phenylecyclobutene, along with other olefinic resonances. No transient abnormalities were apparent in the position of the 1-phenylecyclobutene absorption.

Reactions with Tri-n-butyltin Hydride.—In an nmr tube, there were placed 0.53 ml of a 1.2 M stock solution of tri-n-butyltin hydride in benzene, 0.144 g (0.59 mmole) of 1-chloro-4-bromo-1-phenyl-1-butene, 0.0016 g of arsobisobutonitrile, and 0.020 ml of tetrahydrofuran (as an internal reference). The sample was heated at 80° until the nmr spectrum showed complete disappearance of the Sn-H band (3 2.24 ppm upfield from benzene). The nmr spectrum showed partial disappearance of the chlorobromide olefinic triplet at 1.32 ppm upfield from benzene, and replacement by a new triplet at 8 1.28 ppm. By gas chromatography, components of the mixture were separated and identified as cis-1-phenyl-1-butene (by retention time), trans-1-phenyl-1-butene (by nmr), cis-1-chloro-1-phenyl-1-butene (by nmr), trans-1-phenyl-1-chloro-1-butene (by nmr), and cis and trans isomers of the starting halide (by retention time). The ratio of cis-5-phenylcyclooctanol tosylate and the corresponding p-anisyl derivatives. The results indicate that in these compounds, participation by the transannular hydrogen of the ring by the tert-butyl group, rather than of neighboring group participation in the usual sense. The rearranged olefin is obviously quite bulky, it may well deform appreciably the cyclooctane ring to which it is attached, and hence the earlier experiments did not conclusively rule out the possibility that the unusual rate for the cis isomer was a result of conformational distortion of the ring by the tert-butyl group, rather than of neighboring group participation in the usual sense. The rearranged product in that case would have to be formed by a trans-1-phenyl-1-butene to trans-1-chloro-1-phenyl-1-butene was about 0.1. Reactions at lower concentrations gave less complete reduction and apparent side reactions.

A similar attempt at reduction of 1-phenyl-1-butene led to no disappearance of either hydride or alkene, based on nmr observation. With 1-chloro-1-phenyl-1-butene, disappearance of the hydride occurred, and a product was formed which was identified by nmr and by its retention time as n-butylbenzene. 1-Phenyl-1-butene was formed in less than 10% of the amount of n-butylbenzene.

Transannular hydride shifts across medium rings have been known for almost 20 years. In an effort to understand the stereochemical features of these shifts, the solvolyses of a number of different stereoisomers of three- and five-substituted cyclooctane compounds were studied. It was found that cis-5-tert-butylecyclooctyl tosylate solvolyzed much more rapidly than did the trans isomer, and the product obtained from the cis isomer was mostly rearranged olefin, while that from the trans isomer was mostly the olefin corresponding to simple elimination. From examination of the probable conformations of the molecules, participation by the transannular hydrogen of the cis isomer in the rate-determining step appeared to be indicated (eq 2). Only the cis isomer has a geometry which will permit such participation. The trans isomer reacts without participation, and without much rearrangement. However, the difference in rate between the cis and trans isomers was only a factor of 34, and not large enough to be convincingly attributed to neighboring group participation. Since the tert-butyl group is obviously quite bulky, it may well deform appreciably the cyclooctane ring to which it is attached, and hence the earlier experiments did not conclusively rule out the possibility that the unusual rate for the cis isomer was a result of conformational distortion of the ring by the tert-butyl group, rather than of neighboring group participation in the usual sense. The rearranged product in that case would have to be formed by a trans-1-phenyl-1-butene to trans-1-chloro-1-phenyl-1-butene.

Conformational Analysis. LXXII. Solvolysis Studies with the 5-Phenylecyclooctanol System

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A rate and product study has been carried out on the solvolysis in aqueous ethanol of cis- and trans-5-phenylecyclooctanol tosylate and the corresponding p-anisyl derivatives. The results indicate that in these compounds, and by inference other cyclooctyl derivatives, neighboring group participation is not of importance in determining solvolysis rates. The rather fast rates observed, and rate differences between isomers, are attributed to steric effects.

\[\text{cis} \quad \begin{array}{c} \text{OTs} \\ \text{trans} \end{array} \quad \rightarrow \quad \text{relative rate} = 1 \]

\[\text{cis} \quad \begin{array}{c} \text{OTs} \\ \text{cis} \end{array} \quad \rightarrow \quad \text{relative rate} = 34 \]
annular hydride ion transfer subsequent to the rate-
determining step.

In order to differentiate steric and electronic effects
in such a case, a convenient method involves carrying
out parallel experiments on a phenyl compound, and on
the p-anisyl derivative. The steric effects are essen-
tially the same for these two, but the p-anisyl compound
is able to supply electrons to a much higher degree if
required to do so by an electronic demanding transition
state. One might therefore predict that since a phenyl
group has approximately the same, or somewhat
smaller, bulk as a tert-butyl group¹¹ (depending on how it
is measured), the 5-phenylcyclooctyl derivatives would
solvolyze at rates similar to those of the corresponding
tert-butyl compounds if neighboring group participation
were unimportant in the transition state, but the cis
isomer should be much faster if it were important. The
cis-5-p-anisyl compound should either solvolyze at the
same rate as the phenyl derivative, which would indi-
cate no participation, or at a greatly accelerated rate,
which would indicate a high degree of participation, or
somewhere in between, while the trans isomer should
have a rate similar to trans-phenylcyclooctyl tosylate in
any case.

Synthesis

During the early stages of this work, a paper by
Cope² appeared, in which the syntheses of the isomeric
5-phenylecyclooctyl tosylates were described. We pre-
pared a mixture of the two isomers by substantially the
method described by Cope. There was no particular
need to separate them; so we determined the rates of the
two isomers directly from the mixture. Since the cis
isomer solvolyzes over five times as fast as the trans
isomer, this was easy to do experimentally. The anal-
ogous 5-anisylecyclooctyl tosylates were then prepared,
by the scheme outlined on Chart I. Anisylaldehyde
was converted to 3-anisylglutaric acid (I) via a Knoeven-
agel reaction with ethyl acetoacetate, followed by basic
cleavage (a reverse Claisen reaction) which yielded the
acid. The acid I was esterified and reduced to
3-anisylpentane-1,5-diol (II) with lithium hydride.
Chain extension of this diol via the tosylate IV and
treatment with cyanide yielded 4-anisylpimelonitrile
(V), which was converted to the ester VI, which was in
turn reduced to 4-anisylheptan-1,7-diol (VII). An-
other chain extension via the tosylate VIII gave 5-
anisylazelanitrile (IX). This compound was cyclized
to yield 2-cyano-5-anisylecyclooctenylamine (X) by
means of a Thorpe–Ziegler cyclization. Hydrolysis and
decarboxylation furnished 5-anisylecyclooctanone (XI).
The ketone was reduced with lithium aluminum hy-
dride to give a mixture of the cis- and trans-5-p-anisyl-
ecyclooctanols (XII). The tosylates XIII were pre-

pared and solvolyzed in the usual way; the solvolysis products are given in Table I. For comparison purposes, a number of other cyclooctyl tosylates were solvolyzed, or had previously been solvolyzed, under identical conditions (in 90% ethanol, 25°C, and pH 8.4). The relative rates of these compounds are summarized in Table II.

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<th>Compound solvolyzed</th>
<th>cis-5-tert-Butylycyclooctyl tosylate</th>
<th>trans-5-tert-Butylycyclooctyl tosylate</th>
<th>5-Phenylcyclooctyl tosylate (cis/trans ratio 1.32)</th>
<th>5-Anisylcyclooctyl tosylate (cis/trans ratio 2.3)</th>
<th>cis-3-tert-Butylycyclooctyl tosylate</th>
<th>Cyclooctyl tosylate</th>
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<tr>
<td>Rearranged products, %</td>
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<td>Alcohol</td>
<td>Olefin</td>
<td>Alcohol</td>
<td>Olefin</td>
<td>Alcohol</td>
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<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>5-10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5-Phenylcyclooctyl tosylate (cis/trans ratio 1.32)</td>
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<td>34</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>28</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cyclooctyl tosylate</td>
<td>53</td>
<td>53</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

* Shown to contain 8% of the cis isomer during solvolysis.

We thus conclude that there is no evidence for neighboring group participation by the phenyl.

Results and Discussion

The products of the solvolysis of cis- and trans-5-phenylcyclooctyl tosylate (in formic acid) were studied earlier by Cope and Kinnel. They found that various alcohols were obtained as minor products; the cis isomer gave mostly the olefin obtained by hydride migration from C-5, while the trans isomer gave mostly rearranged olefin, analogous to what was found earlier with the 5-alkylcyclooctyl tosylates.6-8 In general our results seem to agree with Cope's, although our alcohol/olefin ratio was a little larger, as would be expected from the higher nucleophilicity of the solvent we employed. We did not separate our isomeric tosylates for separate study, but the products obtained are consistent with the cis isomer yielding mostly rearranged olefin and the trans isomer yielding mostly olefin without rearrangement (Table I).

The relative solvolysis rates of the tosylates are more informative than the reaction products. Looking now at Table II, we might first compare the relative rates of trans-5-tert-butylcyclooctyl tosylate (9.1) with the corresponding phenyl compound (4.1). The rates differ by only about a factor of 2, indicating that the steric effects are similar and the electronic effect is negligible, or there is some fortuitous cancellation of the two effects. Looking at the corresponding cis isomers, the 5-tert-butylcyclooctyl tosylate has a solvolysis rate of 31, compared to a cis-5-phenylcyclooctyl tosylate rate of 22. Any participation by the phenyl would be expected to accelerate the rate, and since the phenyl compound solvolyzes more slowly by a factor of 14, any acceleration must be pretty small, and more than counterbalanced by a steric or inductive effect. Looking only at the rates of the phenylecyclooctyl tosylates, then, one would conclude that there is no evidence for neighboring group participation by the phenyl.

If we now compare the p-anisylecyclooctyl tosylates with the corresponding p-phenyl compound, we notice that for the trans isomers the phenyl (rate 4.1) is just slightly faster than the p-anisyl (rate 2.9), a difference too small to be of much importance. Looking at the corresponding cis isomers, the p-anisyl (rate 25) is just slightly faster than the p-phenyl (rate 22). We thus conclude that there is no detectable neighboring group participation in the transition state in any of these phenyl- or anisyl-substituted cyclooctyl tosylates. It might be argued that perhaps the phenyl group cannot achieve planarity with the carbonium ion being generated by hydride migration, and therefore it is unable to become involved in neighboring group participation in the transition state. While proof that this is not the case is lacking, it seems improbable that at least a small effect would not be observed if hydride migration is concerted with the solvolysis. For it not to occur, the phenyl would have to remain at almost exactly 90° to the plane of the carbonium ion being generated by hydride migration. This seems highly improbable. The large rate acceleration (34 times) brought about by the cis-5-tert-butyl group therefore seems best interpreted as a steric effect, that is, a relief of strain of some sort in the transition state. It might be noted that the cis-3-tert-butyl group also brings about a substantial rate acceleration (although not so large as in the 5-tert-butyl case), but here participation by hydride is unlikely, as the product obtained shows no hydride migration from the 3 position.

Since we conclude that neighboring group participation is negligible in the transition state, we must also conclude that the cis- and trans-cyclooctyl derivatives do not go through a common intermediate, since they give different products. The cis isomer is geometrically more favorably disposed toward transannular hydride transfer, and it undergoes such transfer in a fast
Experimental Section

3-p-Anisaldehyde (1).—To a mixture of 119.9 g of anisaldehyde and 225 g of ethyl acetocetate was added dropwise 20 ml of pyridine, with stirring. After standing overnight the mixture had solidified. A solution of 200 g of sodium hydroxide in 11.1 of absolute ethanol was added to the solid product. After the solid had dissolved, the solution was heated under reflux with stirring for 24 hr. The majority of the ethanol was then removed by distillation. The solid had dissolved, the solution was heated under reflux with stirring for 24 hr. The major part of the ethanol was then removed by distillation. The precipitate was filtered, washed with ether, and dissolved in 500 ml of water. Acidification with concentrated hydrochloric acid yielded the crude product, 165 g, m.p. 160–162°. Recrystallization from ethyl acetate gave crystals, m.p. 165–167° (lit.1 165°) 1987.

Anal. Caled for C12H18O3: C, 68.55; H, 8.63. Found: C, 68.41; H, 8.56.

Dimethy1 3-p-Anisylglycinate (II).—A mixture of 165 g of crude acid I, 500 ml of methanol, 1.1 of benzene, and 20 ml of concentrated sulfuric acid was heated under reflux for 2 hr. After the reaction mixture was cooled, 1.1 of water was added, the organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic portions were washed again with water and dried over magnesium sulfate. The combined ether solutions were dried over magnesium sulfate and evaporated under reduced pressure. The oily residue was extracted with ether. The organic layer was separated, and the aqueous layer was extracted with ether. The ether layer was washed with water and saturated sodium bicarbonate and dried over magnesium sulfate. After concentration and vacuum evaporation, 0.9 g of naphthalene was added. A solution of 2 g of the tosylate and 4 g of potassium carbonate in 80 ml of water was added until the initial color was maintained. The reaction mixture was heated under reflux for 4.8 g of X in 200 ml of 30% (volume) concentration, the residue was distilled, bp 163–164° (0.7 mm), nD20 1.5091, yield 34 g.


5-p-Anisylheptane-1,7-diol (V).—A solution of 34 g of VI in 170 ml of dry tetrahydrofuran was added dropwise to a stirred solution of 10 g of lithium aluminum hydride in 600 ml of dry ether. The reaction mixture was heated under reflux for 3 hr, cooled, and treated with 200 ml of saturated ammonium chloride solution with stirring and cooling. The precipitate was filtered and washed with ether. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether extract was dried over magnesium sulfate and concentrated to yield 21 g.


5-p-Anisylcyclooctyl-p-Toluenesulfonate (XIII).—To a solution of 25 g of XII in 1 ml of dry pyridine, in an ice-salt bath, 1.8 g of tosyl chloride was slowly added. The reaction mixture was stirred for 2 hr at 0° and treated with 20 ml of water. The aqueous solution was extracted with ether. The ether layer was washed with ice-cold 2 N hydrochloric acid, water, and saturated sodium bicarbonate and was dried over magnesium sulfate. After concentration, 200 ml of pyridine was added to the mixture under reflux for 4 hr. The reaction mixture was refluxed for 4 hr. The reaction mixture was refluxed for 4 hr. The mixture was extracted with chloroform, and the chloroform layer was washed with water and saturated sodium bicarbonate. The combined ether solutions were dried over magnesium sulfate and evaporated under reduced pressure. The oily residue was recrystallized from ethanol twice to yield 30 g of crystals, m.p. 65.5–66°.


5-p-Anisylcyclooctanol (XI).—To a well-stirred, boiling solution of sodium methanilithium, which was prepared from 12 g of sodium, 40.4 g of naphthalene, and 70 g of N-methylacetanilide in 800 ml of ether, a solution of 10.6 g of IX in 1.9 l of dry ether was added dropwise through the high-dilution apparatus over a period of 3 days. The reaction mixture was heated under reflux for 3 hr, cooled, and treated with 500 ml of water with stirring and cooling. The ether layer was separated and the aqueous layer was extracted with ether. After evaporation of solvent from the combined ether layers, the residue was steam distilled to remove 2-hydroxy-1,4-dihydronaphthalene. The material remaining was extracted with chloroform, and the chloroform solution was dried over magnesium sulfate. Evaporation of the solvent gave a residue, m.p. 85–90°. Recrystallization from methanol gave 7.2 g of crystals, m.p. 126–127°.

Anal. Caled for C16H20O: C, 74.97; H, 7.86; N, 10.93. Found: C, 74.85; H, 8.01; N, 10.79.

5-p-Anisylcyclooctane (X).—To a solution of 12 g of sodium, 40.4 g of naphthalene, and 70 g of N-methylacetanilide in 800 ml of ether, a solution of 10.6 g of IX in 1.9 l of dry ether was added dropwise through the high-dilution apparatus over a period of 3 days. The reaction mixture was heated under reflux for 3 hr, cooled, and treated with 500 ml of water with stirring and cooling. The ether layer was separated and the aqueous layer was extracted with ether. After evaporation of solvent from the combined ether layers, the residue was steam distilled to remove 2-hydroxy-1,4-dihydronaphthalene. The material remaining was extracted with chloroform, and the chloroform solution was dried over magnesium sulfate. Evaporation of the solvent gave a residue, m.p. 85–90°. Recrystallization from methanol gave 7.2 g of crystals, m.p. 126–127°.

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Anal. Caled for C16H20O: C, 74.97; H, 7.86; N, 10.93. Found: C, 74.85; H, 8.01; N, 10.79.
of p-toluenesulfonyl chloride in 5 ml of pyridine. The reagent was added as fast as consistent with maintaining the reaction temperature. The resulting solution was then stored at -20° for 2 days. The flask was removed from the freezer, five drops of water were added to the reaction, and the solution was allowed to warm to 0°. The reaction was then poured into 20 ml of ice-cold 5% hydrochloric acid, and the solution was extracted with 30 ml of ether. The ether solution was washed with cold 5% acid and with sodium bicarbonate and was dried over magnesium sulfate. The solution was evaporated to dryness under reduced pressure, and the residue was recrystallized from ether-pentane at -20° to yield crystals, mp 77.5-82°. Kinetic runs were made on this product and showed different batches to be a mixture of epimers of variable composition.

5-Phenylcyclooctyl p-Toluenesulfonate.—This compound was prepared following the procedure used for XI1 and gave crystals, from ether-pentane (-20°), mp 68-70° [lit. 69.5-70.5 (cis isomer) and 70-71.5° (trans isomer)]. Kinetic runs were made on the mixture of epimers, and these runs showed the composition to be 1.3 parts cis epimer to one part trans.

1-Phenylcyclooctene (XV).—The preparation of this compound was accomplished by the dehydration of XIV in ether solution with iodine. This product was shown to be the olefin by thin layer chromatography, gas chromatography, and tetranitromethane tests.

1-p-Anisylcyclooctane.—The method of preparation of this compound was identical with that described for the preparation of XIV, and the preparation of 1-p-anisylcyclooctene was similarly analogous to the preparation of XV. Both compounds were used as ether solutions for the product analysis. Thin layer chromatography and gas chromatography were consistent with the above structures.

Kinetic Experiments.—The rates of solvolysis were measured on a Sargent recording pH-Stat, as discussed earlier.4 Preparation of Solvents and Reagents.—The aqueous ethanol used in the kinetic runs was prepared all at once, and the same solvent was used for the base titrant and the solutions of tosylate. It was stored under dry nitrogen when not being used. Preparation consisted of dilution of commercial 95% ethanol with enough distilled water to make the solvent 90% ethanol by volume. Physical constants of the solution were as follows: nD 1.3624, density 0.8498 g/ml at 25°. The basic titrant was prepared by dissolving reagent potassium hydroxide (0.65 g) in 500 ml of the above solvent. Titration against standard hydrochloric acid showed it to 0.161 N. The reaction vessel was removed from the titrator, excess base was added to the solution, and the solution was transferred to a 20-ft dual column, the first half packed with XE-60 on 60-80 mesh firebrick, the second half packed with triericyl phenol.

Product Analysis.—Product analyses of the tosylate solvolyses were done by gas chromatography, and the results were checked by thin layer chromatography. The actual solvolysis runs were used for the analysis, rather than separate runs. This eliminated any uncertainty due to variable composition of epimers in the mixtures, which appears to occur with the p-anisyl derivative. A typical work-up of a solvolysis for analysis follows.

The reaction vessel was removed from the titrator, excess base was added to the solution, and the solution was transferred to a second flask and stored at 25° until work-up was convenient. (In the case of the slower reactions, the reaction was left for several more half-lives to ensure complete reaction.) The reaction mixture was then diluted with 50 ml of pentane and extracted twice with 50 ml of distilled water. The water extracts were washed with pentane, and the organic fractions were combined and dried over magnesium sulfate. The pentane was then distilled carefully, using a 12-in. column packed with stainless steel gauze, and equipped with a head in which the reflux ratio could be varied. Distillation was continued until only 0.5-1 ml of liquid remained in the pot. This solution was stored in the freezer until needed.

The actual analyses were done on an aluminum column, 4 m × 0.25 in., packed with 10% SE-60 on 40-60 mesh firebrick, and the second half packed with triericyl phenol.

Allinger, Neumann, and Sugiyama

Table III

<table>
<thead>
<tr>
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kcis = 7.07 × 10^-5 sec^-1; ktrans = 1.244 × 10^-4 sec^-1

Ratios of cis/trans = 1.34

Run no. 3: 13.50 mg of p-toluenesulfonate in 15 ml of 80% ethanol maintained at pH 6.4 ± 0.4.

Cope and Tiffany were apparently the first workers to observe an unusual base-catalyzed rearrangement of an epoxide when dealing with cyclooctatetraene oxide. Subsequent work with phenyl-substituted ethylene oxides, medium-ring cycloalkene oxides, and open-chain epoxides established several novel reaction pathways on treatment with strong base. The extensive work of Crandall and his coworkers amplified these and brought to light additional reactions.

This paper deals with our continuing study of the lithium diethylamide induced rearrangement of a series of propylidenecycloalkane oxides to allylic alcohols. Formally an elimination, this reaction is remarkable for its very high selectivity, requiring in excess of 95% of the alternate, tertiary allylic alcohol. A series of ethylidenecycloalkane oxides, where preference for endocyclic elimination competes with proton abstraction from primary carbon, was also examined. The results of both series support a syn elimination mechanism, with very specific cis-coplanar transition state geometrical requirements.

Course of the reaction was followed by vpc, and the mixture quenched with water when the epoxide was consumed. The results are shown in Table I.

| TABLE I PRODUCT DISTRIBUTION FROM THE REACTION OF PROPYLIDENECYCLOALKANE OXIDES (1) WITH LITHIUM DIETHYLAMIDE |
| Time, hr | 1 | 2 | 3 |
| + | 4 | 6 | 77 |
| b | 5 | 1 | 100 |
| c | 6 | 5 | 98 |
| d | 7 | 5 | 98 |
| e | 8 | 2 | 100 |
| f | 12 | 22 | >84 |

The reactions were followed by vpc; this is the time required for effective complete loss of starting epoxide. The product mixture in this case contained 5% cyclobutyl ethyl ketone and 3% unidentified material. At this time 95% unreacted epoxide remained. Not directly determined; see Experimental Section.

In this series, proton abstraction from secondary cyclic carbon competes with that from a secondary acyclic center. The data in Table I show not only high selectivity depending on ring size, but a striking reversal in the direction of elimination in the series cyclopentyl (endoacic), cyclohexyl (acyclic), and cycloheptyl (endoacic olefin preferred).

It is apparent that subtle conformational effects can significantly diminish the activation energy for elimination into the carbocyclic ring. The propylicenecyclohexane oxide 1c serves as a basis for comparison; reaction to form the acyclic double bond (as strongly favored in 1c) requires in excess of 49 hr for complete conversion. All other systems shown in Table I react more rapidly, from a great deal faster in the completely