

Isomerization of Vinylcyclopropanes by a Homogeneous Rhodium Catalyst

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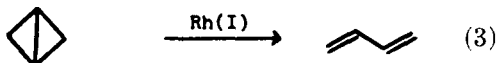
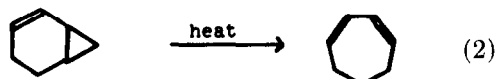
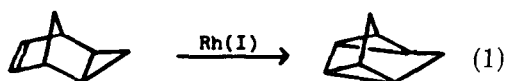
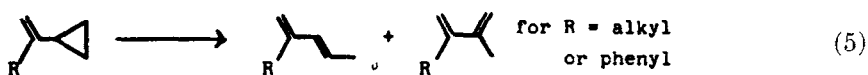
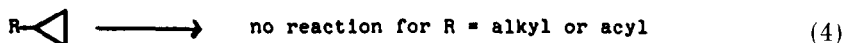
Vinyl and phenyl cyclopropane derivatives are shown to be generally reactive in the presence of di- μ -chlorotetracarbonyldirrhodium (I) in chloroform solution to yield mainly *trans*-1,3-pentadiene compounds. The most unusual feature of the reaction is that the vinylcyclopropanes possess an uncatalyzed "thermally allowed" concerted reaction path (to yield cyclopentene derivatives), but the rhodium catalyst alters the route and yields a new group of products by a step-wise mechanism. The reaction is subject to steric and conformational effects which influence the rate of the reaction. The most reasonable mechanism is one involving a rhodium coordinated cyclopropyl carbinyl cation.

INTRODUCTION

The photochemical ring closure of conjugated and nonconjugated dienes to yield dicyclopropyl derivatives has been well described (1). The reverse process (ring opening) has been shown to be feasible through thermal (2) and homogeneous metal catalytic processes, the latter involving principally Ag (I) (3-6) and especially Rh(I) complexes (7-10). Bicyclobutanes have similarly been ring opened by silver and rhodium catalysts (3-6, 11-16).

Relatively few reports of the isomerization of unsubstituted and "strain-free" cyclopropanes have appeared. Those reports available have dealt with this reaction with respect to the formation of allyl complexes (with palladium) (17-19) and with the formation of saturated propanes (17-22).

We have confirmed the inertness of alkyl- and acyl-substituted cyclopropanes toward isomerization with di- μ -chlorotetracarbonyldirrhodium (I), but wish to report the general reactivity of vinyl and phenyl (conjugated) derivatives of cyclopropane.



The reaction is of some current interest because of its analogy to various cyclopropyl carbinyl and strained ring isomerizations.

EXPERIMENTAL

Compounds

Vinyl cyclopropane (V), phenyl cyclopropane (VI), dicyclopropyl methane

(XII), methyl cyclopropyl ketone (XIV), and dicyclopropyl ketone (XV) were obtained from the Aldrich Chemical Co. The rhodium dicarbonyl chloride dimer was obtained from the Research Organic/Inorganic Chemical Corp. Quadricyclane (I) was prepared as previously described (23). *Exo*-tri-cyclo[3.2.1.0^{2,4}]oct-6-ene (II), 2-norcarene (III), *exo*-tri-cyclo[3.2.1.0^{2,4}]octane (IX), *exo,exo*-tetracyclo[3.3.1.0^{2,4}0^{6,8}]nonane (X), and tricyclo[5.1.0.0^{2,4}]octane (XI) were prepared from the appropriate alkene or diene by the procedure of LeGoff (24). These hydrocarbons were purified by preparative gas-liquid chromatography after synthesis. The purity achieved was greater than 99% for all compounds either purchased or purified in this manner. 1-Cyclopropyl-1-phenylethene (IV), 1,1-dicyclopropylethene (VII), 2-cyclopropylpropene (VIII), and 1,1-dicyclopropyl-2-phenylethene (XIII) were prepared from the appropriate ketone and alkyl halide by the method of Wittig (25). These compounds were similarly isolated by preparative gas-liquid chromatography to a purity in excess of 99%. 3-Phenyl-2-methyl-1,3-butadiene was prepared from methyl methacrylate by conversion to the acid chloride (26), which in turn was used to acylate benzene (27), and the ketone produced was converted to the diene by the Wittig reaction (25). A serious side reaction which occurred during the last step was an efficient Diels-Alder cycloaddition reaction, so that the overall yield of 3-phenyl-2-methyl-1,3-butadiene was only about 10%. 2-Phenyl-1,3-pentadiene was prepared via acylating benzene with 2-butenoyl chloride, followed by the Wittig reaction; the desired product was obtained in 35% yield. 2-Phenyl-1,4-pentadiene was prepared from vinyl acetic acid (28) via the acid chloride (26), acylation of benzene (27), and Wittig reaction (25) in 13% overall yield.

Reactions

All solutions were prepared using freshly degassed spectrograde quality chloroform (Matheson, Coleman, and Bell). Solutions were prepared and stored (if necessary) in a nitrogen filled dry-bag; the transfer of

solutions was also conducted in the dry-bag. A stock solution of $9.33 \times 10^{-3} M$ $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was made up and used throughout, with no apparent change in the appearance or activity. Reactions were conducted in either a 15 ml nitrogen or hydrogen filled round-bottomed flask or a sealed, nitrogen filled NMR sample tube. The reaction vessel was immersed in a well-stirred oil bath regulated at the desired temperature. The reaction vessels were filled with the desired amount of compound and chloroform solvent, degassed on a vacuum line, refilled with nitrogen or hydrogen gas, and then the catalyst solution was introduced. The vessel was then immediately immersed in the oil bath.

Analyses

All synthesized compounds had structures verified by recording and comparing the infrared and nuclear magnetic resonance (NMR) spectra. Infrared spectra were obtained employing a Perkin-Elmer Model 337 and/or Model 710 recording spectrophotometers with sodium chloride liquid-film plates. Nuclear magnetic resonance spectra were also always obtained to both verify structure and monitor reaction mixtures. NMR spectra were recorded employing a Varian A-60D spectrometer operated at a probe temperature of 38°C. Gas-liquid chromatography (GLC) analyses were performed with Varian Aerograph Model 90-75 or Wilkens Aerograph A-90P single column, thermal conductivity detector instruments. GLC was used to monitor the progress of syntheses and kinetic reaction runs, to determine the purity of starting materials and synthesized compounds, and to purify reagents. Chromatography columns employed were constructed of one-quarter inch copper tubing; the columns were packed with 8% Carbowax 20M on Chromosorb P (10-foot), 20% QF-1 on Chromosorb W (10-foot), and 3% SE-30 on firebrick (6-foot). The on-column injection technique was used with these columns. All columns were preconditioned and maintained at the desired temperature for at least 6 hr. The isomeric phenyl pentadienes could not be prepara-

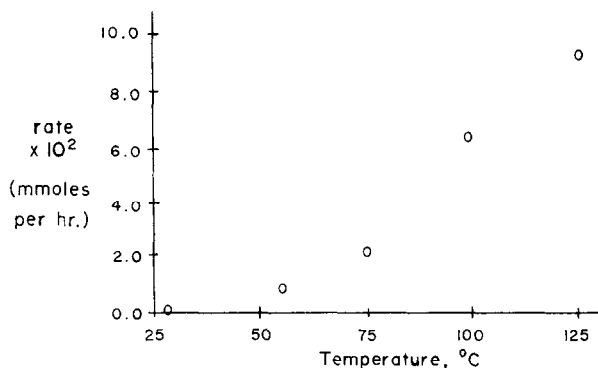


Fig. 1. Temperature dependence of the rate of isomerization of IV.

tively separated by these columns, nor could they be isolated by a 10% silver nitrate-benzyl cyanide-on-firebrick column. Product mixture composition for the reaction of IV was determined by mixing authentic samples of the isomers until the NMR spectrum of the product mixture was duplicated.

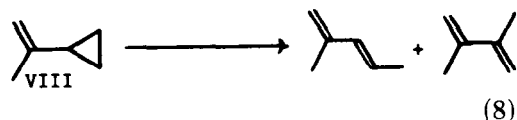
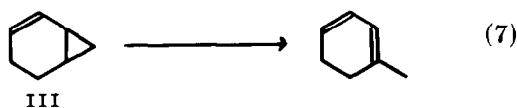
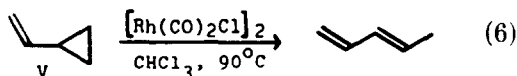
RESULTS

The rhodium complex-catalyzed reaction with vinylcyclopropanes was found to produce a variety of conjugated dienes (Table 2). These results are unlike those found with the often selective thermal reaction pathway, which leads to cyclopentene derivatives (1, 29), or the similar isomerization of norcarene which yields cycloheptadienes and related "fluxional" isomerization products (29, 34). The low selectivity also contrasts with the simplicity of the heterogeneous palladium-catalyzed hydrogenolysis of similar cyclopropane derivatives (31-33). Significantly, no "thermal" reaction products could be detected and the compounds studied did not undergo any detectable isomerization under the reaction conditions in the absence of the rhodium catalyst. The catalyzed reaction is, however, strongly temperature dependent. Except for compounds I and II, no detectable reaction was observed at room temperature for the vinyl-

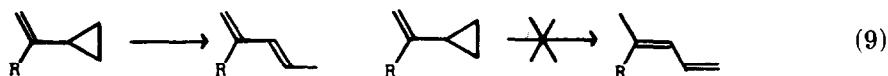
cyclopropanes after periods of several days, but at temperatures of 50°-90°C, the reaction proceeded at a moderate rate. The temperature dependence of the rate for compound IV is shown in Fig. 1.

Conjugation

In spite of the poor selectivity, definite trends in the mode of ring opening can be observed in the compounds produced (Table 2). Ring opening adjacent to vinyl or phenyl (1,2-opening) was largely preferred. Conjugated products predominated, with the new double bond usually of the *trans* configuration.



Significantly, the variety of products did not, however, include any which could be identified as arising from isomerization of the original double bond, even though other isomeric dienes were structurally possible.



Although the vinyl group did not itself isomerize, the presence of a conjugated carbon-carbon unsaturation site adjacent to the cyclopropyl ring is obviously a requirement of the reaction, since other alkyl and carbonyl substituted compounds did not react observably under the same conditions which readily produced reaction in the vinylcyclopropanes (Table 1). Also, except for norcarene, the reaction showed a preference for terminal adjacent vinyl groups, that is, 1-substituted vinylcyclopropanes. Compound XIII, a conjugated but 2-phenyl substituted vinylcyclopropane did not react even after several days.

Steric Effects

An apparent steric effect can be observed from examining the series of compounds V to VIII in Table 1: the rate dropped slightly with an increase in size of the substituent which is bound to the same carbon atom as the cyclopropyl group. A steric effect may also be responsible for the preference of the reaction for terminal vinyl

group double bonds and the lack of reactivity of compound XIII. These apparent steric effects may be caused by difficulty of coordination of the rhodium complex with the double bond terminus due to the bulkiness of nearby substituents. It is noteworthy in this context that norcarene, a *cis* disubstituted double bond compound, is significantly faster in rate of reaction than any of the other vinylcyclopropanes.

Hydrogen Migration

The isomerization reaction is necessarily accompanied by a hydrogen migration. In an attempt to ascertain whether this feature of the reaction was intermolecular, the reaction was performed with compound VIII in the presence of deuterium gas (instead of nitrogen) and deuteriochloroform solvent (instead of chloroform), but no change or reduction in the size of the NMR multiplets due to the products or reactants could be detected. Also, no change in the product distribution could be observed and

TABLE 1
RATES OF ISOMERIZATION OF CYCLOPROPYL COMPOUNDS

Compound		Compound ^a / catalyst	Temp (°C)	Relative rate ^b
No.	Name			
I	Quadricyclane	52.1	38	2.10×10^3
II	<i>exo</i> -Tricyclo [3.2.1.0 ^{2,4}]oct-6-ene	58.2	38	4.65×10^2
III	2-Norcarene	61.8	75	2.43×10^2
IV	1-Phenyl-1-cyclopropylethene	71.5	90	3.90
V	Vinylcyclopropane	262	88	(1.00) ^c
VI	Phenylcyclopropane	91.5	90	0.48
VII	1,1-Dicyclopropylethene	73.5	90	0.21
VIII	2-Cyclopropylpropene	78.1	90	0.067
IX	<i>exo</i> -Tricyclo [3.2.1.0 ^{2,4}]octane	51.5	75	0 ^d
X	<i>exo,exo</i> -Tetracyclo [3.3.1.0 ^{2,4} .0 ^{6,8}]nonane	48.6	90	0
XI	Tricyclo [5.1.0.0 ^{2,4}]octane	63.4	90	0
XII	Dicyclopropylmethane	25	90	0
XIII	1,1-Dicyclopropyl-2-phenylethene	67.1	90	0
XIV	Methyl cyclopropyl ketone	25	90	0
XV	Dicyclopropyl ketone	25	90	0

^a Molar ratio in chloroform solvent; catalyst concentration was 4.66×10^{-3} M.

^b Relative to vinylcyclopropane (V); the rate of disappearance of the starting materials measured by NMR multiplet integration or gas chromatogram peak integration; values are ± 0.05 .

^c First-order rate constant was found to be 1.00×10^{-1} hr⁻¹ at 88°C.

^d Reactions with relative rate values of 0 indicate no decrease in the concentration of the starting materials after 24-100 hr.

TABLE 2
 ISOMERIZATION PRODUCTS

Compound		
No.	Name	Products (% yield) ^a
I	Quadricyclane	Bicycloheptadiene (100) ^b
II	<i>exo</i> -Tricyclo[3.2.1.0 ^{2,4}]octane	Tetracyclo[3.2.1.0 ^{1,7} .0 ^{4,6}]octane (100) ^b
III	2-Norcarene	1-Methylcyclohexadiene-1,3 (major) ^c
IV	1-Cyclopropyl-1-phenylethene	2-Phenyl-3-methylbutadiene (67) ^d 2-Phenyl-1,3-pentadiene (<i>trans</i>) (23) ^d 2-Phenyl-1,4-pentadiene (3) ^d
V	Vinylcyclopropane	<i>trans</i> -1,3-Pentadiene (major) ^c
VI	Phenylcyclopropane	<i>cis</i> -1-Phenylpropene (70) 2-Phenylpropene (30)
VII	1,1-Dicyclopropylethene	Five products
VIII	2-Cyclopropylpropene	2-Methyl-1,3-pentadiene (<i>trans</i>) (90) 2,3-Dimethylbutadiene (10)

^a Measured by gas chromatogram peak area determination, unless otherwise specified. Values are $\pm 0.5\%$.

^b See references (7-9).

^c Identified from the NMR spectrum of the reaction mixture.

^d Mixture not separated; the composition was determined by reproducing the mixture with authentic samples. Values are $\pm 1\%$.

no reduced products (alkanes or alkenes) could be found.

DISCUSSION

Conformational Effects

The isomerization reaction must depend at some stage on an apparently important conformational effect, closely related to the steric effects mentioned above. Vinylcyclopropane (V) should be the least sterically hindered compound of those studied, since it is the parent homolog of the other compounds. Yet norcarene (III) is significantly faster in rate of reaction, even though this compound is a symmetrically disubstituted one. Since the principal difference between III and V is one of freedom of rotation about the vinyl-cyclopropyl bond, one of the crucial steps in the isomerization reaction must be due to conformational effects. In this context, the mode of ring opening of norcarene is also worthy of scrutiny, since the compound provides three distinct opportunities for ring opening, each of which would yield distinguishable isomers. The fact is that norcarene ring-opened to yield mainly 1-methyl-1,3-cyclohexadiene, but

little or no cycloheptadiene or 2-methyl-1,3-cyclohexadiene. This preferred mode of ring opening, taken together with the rate enhancement, suggests an orientation of vinyl and cyclopropyl bond orbitals which would be suitable for concurrent coordination with the rhodium complex (3-6, 11-16, 34, 35) and/or proper alignment of cyclopropyl and *p*-orbitals for subsequent double bond formation. This orientational preference is similar to that observed for solvolytic and free radical ring opening of cyclopropylcarbinyl derivatives (3-6, 36-39) (Fig. 2).

Mechanism

Several distinct processes must occur in order for this reaction to proceed: coordi-

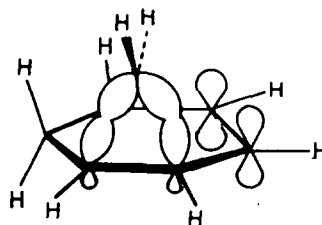
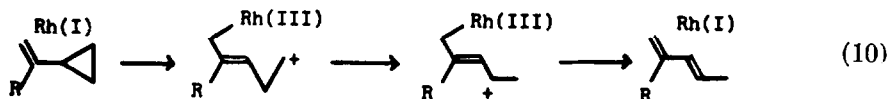


FIG. 2. Preferred conformation for isomerization.

nation of the catalyst with the vinylcyclopropane, ring opening, and a hydrogen transfer (1,3-migration). Other steps are possible, but these must occur, either as separate steps or in concerted combinations. Compounds I and II may be distinguished from all of the vinylcyclopropanes studied in that these need not employ a hydrogen-transfer process in order for isomerization to occur. Significantly, these compounds reacted much faster (even at a lower temperature) than the others except for III.

The critical hydrogen-transfer step must be intramolecular since the use of deuterium gas or deuteriochloroform solvent failed to incorporate any deuterium into the isomerization products.

Compound I has been reported to react in a concerted manner, employing rhodium *d* orbitals to alter the thermally "forbidden" pathway (7-9, 34-35). It does not appear that the vinylcyclopropanes react in this manner, since the reaction was found to be first order (for IV), several processes must occur, and the reaction was not highly regiospecific (as most concerted reactions are). A step-wise mechanism, which maintains the integrity of the vinyl double bond and accounts for the observed steric and conformational effects would seem to be in order (7-10, 40-41).



This suggested reaction sequence, employing σ -bonded carbon-rhodium intermediates, is similar to that proposed for the bicyclo-butane isomerization reaction (11-16), but differs from it in that a hydrogen-transfer step is necessary.

ACKNOWLEDGMENT

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