Table I. Heats of Hydrogenation ($-\Delta H_{H_2}$, kcal/mol)[a] for the Cyclooctenes

Cis	*Trans*	Solvent	Ref
22.98 ± 0.10	32.24 ± 0.21	Acetic acid	6
23.53 ± 0.04	–	Gas phase	5
23.04 ± 0.17	34.41 ± 0.43	Hexane	This work

[a] Under Turner's conditions in acetic acid, the magnitude of the heat of hydrogenation will be smaller than the gas-phase value by the heat of solvation of cyclooctane in acetic acid (about 0.4 kcal/mol). Kistiakowsky's measurements were at 82 °C, and heats of hydrogenation are generally slightly greater in magnitude at elevated temperatures.

is quite comparable with earlier values, as anticipated. The *trans*-cyclooctene value is approximately 2 kcal greater in magnitude than that reported by Turner. The difference is attributed in part to solvation but mainly to sample purity, as discussed above. The predictive value of the force field calculations is again borne out. From the heat of hydrogenation obtained herein, we can estimate the heats of formation and strain energies of the cyclooctenes. Taking the heat of formation of cyclooctane[4a] as −29.73 ± 0.28, we obtain $H_f°$ values for the gas phase at 25 °C, as: trans, +4.68 ± 0.71 kcal/mol, and cis, −6.69 ± 0.45 kcal/mol. An independent literature value[4a] gives: cis, −6.45 ± 0.30 kcal/mol.

The calculated inherent strain energies[3a] for cyclooctane, and *cis*- and *trans*-cyclooctene are respectively 14.15, 10.36, and 21.99 kcal/mol.[13] While these numbers are quantitatively different from earlier values, the interpretation is the same, namely that cyclooctane contains considerable strain from van der Waals repulsion and unfavorable torsion, which is partly relieved in *cis*-cyclooctene. The *trans*-cyclooctene, on the other hand, contains a large amount of bending and twisting strain about the double bond.

Experimental Section

The apparatus and technique used for the heat of hydrogenation measurements has been previously described.[8] 1-Hexane was used as the standard (H_{H_2} = −30.00[4b] kcal/mol). Samples of compound, 0.15–0.30 g, were weighed to ±0.01 mg and made up to volume with hexane. Forty-microliter aliquots were added to the hydrogenation vessel, which contained the Pd/C catalyst suspended in hexane.

cis-Cyclooctene was purchased from Columbia Carbon Co., Princeton, N.J., and was distilled. GLC showed it to be quite pure (SE 30 capillary column). The trans isomer was furnished by Dr. R. Bach, and had been prepared by elimination from the 1,2-diol. It was shipped in pentane. The pentane was removed by distillation and the *trans*-cyclooctene was distilled. A polymeric residue remained. This sample of *trans*-cyclooctene was shown by GLC not to contain any detectable amount of the cis isomer. It did contain 1.8 ± 0.5% pentane, which was allowed for in calculation of the heat of hydrogenation.

The *trans*-cyclooctene sample described above was both used as described and partly redistilled (to give a second sample), which now was found by GLC to contain 0.45 ± 0.15% pentane. The heat of hydrogenation was also measured with this sample. Uncertainties in Table I are 95% confidence limits on nine replicate samples plus an estimated uncertainty on the correction due to pentane in the trans sample.

Acknowledgment. The authors are grateful to Dr. Robert D. Bach, Wayne State University, for furnishing them with the *trans*-cyclooctene sample used in this work.

Registry No.—*cis*-Cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5.

References and Notes

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(2) On leave from the Chemistry Department, The Brooklyn Center, Long Island University, Brooklyn, N.Y. 11201.
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Reaction of Methyl and *tert*-Butyl Hypochlorite with Cyclopentadiene

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Recently, we reported studies on the ionic and radical addition of methyl hypochlorite to acyclic, conjugated dienes.[1] In order to examine the stereochemistry of this reaction, we decided to explore the addition of alkyl hypochlorites to cyclopentadiene (1). The reaction of 1 with *tert*-butyl hypochlorite has been reported[2] but without identification of the stereoisomers and without a discrimination between ionic and radical addition mechanisms.

The products obtained from 1 and methyl and *tert*-butyl hypochlorite are identified in Scheme I. The ratios of products obtained under ionic and radical conditions are listed in Tables I and II, respectively. Both of the hypochlorites give a rapid radical reaction (molecule-induced homolysis) with the

Scheme I

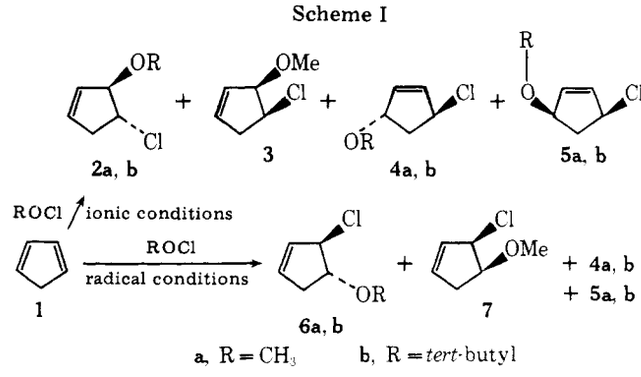

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Table I. Reactions of Cyclopentadiene with Methyl and *tert*-Butyl Hypochlorite under Ionic Conditions

Expt no.	Conditions[b,c]	Products, %[a] 1,2 addn (Markownikoff) 2a,b	3	1,4 addn 4a,b	5a,b	Yield of alkoxy chlorides, %	Yield of dichlorides, %
1	MeOCl, MeOH (98%)	36	7	26	31	72	
2	Cl_2, MeOH (98%)	34	6	27	33	60	16[d]
3	Cl_2, MeOH (98%), 0.1 M LiCl	36	8	25	31	55	17[d]
4	Cl_2, *t*-BuOH (98%)	66		10	24	14	28[d]
5	MeOCl, MeOH (98%), BF_3	26	9	30	35	82	
6	MeOCl, HOAc (98%)	14	28	4	54	5	
7	MeOCl, HOAc (2%), CH_2Cl_2 (96%)	24	39	10	32	16	
8	MeOCl, $PhCO_2H$ (2%), CH_2Cl_2 (96%)	27	42	9	22	18	
9	MeOCl, $ClCH_2CO_2H$ (2%), CH_2Cl_2 (96%)	24	37	10	29	21	
10	MeOCl, CH_2Cl_2 (98%), BF_3	30	27	16	27	47	

[a] Percentages of alkoxy chloride products are normalized to 100%. [b] Reactions were carried out by saturating the reaction mixtures with oxygen gas before addition of the hypochlorite. [c] Percentages in parentheses refer to the mole percentage of that reagent before addition of the hypochlorite solution. The concentration of 1 was always 0.02 mole fraction. [d] The dichlorides[7] are *trans*-3,4-dichlorocyclopentene (**8**), *cis*-3,4-dichlorocyclopentene (**9**), *trans*-3,5-dichlorocyclopentene (**10**), and *cis*-3,5-dichlorocyclopentene (**11**); the percentage of each of the dichlorides is, respectively in expt 2: 43, 13, 22, 22; in expt 3: 42, 14, 22, 22; and in expt 4: 27, 27, 15, 31.

Table II. Reactions of Cyclopentadiene with Halogenating Reagents under Radical Conditions

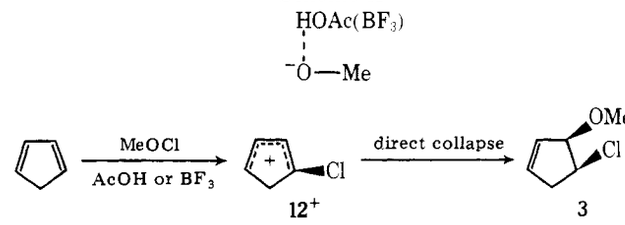
Reagent[a]	Yield	Products, % 1,2-Addition[b] trans	cis	1,4-Addition trans	cis
CH_3OCl	97	28[b]	5[b]	50	17
t-BuOCl	100	39[b]	0	52	9
NCl_3[c]	55	38	12	25	25
$PhICl_2$[c]	88	41	0	29	30

[a] Reactions were carried out by adding the reagent in methylene chloride to neat 1 which was saturated with nitrogen before addition. The reaction mixture was illuminated with ultraviolet light from a 275-W sunlamp. [b] The 1,2-alkoxy products are anti-Markownikoff. [c] Data from ref 11.

neat diene, affording near-quantitative yields of the alkoxy chloride adducts (Table II). Ionic addition to 1 was achieved under a variety of conditions. In line with our previous observations with acyclic dienes,[1] 1 did not react with the hypochlorites in dilute methylene chloride solution under oxygen as a radical inhibitor.[3] In dilute methanol a complete reaction was observed in 30 min (Table I, expt 1). A more rapid reaction occurs when BF_3 is present in the methanol (expt 5).[4] The reaction between 1 and *tert*-butyl hypochlorite in *tert*-butyl alcohol was much slower and, since the product ratios showed some variation over this long time period, the results are not reported in Table I.[5] The products from the chlorination of 1 in methanol and *tert*-butyl alcohol are also reported in Table I (expts 2 and 4).[5]

We designed experiments in which the addition of methyl hypochlorite to 1 occurred in the absence of methanol, thus avoiding the complication of methoxide incorporation from the solvent. For example, reaction between 1 and methyl hypochlorite in glacial acetic acid (expt 6) gave a 5% yield[6] of methoxy chlorides. The yield was increased to 16% by using only 2% acetic acid in methylene chloride (expt 7). Benzoic acid (expt 8) and chloroacetic acid (expt 9) under the same conditions gave methoxy chlorides in yields of 18 and 21%, respectively. The highest yield (47%) under these conditions was obtained by adding a few drops of boron trifluoride etherate (expt 10) to the mixture of 1 and methyl hypochlorite in methylene chloride.

Scheme II



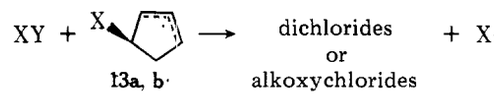
Turning to the mechanistic significance of our results, we wish to make several observations. First, concerning the 1,2 addition under ionic conditions, we note that, while some syn 1,2 addition was observed with methyl hypochlorite,[5] the amount of syn addition is greatly increased when methanol is not the solvent. Apparently, the carboxylic acids or BF_3 catalyze formation of the ion pair **12** by stabilizing the methoxide ion as shown in Scheme II. The methoxide ion can then collapse directly to give the cis product **3**. Reactions in methanol give mainly the trans-1,2-product evidently because solvent collapse happens very rapidly from the back-side.

It is interesting that the four reactions (expts 1, 2, 3, and 5) employing methanol solvent all give very similar product ratios. Apparently, chlorine and methyl hypochlorite produce essentially identical carbonium ion intermediates, a conclusion previously reported.[1] The addition of excess chloride ion (expt 3) did not increase the percentage of dichlorides formed in chlorination, suggesting as previously reported in the chlorination of styrenes[8a] and pentenes[8b] that the dichlorides are formed from the collapse of an intimate ion pair.

The data show that the stereochemical results from 1,4 addition are similar to those of 1,2 addition. For example, much more syn 1,4 addition is obtained when methanol is not the solvent. However, in contrast to the 1,2 addition, the 1,4 addition is slightly more syn than anti, even for the reaction in methanol of 1 with methyl hypochlorite or chlorine. This may be due to the lower degree of steric hindrance which would be encountered for syn 1,4 addition of methoxide (or methanol) compared to syn 1,2 addition.

Under radical conditions (molecule-induced homolysis) the *trans*-1,4-adduct predominates[9] and the 1,2-adduct is the anti-Markownikoff product. A steric effect is observed in the chain-propagating step for the formation of cis-1,2-adducts.[10] The steric effect is indicated by the absence of cis-1,2-products

when *tert*-butyl hypochlorite or iodobenzene dichloride[11] react with radical intermediate **13a** or **13b** (Table II).



13a, b·

13a, X = OBu^t; Y = Cl
13b, X = Cl; Y = PhICl

Experimental Section

General. Cyclopentadiene was obtained from its dimer and distilled just prior to use. The hypochlorites were prepared by a modification of the method used by Jenner to prepare *n*-butyl hypochlorite.[12] NMR spectra were obtained on a Varian T-60A spectrometer and IR spectra on Beckman IR-10 or Perkin-Elmer 337 spectrophotometers. VPC analysis was done with a Hewlett-Packard 5750 flame-ionization chromatograph.

Reaction Conditions. Reactions in methanol and radical reactions were done under the same conditions as described previously.[1] In expt 5 (Table I) two drops of boron trifluoride etherate were added to 30 mL of methanol, and in expt 10 six drops of boron trifluoride were added last to a solution of 1.2 mL of 1 and 2.5 mL of 1.5 M methyl hypochlorite in 47 mL of methylene chloride.

Analysis and Identification of Products. Methoxy chlorides and dichlorides were analyzed by VPC as follows: 2.5% β,β-oxydipropionitrile on 80–100 mesh Chromosorb W(AW-DMCS), 70 °C, 4 ft × 0.25 in. SS. Retention times were 2.2, 2.5, 2.5, 3.6, 4.2, 7.4, 8.4, 8.4, 9.6, and 10.2 min for **8, 2a, 6a, 10, 4a, 5a, 3, 7, 9,** and **11,** respectively.

tert-Butyl chloride products were analyzed as follows: 6% SE-30 on 80–100 mesh Chromosorb W(AW-DMCS), 65 °C, 8 ft × 0.25 in. SS. Retention times were 33, 33, 41, and 47 min for **2b, 6b, 4b,** and **5b,** respectively.

Products were isolated by preparative VPC or spinning-band distillation and structures assigned mainly on the basis of the NMR spectra reported below. The compound assigned structure **7** was not isolated. The structure is tentatively assigned on the basis that this VPC peak had the same retention time as **3** and that the peak was removed by methanol solvolysis described below.

The most suitable column for VPC collection of the methoxy chloride products was 5% DC-550 silicone in 8 ft × 10 mm glass. *tert*-Butoxy chloride products were collected by VPC on the same column as was used for analysis. The *tert*-butoxy chloride **6b** was isolated in large amounts by spinning-band distillation, bp 64 °C (14 mm).

Additional evidence for the structure of the methoxy chloride product was obtained by solvolysis to dimethoxycyclopentenes in methanol, thus producing diethers. Three of the expected dimethoxy products were isolated by VPC collection: *trans*-3,4-dimethoxycyclopentene (**12**), *trans*-3,5-dimethoxycyclopentene (**13**), and *cis*-3,5-dimethoxycyclopentene (**14**). The VPC retention times of **12, 13,** and **14** on the propionitrile column (70 °C) described above are 3.0, 4.9, and 6.8 min, respectively. The allylic methoxy chlorides **2a, 3, 4a,** and **5a** were distinguished from the nonallylic (anti-Markownikoff adducts) methoxy chlorides **6a** and **7** by subjecting each to solvolysis in methanol at 50 °C. After 24 h, peaks corresponding to **2a, 3, 4a,** and **5a** had essentially disappeared, whereas **6a** and **7** were unaffected.

NMR Spectra. Structures were assigned on the basis of NMR. The spectra of the cyclopentadiene dibromides and dichlorides where spectra had been assigned previously served as important models.[1,7,13] Spectra were obtained in carbon tetrachloride (reported in parts per million downfield from Me_4Si).

Chloromethoxy Cyclopentenes. 2a: NMR δ 2.48 (dd, 1, *trans*-C**H**(H)CH, $J_{5'5}$ = 17.6, J_{45} = 4.4 Hz, other fine coupling), 3.08 (dd, 1, *cis*-CH(**H**)–CH, $J_{5'5}$ = 17.6, J_{45} = 7.0 Hz, other fine coupling), 3.40 (s, 3, CH_3O), 4.12 (ddd, 1, CHCl, J_{45} = 4.4, $J_{45'}$ = 7.0, J = 3.2 Hz), 4.32–4.52 [m (narrow), 1, C**H**OCH_3], 5.73–5.92 (m, 2, Ch=CH); **3:** NMR δ 2.72 (d, 2, CH_2, J_{45} = 5.2 Hz), 3.37 (s, 3, CH_3O), 4.20 (br d, 1, C**H**OCH_3, J_{34} = 5.2 Hz), 4.37 (dt, 1, CHCl, J_{45} = 5.2, J_{34} = 5.2 Hz), 5.87 (m, 2, CH=CH); NMR δ **4a;** 2.23–2.47 (m, 2, CH_2), 3.28 (s, 3, CH_3O), 4.47–4.77 (m, 1, $CHOCH_3$), 4.83–5.12 (m, 1, CHCl), 6.02 (s, 2, CH=CH); **5a:** NMR δ 1.93 [dt, 1, *trans*-C**H**(H)CH, $J_{44'}$ = 13.8, $J_{4'3(5)}$ = 4.4 Hz], 2.83 [dt, 1, *cis*-CH(**H**)CH, $J_{44'}$ = 13.8, $J_{4'3(5)}$ = 7.0 Hz], 3.27 (s, 3, CH_3O), 4.35 (dd with fine structure, 1, C**H**OCH_3, J_{45} = 7.0, $J_{4'5}$ = 4.4 Hz), 4.72 (dd with fine structure, 1, CHCl, J_{34} = 7.0, $J_{34'}$ = 4.4 Hz), 5.97 [m (narrow), 2, CH=CH]; **6a:** NMR δ 2.32 [br d, 1, *trans*-C**H**(H)-CH, $J_{45'}$ = 17.0 Hz], 2.85 [dd with fine structure, 1, *cis*-CH(**H**)–CH, J_{55} = 17.0, J_{45} = 7.0 Hz], 3.40 (s, 1, CH_3O), 3.95–4.23. (m, 1, C**H**OCH_3), 4.65–4.87 (m, 1, CHCl), 5.58–6.10 (m, 2, CH=CH).

Dimethoxycyclopentenes. 12: NMR δ 2.15 (dd with fine splitting, *trans*-C**H**(H)CH, $J_{5'5}$ = 16, $J_{5'4}$ = 4.5 Hz), 2.72 (dd with fine splitting, 1, *cis*-CH(**H**)CH, $J_{55'}$ = 16, J_{54} = 6.8 Hz), 3.32 (s, 6, CH_3O), 3.78 (ddd, 1, C**H**CH_2, J_{45} = 6.8, $J_{45'}$ = 4.5, J_{43} = 3.3 Hz), 4.12–4.33 (m, 1, C**H**CH=CH), 5.75 [m (narrow), 2, CH=CH]; **13:** NMR δ 1.92 (t, 2, CH_2, $J_{43(5)}$ = 4.8 Hz), 3.23 (s, 6, CH_3O), 4.48 (dt, 2, C**H**CH_2, $J_{3(5)4}$ = 4.8, $J_{13(5)}$ = 0.9 Hz), 6.02 (dd, 2, CH=CH, $J_{13(5)}$ = 0.9 Hz); **14:** NMR δ 1.50 [dt, 1, *trans*-C**H**(H)CH, $J_{4'4}$ = 13.2, $J_{4'3}$ = 4.8 Hz], 2.50 [dt, 1, *cis*-CH(**H**)CH, $J_{44'}$ = 13.2, J_{45} = 7.0 Hz], 3.25 (s, 6, CH_3O), 4.20 (dd, 2, C**H**OCH_3, $J_{3(5)4'}$ = 4.8, $J_{3(5)4}$ = 7.0 Hz), 5.95 (s, 2, CH=CH).

Chloro-*tert*-butoxycyclopentenes. 2b: NMR δ 1.20 (s, 9, Bu^tO), 2.43 [m, 1, *trans*-C**H**(H)CH], 3.07 [m, 1, *cis*-CH(**H**)CH], 4.03 (ddd, 1, CHCl, J = 7.0, J = 4.0, J = 3.5 Hz), 4.50–4.73 (m, 1, CH-OBu^t), 5.57–5.93 (m, 2, CH=CH); **4b:** NMR δ 1.18 (s, 9, Bu^tO), 2.15–2.45 (m, 2, CH_2), 4.72–5.05 (m, 2, CHCl and **H**C-OBu^t), 5.90 [m (narrow), 2, CH=CH]; **5b:** NMR δ 1.18 (s, 9, Bu^tO), 1.88 [dt, 1, *trans*-C**H**(H)CH, $J_{4'4}$ = 13.2, $J_{4'3(5)}$ = 5.0 Hz], 2.85 [dt, 1, *cis*-CH(**H**)CH, $J_{44'}$ = 13.2, $J_{43(5)}$ = 6.8 Hz], 4.38–4.80 (m, 2, CHCl and **H**COBu^t), 5.82 [m (narrow), 2, CH=CH]; **6b:** NMR δ 1.22 (s, 9, Bu^tO), 2.17 [m, 1, *trans*-C**H**(H)CH, $J_{5'5}$ = 16, $J_{5'4}$ = 3.4 Hz, other coupling], 2.83 [m, 1, *cis*-CH(**H**)CH, $J_{55'}$ = 16, J_{54} = 7.2 Hz, other coupling], 4.30 (ddd, 1, C**H**OBu^t, J_{45} = 7.2, $J_{45'}$ = 3.4, J_{43} = 2.8), 4.53–4.70 (m, 1, CHCl), 5.67–5.97 (m, 2, CH=CH).

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Registry No.—**1,** 542-92-7; **2a,** 63866-22-8; **2b,** 63866-23-9; **3,** 63866-24-0; **4a,** 63866-25-1; **4b,** 63866-26-2; **5a,** 63866-27-3; **5b,** 63855-28-4; **6a,** 63966-29-5; **6b,** 63866-30-8; **8,** 31572-43-7; **9,** 51502-28-4; **10,** 31572-44-8; **11,** 31572-45-9; **12,** 59415-73-5; **13,** 59415-71-3; **14,** 59415-72-4; methyl hypochlorite, 593-78-2; *tert*-butyl hypochlorite, 507,40-4.

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(5) The *tert*-butoxy chloride cis-1,2-adduct was not detected under ionic conditions when *tert*-butyl hypochlorite or chlorine was added to **1** in *tert*-butyl alcohol. Apparently, steric effects preclude the formation of this product.
(6) The main product formed in the presence of carboxylic acids is undoubtedly a mixture of chloro esters. Riemschneider and Nehring[2] isolated chloroacetates from the reaction of **1** with *tert*-butyl hypochlorite in acetic acid. We observe several large VPC peaks of long retention time in the product from **1,** methyl hypochlorite, and acetic acid, but these peaks were not identified.
(7) For identification and spectra of the dichlorides, see: G. E. Heasley, V. L. Heasley, P. D. Davis, D. C. Hayse, D. M. Ingle, G. R. McClung, K. D. Rold, D. K. Strickland, and T. S. Ungermann, *J. Org. Chem.*, **41,** 334 (1976) and V. L. Heasley, G. E. Heasley, P. D. Davis, D. M. Ingle, and K. D. Rold, *ibid.*, **39,** 736 (1974).
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(10) We make the same assumption we made in a previous paper,[11] that the cis/trans 1,2- and 1,4-product ratios are a consequence of steric approach in the chain-propagating step and not the result of steric crowding in the developing product.
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