found to be **9k** ($R_4 = C_6H_5$) > **9i** (R_4 = Br) > **9h** (R_4 = Cl) > **9b** (R_4 = H).

Complexes of type **10** were generally stable to work-up conditions and repeated recrystallizations. Prolonged exposure to air or heat sometimes resulted in partial decomposition, particularly in those compounds containing halogen on the ring.

Yields.—With the exception of **7p**, which gave 20–30% yields of cyclohexenone derivatives, more than 70% of the organic substrate was recovered on work-up of reaction mixtures. The bistricarbonyliron complexes presented in Table IV were obtained in yields of <1 to 8% after 3-hr irradiation with a 70-W light source. Greater yields (up to 20%) of **2**, **4**, **11**, and **12** were obtained under the same conditions.

Reactions of α-Methylstyrene (7b) under Reflux Conditions. A.—A solution in hexane of **7b** (0.9 g) and $Fe(CO)_5$ (1.05 g) was irradiated for 0.75 hr with water flow in the inner jacket regulated for mild reflux of the reaction solution. Only $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were detected in ir analysis of the metal carbonyl region, and the bulk of **7b** was recovered on work-up.

B.—A solution similar to that in part A was irradiated at room temperature for 1 hr, then refluxed with continued irradiation for an additional 0.5 hr. Work-up of the reaction mixture afforded only **7b** and a small quantity of **10b**.

Reaction of α-Methyl-4-phenylstyrene (7k).—A solution of **7k** (0.1 g) in 15 ml of hexane was stirred with 1.0 g of $Fe_2(CO)_9$ for 48 hr under nitrogen. Ir analysis indicated early formation of **8k** and $Fe_3(CO)_{12}$. Work-up on a short column of Florisil yielded $Fe_3(CO)_{12}$ and a mixture of **7k** and **8k**.

Reaction of 2-Bromostyrenetetracarbonyliron (8v).—A solution of **8v** (0.5 g) in 110 ml of hexane was irradiated for 6 hr and analyzed by ir monitoring of the metal carbonyl region. After 20 min only a small concentration of **8v** was still present while the bands typical of diene–$Fe(CO)_3$ (~2055, 1993, 1983 cm^{-1}, **9v**) were at a maximum. Continued irradiation produced bands characteristic of the diiron complex **10v**. Preparative tlc of the residue after evaporation afforded separation of 2-bromostyrene (**7v**) and two complexes, one identical by ir and melting point with **10v**, and the other identical [mp 120°; ν_{CO} (hexane) 2070, 2036, 2000, 1993 cm^{-1} (sh)] with **13** (see ref 12).

Reactions of 4-Chloro-α-methylstyrenetricarbonyliron (9h). A.—A solution of **9h** (0.10 g) in 110 ml of hexane was irradiated for 3.75 hr. Consumption of **9h** and an increase in bands characteristic of **10h** were observed in the ir throughout the irradiation. Work-up of the residue after evaporation gave **7h** and a considerably smaller amount of **10h**.

B.—Heating a solution similar to that in part A at 45° for 1 hr resulted only in a small decrease in the concentration of **9h**. At reflux temperature of hexane **9h** in this solution decomposed completely within 10 min, and no other organometallic materials were observed.

C.—Irradiation of a solution similar to that in part A with 0.5 g of $Fe(CO)_5$ for 2.5 hr yielded **10h** at a rate greater than that in part A on comparison of ir concentrations of **10h** at any given time.

Reaction of α-Methyl-4-phenylstyrenetricarbonyliron (9k).—A solution of **9k** (0.2 g) in 15 ml of hexane was stirred with $Fe_2(CO)_9$ for 1.5 hr under nitrogen. Carbonyl bands of **10k** and $Fe(CO)_5$ were apparent throughout the period allotted. Work-up of the evaporated residue permitted isolation of **10k** (ir, melting point data).

Acknowledgment.—The authors are grateful to Badische Anilin und Soda Fabrik, Germany, for a gift of iron pentacarbonyl.

Solvomercuration–Demercuration. III. The Relative Rates of Oxymercuration of Representative Olefins in an Aqueous Tetrahydrofuran System

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The relative reactivities of a number of olefins have been determined in aqueous tetrahydrofuran in order to provide a basis for predicting the possibilities of the oxymercuration–demercuration procedure for the selective reaction of one olefin in the presence of a second or the selective reaction of one of the two double bonds in a diene. The results reveal the following reactivity trends with respect to the position of the double bond and the degree of substitution: terminal disubstituted > terminal monosubstituted > internal disubstituted > internal trisubstituted > internal tetrasubstituted. In the case of disubstituted internal olefins, RCH=CHR′, cis olefins are more reactive than the corresponding trans. The rates of oxymercuration reveal marked decreases with increasing branching of the alkyl groups attached to the double bond. This is true irrespective of whether the branched alkyl group is attached to the carbon atom which receives the mercury addendum or the entering hydroxyl group. Inclusion of the double bond in ring systems causes a relatively moderate rate increase which varies modestly with structure: cyclohexene > cyclopentene ≫ cyclooctene; norbornene ≫ bicyclo[2.2.2]oct-2-ene. Conjugation of the double bond with the benzene ring results in a rate decrease. The results can be rationalized in terms of carbonium ion stability, the strain in the double bond, and steric interactions. However, irrespective of the precise interpretations, the results provide a basis for predicting the course of selective oxymercuration–demercuration of mixtures of olefins or unsymmetrical dienes.

In previous papers the broad synthetic utility of the solvomercuration–demercuration process has been indicated. Thus, alcohols,[3] ethers,[4] and amines[5] with the Markovnikov orientation are readily prepared from a wide variety of olefins in excellent yield. Oxymercuration–demercuration has also been extended to dienes and unsaturated alcohols to produce diols, tetrahydrofurans, and tetrahydropyrans.[6]

It then appeared appropriate to undertake a systematic study of the utilization of this procedure for the monohydration of dienes.[7] However, such a study required quantitative data on the effect of modifications in the olefin structure on the rate of oxymercuration under the conditions of the proposed procedure. In this way we could hope to establish the practicality of predicting the point of attack of the reagent in the proposed monohydration of dienes.

Only a limited number of studies have been described in which data have been obtained on the rates of oxymercuration of several nonfunctionally substituted olefins. Indeed, most of the kinetic studies have

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involved methoxymercuration. Thus, the study of Spengler and coworkers involved the reaction of various isomeric hexenes and nonenes with mercuric acetate in methanol.[8] Similarly, Asinger and coworkers examined the reaction of various isomers of *n*-undecene with mercuric acetate in methanol.[9]

Their results are quite interesting. Thus, Spengler, *et al.*,[8] noted that in the case of the normal straight-chain olefins the 1-alkene reacts about ten times faster than the 2-alkene and about 100 times faster than the 3-alkene. Branching in the alkyl group results in a decrease in rate. Thus, 1-hexene is converted to product at four times the rate of 4-methyl-1-pentene. Terminal-disubstituted olefins, such as 2-methyl-1-pentene, react about twice as fast as the monosubstituted isomer, such as 1-hexene. Branching in a remote position has little effect upon the rate, as indicated by the comparable rates for 3,6-dimethyl-1-heptene and 3-methyl-1-octene.

According to the results of Asinger and coworkers,[9] both *cis*- and *trans*-2-undecene react considerably slower than 1-undecene. Moreover, the *trans*-x-undecenes always react at a slower rate than the corresponding cis isomer ($x = 2, 3, 4$, and 5). The rates of reaction of both *cis*- and *trans*-x-undecene decrease as x increases, that is, with the positioning of the double bond further toward the center of the chain. Finally, the ratio $k_{\text{cis-}x}/k_{\text{trans-}x}$ increases as x increases.

Halpern and Tinker examined the rates of oxymercuration of a number of unsaturated compounds in aqueous mercuric perchlorate solution.[10] In order to achieve adequate solubility of the substrate in the water medium, most of the olefins utilized carried functional substituents. However, their data do reveal, in agreement with the methoxymercuration data,[8] that terminal-disubstituted olefins react faster than monosubstituted olefins, that internal olefins react slower than terminal olefins, and that cis olefins react faster than the corresponding trans isomer.

We were interested in a far broader range of olefin structures than the previous studies provided. Moreover, we were interested in reactivities for the aqueous tetrahydrofuran system utilized in our general procedure.[3] Accordingly, we decided to undertake a determination of the relative reactivities of a wide variety of representative olefin structures by a competitive technique.

Results and Discussion

The standard oxymercuration–demercuration procedure utilizes a 50:50 (v/v) mixture of water and tetrahydrofuran. In many cases the olefin is only partially soluble in this medium. For the usual oxymercuration–demercuration synthesis, such partial solubility offers no difficulty. However, for the competitive reaction of two olefins or one double bond of a diene it was highly desirable to avoid complications in the data arising from partial miscibility. Accordingly, we adopted for the medium a 20:80 (v/v) mixture of water and THF. Cyclohexene was adopted as the standard ($k_r = 1.00$) and the relative reactivities of all other olefins referred to this standard.

The standard procedure used to determine the relative reactivities of the various olefins follows. Ten millimoles of each of two olefins was measured volumetrically and introduced into 50 ml of 80% aqueous THF. The solution was cooled to 0°. Generally the solution was observed to be homogeneous at this point. If it was not homogeneous, an additional 50 ml of solvent was added. Then 10 mmol of mercuric acetate was added to the stirred solution. After 1 hr (2 hr if 100 ml of solvent had been used, or if the two olefins were of relatively low reactivity), 10 ml of 3.0 *M* sodium hydroxide was added, followed by 10 ml of 0.5 *M* sodium borohydride in 3.0 *M* sodium hydroxide. A suitable glpc standard was added. After the precipitated mercury had coagulated, the aqueous phase was saturated with sodium chloride and potassium carbonate. A portion of the organic layer was removed, dried with potassium carbonate, and analyzed with a Hewlett-Packard Model 5750 gas chromatograph on a 10 ft × 0.25 in. Carbowax 20M on Chromosorb W (60/80) AW-DMCS column (1% Armeen 18D added).

The relative rates, k_r, were calculated according to the relationship $k_r = \log (A/A_0)/\log (A'/A_0')$, where A_0 and A_0' are the initial concentrations of olefins A and A', respectively, and A and A' are the final concentrations of olefins A and A'. Both A and A' were measured in terms of the per cent recovery of the respective olefins. Each competitive experiment was run in duplicate. Generally the relative rates from duplicate experiments were well within 5% of the average value, k_r, reported in the tables.

If the conclusions as to the effect of structure on the rate of the oxymercuration stage are to be relied upon, it is necessary to consider both the accuracy and the reliability of the results. The initial olefin concentrations are probably accurate to within ±0.5% by the volumetric method employed. However, the uncertainties of the glpc analysis probably make the uncertainty in the final olefin concentrations to be no greater than ±3%. Moreover, owing to the nature of the relationship between k_r and the initial and final olefin concentrations, the uncertainty in k_r depends not only upon the uncertainty in each of the A terms, but also on the absolute value of each A term. Accordingly, the uncertainty is minimal when the two olefins have approximately the same reactivity, but increases rather severely as the difference in the reactivities of the two olefins become greater.

In order to check the internal consistency of the results, four pairs of olefins for which individual k_r values had been determined previously were oxymercurated competitively, utilizing the standard procedure. The relative reactivities were then calculated from results of the actual experimental data. These experimental relative reactivities were then compared to the relative reactivities calculated from the previously determined values for k_r. The results are summarized in Table I. The data reveal that the experimental and calculated values of the relative reactivities are reasonably consistent.

The olefins we selected for relative rate determinations were chosen to indicate the effects of specific types of structural features on the relative reactivity. Each

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TABLE I

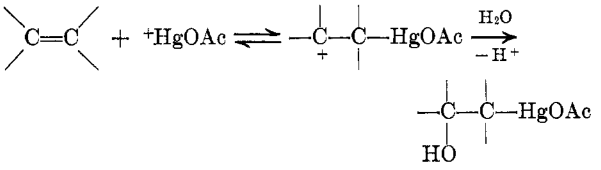
COMPARISON OF THE RELATIVE REACTIVITIES DETERMINED BY DIRECT EXPERIMENTAL COMPARISON AND CALCULATED FROM THE k_r VALUES

Olefin A	k_{r_A}[a]	Olefin B	k_{r_B}[b]	Rel reactivity Calcd[c]	Rel reactivity Exptl[d]
3-Methyl-1-butene	2.5	2,4-Dimethyl-2-pentene	0.056	44.7	39.9
1-Hexene	4.8	Cyclopentene	0.78	6.17	6.26
3,3-Dimethyl-1-butene	0.15	*cis*-4-Methyl-2-pentene	0.090	1.66	1.28
1-Pentene	6.6	1-Hexene	4.8	1.37	1.33

[a] Reactivity of olefin A relative to cyclohexene. [b] Reactivity of olefin B relative to cyclohexene. [c] k_{r_A}/k_{r_B}. [d] Calculated from the direct experimental comparison of the pairs of olefins A and B.

of these structural features are considered individually in the following sections.

Although this study was undertaken primarily with the objective of defining structural effects on reactivity, without considering the detailed mechanism of the reaction, it appears desirable at this point to mention the simple working hypothesis we have adopted. The electrophilic nature of the mechanism has been repeatedly demonstrated. The directive effects clearly point to an intermediate with cationlike properties. However, the precise structure of the intermediate ion as well as of the transition state leading to it remains a matter of some debate.[11] In the absence of any definite evidence supporting a mercurinium ion intermediate, we shall view it as essentially a carbonium ion with a large fraction of the charge remaining on the mercury moiety (eq 1). In terms of this hypothesis, the difference in properties of the intermediates produced by adding protons or mercuric ions to olefins is primarily the result of major differences in the amount of positive charge which is transmitted to the cationic centers of the intermediates.


(1)

Effect of Increased Branching in the Alkyl Group of 1-Alkenes.—In the oxymercuration of 1-alkenes the mercury atom invariably becomes attached to the 1-carbon atom and the nucleophile, water, becomes attached to the 2-carbon atom. Increased branching of the alkyl group results in a significant decrease in the relative rates of reaction (Table II).

TABLE II

EFFECT OF INCREASED ALKYL BRANCHING ON THE RELATIVE REACTIVITY

Olefin	Rel reactivity, k_r[a]
1-Pentene	6.6
1-Hexene	4.8
3-Methyl-1-butene	2.5
3,3-Dimethyl-1-butene	0.15

[a] Relative to cyclohexene.

Since the increased branching should not affect significantly the rate of attachment of the mercury atom to the terminal position, the decrease in relative reactivity is presumably the result of a steric retardation of the addition of water.

Effect of the Position of the Double Bond.—The results reveal that 1-alkenes are considerably more reactive than the corresponding 2-alkenes (Table III).

TABLE III

EFFECT OF THE POSITION OF THE DOUBLE BOND

Olefin	Rel reactivity, k_r[a]	k_{cis}/k_{trans}
1-Pentene	6.6	
cis-2-Pentene	0.56	3.29
trans-2-Pentene	0.17	
cis-4-Methyl-2-pentene	0.090	3.46
trans-4-Methyl-2-pentene	0.026	

[a] Relative to cyclohexene.

Effect of Cis–Trans Isomers.—In agreement with the results of previous workers,[9] the cis isomers are considerably more reactive than the trans. Data for two isomeric pairs are given in Table III. The lower rate for the 4-methyl-2-pentene derivatives as compared to the parent 2-pentenes is presumably the result of the larger steric requirements of the more branched alkyl substituent, as discussed earlier.

Effect of the Number of Alkyl Substituents on the Double Bond.—The introduction of a methyl group in the 2 position of a 1-alkene results in a considerable increase in reactivity. Thus the reactivity of 2-methyl-1-pentene is seven times greater than that of 1-pentene. Similarly, the reactivity of 2-methyl-2-pentene is higher than those of *cis*- and *trans*-2-pentene (Table IV). This effect can be rationalized in terms of the fact that the addition of the mercury ion to the less substituted carbon atom in the more reactive systems puts the positive charge at a tertiary position. The relatively small effect which is observed is consistent

TABLE IV

EFFECTS OF SUBSTITUENTS ON THE DOUBLE BOND

Olefin	Rel reactivity, k_r[a]
1-Pentene	6.6
2-Methyl-1-pentene	48
cis-2-Pentene	0.56
trans-2-Pentene	0.17
2-Methyl-2-pentene	1.24
2,4-Dimethyl-2-pentene	0.056
2,4,4-Trimethyl-2-pentene	0.020
2,3-Dimethyl-2-butene	0.061

[a] Relative to cyclohexene.

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(11) For a recent review of the literature, see W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

with the proposal that very little positive charge is actually transmitted from the mercury ion to the carbon atom in the transition state.

It was earlier pointed out that increased branching in the alkyl group adjacent to the position adding the nucleophile results in decreased reactivity (Table II). The data for 2-methyl-2-pentene and 2,4-dimethyl-2-pentene (Table IV) indicate that steric crowding about the carbon atom to which the mercury atom is becoming attached likewise results in decreased rates. The further decrease observed for 2,4,4-trimethyl-2-butene agrees with this conclusion. It appears, therefore, that branching of the alkyl group attached to the double bond results in a decrease in reactivity irrespective of whether it is located at the carbon atom of the double bond where the mercury atom is becoming attached or at the carbon atom where the nucleophile is adding.

Effect of Ring Systems.—The results reveal that olefins derived from cyclopentyl and cyclohexyl systems exhibit reactivities slightly greater than the corresponding acyclic structures. The reactivity of cyclooctene is quite low. On the other hand, norbornene is quite reactive, while bicyclo[2.2.2]oct-2-ene exhibits a low reactivity.

The results are summarized in Table V.

TABLE V

EFFECT OF RING SYSTEMS

Olefin	Rel reactivity, k_r[a]	Acyclic analog	Rel reactivity, k_r[a]
Cyclopentene	0.78	*cis*-2-Pentene	0.56
Cyclohexene	1.00		
1-Methylcyclopentene	1.86	2-Methyl-2-pentene	1.24
Methylenecyclopentane	59	2-Methyl-1-pentene	48
Cyclooctene	0.002		
Norbornene	3.7		
Bicyclo[2.2.2]-octene	0.01		

[a] Relative to cyclohexene.

It is of interst that cyclooctene, which has an exceptionally low heat of hydrogenation,[12] has the lowest rate of reaction, and norbornene, with a very high heat of hydrogenation, is quite reactive in the oxymercuration reaction. However, with steric effects at both positions of the double bond influencing strongly the relative reactivity, the situation is obviously too complex to permit such simple correlations.

Effect of Conjugation of the Double Bond to a Benzene Ring.—The relative reactivities of four phenyl conjugated olefins are summarized in Table VI.

The results reveal that compared to an alkyl group the phenyl substituent results in a marked rate retardation. For example, styrene reacts only at $^1/_{17}$ the rate of 1-hexene. Conjugative resonance stabilization of the incipient cationic intermediate either is absent or is surpassed in magnitude by some opposing factor. The weak sensitivity of the reaction to stabilization of the incipient carbonium ion by alkyl groups, pointed out earlier, indicates that only a small amount of positive charge is transmitted to the incipient cationic center in the transition state. On this basis, it is not surprising that resonance stabilization by the phenyl substituent fails to dominate the situation. Conjugation of the benzene ring to the double bond should lower the ground state energy and thereby decrease the rate. Secondly, the steric requirements of the aromatic ring may be comparable to those of an isopropyl and *tert*-butyl group. Indeed, the reactivity of styrene falls between that of 3-methyl-1-butene and 3,3-dimethyl-1-butene. Consequently, the observed low rate may in part be due to steric effects.

TABLE VI

EFFECT OF CONJUGATION OF THE DOUBLE BOND TO A BENZENE RING

Olefin	Rel reactivity, k_r[a]
Styrene	0.28
α-Methylstyrene	1.18
cis-Propenylbenzene	<0.02
trans-Propenylbenzene	<0.02

[a] Relative to cyclohexene.

Comparison with Previous Data.—Although the present results were obtained under very different conditions, it is of interest to compare them with previous data and conclusions. Spengler and coworkers[8] report that 2-hexene reacts twice as fast as 4-methyl-2-pentene; we find that *trans*-2-pentene reacts six times faster than *trans*-4-methyl-2-pentene. They report that 1-hexene reacts ten times as fast as 2-hexene; we find that 1-pentene reacts 41 times as fast as *trans*-2-pentene and 12 times as fast as *cis*-2-pentene. Finally, Spengler reports that 2-methyl-1-pentene reacts twice as fast as 1-hexene; for these same two olefins we obtain a relative reactivity of seven. Thus, in spite of the fact that Spengler's data refer to the reaction of mercuric acetate in methanol at 20°, whereas ours refers to the addition of the same salt in 80% aqueous THF at 0°, the qualitative agreement is quite good.

The relative reactivities of 1- (1.000), *cis*-2- (0.086), and *trans*-2-undecene (0.022), obtained by Asinger and coworkers for methoxymercuration,[10] are almost identical with our relative reactivity values for the oxymercuration of a related series: 1- (1.000), *cis*-2- (0.085), *trans*-2-pentene (0.024).

Several olefins oxymercurated by Halpern and Tinker[10] exhibit structural features similar to some of those included in the present investigation. A comparison of the two sets of data (Table VII) reveals agreement that can only be considered remarkable in view of the difference in the experimental conditions.

TABLE VII

COMPARISON OF OXYMERCURATION REACTIVITIES

Study of Halpern and Tinker[10]		Present study	
Olefin	Rel reactivity[a]	Olefin	Rel reactivity[b]
2-Methyl-1-propene	>600	2-Methyl-1-pentene	282
1-Butene	47 ± 12	1-Hexene	28
Cyclohexene	2.9 ± 0.6	Cyclohexene	5.9
cis-2-Butene	3.4	*cis*-2-Pentene	3.3
trans-2-Butene	1.00	*trans*-2-Pentene	1.00

[a] Relative to *trans*-2-butene, using aqueous mercuric perchlorate. [b] Relative to *trans*-2-pentene, using 80% aqueous THF.

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[12] R. B. Turner, "Theoretical Organic Chemistry," The Kekule Symposium, Butterworths, London, 1959, pp 67–83.

Conclusion

The oxymercuration–demercuration of olefins has previously been shown to be a highly convenient synthetic method for the Markovnikov hydration of olefins. The present paper has demonstrated a wide range of reactivity accompanying variation of olefin structure. Accordingly, considerable selectivity in the monooxymercuration of dienes is expected. Steric factors play a major role in determining the reactivity of hydrocarbon olefins. Thus, increased substitution on the double bond (as long as the carbonium ion stability remains the same) and increased steric hindrance at the site of hydroxyl or mercury substituent attachment decrease the rate of reaction. Increased stability of the carbonium ion or decreased stability of the olefinic ground state due either to increased cis interactions or constraint in a bicyclic ring system increase the reactivity of the double bond. However, since the situation appears to be relatively complex, it appears best to proceed from experimental data on the relative reactivities of known structures to predict the results of competitive oxymercuration of mixtures of olefins. As will be pointed out in the following paper,[7] the data are helpful in predicting the course of monohydration of dienes.

Experimental Section

Materials.—All olefins used were commercially available and were used as obtained unless vpc or index of refraction data indicated impurities. Mercuric acetate (Mallinckrodt Chemical Works), sodium borohydride (Metal Hydrides, Inc.), and tetrahydrofuran (Fisher Scientific Co.) were used without further purification.

Oxymercuration Procedure.—The general procedure used has been discussed in the text. Cyclohexene was used as the reference olefin in all cases except the following. Norbornene was determined relative to styrene and also relative to 1-pentene. α-Methylstyrene was determined relative to styrene. 2,4,4-Trimethyl-2-pentene, bicyclo[2.2.2]oct-2-ene, and cyclooctene were all determined relative to 2,3-dimethyl-2-butene. In all cases where a reference olefin other than cyclohexene was used, the k_r value was back-calculated to cyclohexene for purposes of presentation in the text.

Control Experiment.—In order to establish that the mercurials do not equilibrate under the reaction conditions employed, the following experiment was performed. Cyclohexene and 1-hexene were oxymercurated separately for 15 min on a 10-mm scale employing 10 mm of mercuric acetate, 10 ml of water, and 10 ml of THF for each olefin; 30 ml of THF was then added to each reaction mixture and the solutions were cooled to 0°. To each reaction mixture was added 10 mm of the other olefin and the solutions were stirred for 8 hr at 0°. Reduction of the mercurials and subsequent vpc analysis showed that no more than 3% of the mercurial from either olefin was converted into the mercurial of the other olefin.

Registry No.—3-Methyl-1-butene, 563-45-1; 1-hexene, 592-41-6; 3,3-dimethyl-1-butene, 558-37-2; 1-pentene, 109-67-1; 2,4-dimethyl-2-pentene, 625-65-0; cyclopentene, 142-29-0; *cis*-4-methyl-2-pentene, 691-38-3; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; *trans*-4-methyl-2-pentene, 674-76-0; 2-methyl-1-pentene, 763-29-1; 2-methyl-2-pentene, 625-27-4; 2,4,4-trimethyl-2-pentene, 107-40-4; 2,3-dimethyl-2-butene, 563-79-1; cyclohexene, 110-83-8; 1-methylcyclopentene, 693-89-0; methylenecyclopentane, 1528-30-9; cyclooctene, 931-88-4; norbornene, 498-66-8; bicyclo[2.2.2]octene, 931-64-6; styrene, 100-42-5; α-methylstyrene, 98-83-9; *cis*-propenylbenzene, 766-90-5; *trans*-propenylbenzene, 873-66-5; 2-methyl-1-propene, 115-11-7; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6.

Solvomercuration–Demercuration. IV. The Monohydration of Representative Dienes *via* Oxymercuration–Demercuration

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The oxymercuration–demercuration of dienes with 1 mol of mercuric acetate per mole of diene under standard conditions (80% aqueous tetrahydrofuran) provides a convenient procedure for the Markovnikov monohydration of one of the two double bonds in the diene. In the case of symmetrical nonconjugated dienes, such as 1,5-pentadiene, 1,7-octadiene, and 1,11-dodecadiene, the yield of enol is lower than predicted for a statistical reaction (50% enol) but approaches the statistical value with the longer chains. The yields can be raised by using mercuric trifluoroacetate. In the case of unsymmetrical dienes, such as 2-methyl-1,11-dodecadiene, 11-methyl-1,10-dodecadiene, 4-vinylcyclohexene, and limonene, the yields of enols are higher and involve selective hydration of the double bond whose structural features indicate it to be the more reactive on the basis of the related study of the relative reactivities of representative olefins under these conditions. Good yields of enols can also be realized from conjugated dienes provided that the reaction time is minimized.

Hydroboration–oxidation provides a convenient procedure for the anti-Markovnikov hydration of the carbon–carbon double bonds in olefins and dienes.[5,6] Oxymercuration–demercuration provides an equally convenient procedure for the Markovnikov hydration of the carbon–carbon double bonds in olefins[7] and dienes.[8]

Although there have been a number of reports of the monosolvomercuration of dienes, a systematic study of the synthetic utility of the reaction for the synthesis of enols *via* the monohydration of dienes has not been

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