distilled, giving 13.6 g (91%), bp 70–78 °C (1 mm), of a mixture of 89% 2,6- and 11% 2,5-cyclooctadienols as determined by GC. The isomers were separated by GC.

Anal. Calcd for $C_8H_{12}O$: C, 77.36; H, 9.74. Found for 2,6 isomer: C, 77.21; H, 9.86. For the 2,5 isomer: C, 77.59; H, 9.89.

2,5- and 2,6-Cyclooctadienyl Methyl Ethers. A mixture of 2,5- and 2,6-cyclooctadienol (10.0 g, 0.08 mol) was added slowly to 200 ml of ether containing 10 g (0.17 mol) of a 40% sodium dispersion (5 μ) in xylene. The mixture was stirred for 1 h, whereupon 20 g (0.14 mol) of methyl iodide was added. After the mixture was stirred for 12 h and refluxed for 2 h, methyl alcohol was added dropwise consuming the excess sodium. More ether was added, and the solution was washed with water and dried. After the ether was removed, the residue was distilled giving 7.9 g (72%), bp 42–45 °C (2 mm), of a mixture of 86% 2,6- and 14% 2,5-cyclooctadienyl methyl ether by GC. The isomers were separated by GC.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found for the 2,5 isomer: C, 77.96; H, 10.07. For the 2,6 isomer: C, 78.07; H, 10.13. NMR spectrum for 2,5 δ 1.00–1.70 (m, 2), 1.70–2.10 (m, 2), 2.70–2.90 (m, 2), 3.21 (s, 3), 4.00–4.50 (m, 1), 5.05–5.80 ppm (m, 4); for 2,6 δ 1.80–2.80 (m, 6), 3.21 (s, 3), 4.50 (m, 1), 5.40 ppm (m, 4).

3,5-Cyclooctadienyl Acetate. Employing the method of Crandall,[11] 10 g (0.093 mol) of 1,3-cyclooctadiene and 10 g (0.09 mol) of selenium dioxide in 60 ml of acetic acid were refluxed for 13 h. After 150 ml of water was added, the solution was neutralized with sodium carbonate and steam distilled. The distillate was extracted with ether. After the ether solution was dried, the ether was removed and the residue was distilled, giving 4.8 g (31%) of the 3,5-acetate, bp 63–65 °C (2 mm). If this reaction was terminated after 4 h, the product was 2,4-cyclooctadienyl acetate, 5.2 g (33%), bp 69–72 °C (3 mm) [lit.[17] 56–57 °C (0.6 mm)]. Mercuric acetate oxidation of 1,3-cyclooctadiene gave similar results. The 3,5-acetate was also obtained by brominating cyclooct-4-enyl acetate with *N*-bromosuccinimide (as described above) and eliminating the elements of hydrogen bromide by treating the bromocyclooct-4-enyl acetate with magnesium hydrogen orthophosphate trihydrate in dimethylformamide at 80 °C for 36 h. NMR spectrum for 3,5 isomer δ 1.70 (m, 2), 2.30 (m, 4), 1.98 (s, 3), 4.75 (m, 1), 5.70 ppm (m, 4).

3,5-Cyclooctadienyl Methyl Ether. Cycloocta-3,5-dienyl acetate (2 g, 0.012 mol) in 10 ml of ether was added dropwise to 1 g (0.026 mol) of lithium aluminum hydride in 25 ml of ether, and the mixture was stirred for 30 min. Water was added dropwise until the excess hydride had reacted. After 10 ml of saturated ammonium chloride solution was added, the ether solution was separated, washed with water, and dried. After the ether was removed, the alcohol was etherified in procedure similar to that above for the cyclooct-4-enyl methyl ether. The ether product distilled, bp 40–42 °C (1 mm), giving 1.2 g (72%).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.23; H, 10.34. NMR spectrum δ 1.44–2.20 (m, 2), 2.20–2.50 (m, 4), 3.22 (s, 3), 3.20–3.40 (m, 1), 5.40–5.80 ppm (m, 4).

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