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Isomerization of Phenylcyclopropanes by a Homogeneous Rhodium Catalyst

PAK-WING (STEVE) CHUM[1] AND JEROME A. ROTH[2]

Northern Michigan University, Marquette, Michigan 49855

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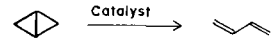
The homogeneous isomerization of the isomeric phenylmethylcyclopropanes in chloroform by di-μ-chlorotetracarbonyldirhodium (I) is discussed. The reaction yields conjugated phenyl alkenes; the rate of reaction and isomer distribution appear to be mainly influenced by conformational, conjugative, and steric interactions of the substituted cyclopropanes. Further evidence for the previously proposed rhodium–carbocation mechanism is discussed and the relationship of this pathway to analogous heterogeneous reactions is briefly examined.

INTRODUCTION

The previously reported isomerization of vinylcyclopropanes with di-μ-chlorotetracarbonyldirhodium (I), $[Rh(CO)_2Cl]_2$, was found to depend strongly on conjugative and steric effects (*1*). These results were interpreted as a rhodium-coordinated carbocation which is able to undergo a classical 1,2-hydride shift, and ultimately may yield mainly linear conjugated dienes. The reaction appears to be similar to certain rhodium, palladium, and silver ion catalyzed isomerizations of bicyclobutyl compounds (*2–5*).



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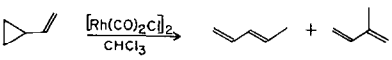


(2)

Two conjugative features were observed with the vinylcyclopropanes: mainly conjugated products predominated and ring-opening was greatly facilitated by conjugation of vinyl groups with the cyclopropyl ring. The phenomenon of "conjugation" of C–C pi-bonds with the cyclopropyl ring has been well-documented, but the theoretical understanding of this point is less clear than with, e.g., dienes (*7*). Recent molecular orbital calculations indicate that cyclopropane (*6–8*) and alkylidenecyclopropane (*9*) possess either pi-type or high energy sigma-type MO's which not only account for the well-known alkenyl behavior of cyclopropane but also for its ability to conjugate with adjacent unsaturated (pi-type) groups (*7,9*). Conjugated groups take the "bisected" conformational position with respect to the cyclopropyl ring, such that the *p*-orbitals of the adjacent pi-bonds are coplanar with the three-membered ring (*7,10,11*). The "bisected" conformation of vinylcyclopropanes was found to be the *most* reactive for isomerization by homogeneous $[Rh(CO)_2Cl]_2$.

We report further compelling evidence in support of the rhodium-coordinated carbocation mechanism. A study was made of the isomerization of methyl- and phenyl-substituted cyclopropanes. Several features were observed in common with the vinylcyclopropane case: a remarkable conformational and steric influence on the rate, a requirement for unsaturated hydrocarbon conjugation, and the production of a variety of conjugated products with the

[1] Present address: Chemistry Department, Oregon State University, Corvallis, OR.

[2] To whom correspondence should be addressed.

most stable ones forming the major fractions.

EXPERIMENTAL METHODS

Compounds. Phenylcyclopropane (I) was purchased from Aldrich Chemical Co., Inc.; it was found to be greater than 98% pure and was used as received. 1-Methyl-1-phenylcyclopropane (II), *trans*-2-methyl-1-phenylcyclopropane (III), and *cis*-2-methyl-1-phenylcyclopropane (IV) were prepared via the LeGoff modification of the Simmons–Smith reaction (12,13) from the corresponding alkenes, with yields in excess of 75%. Cyclopropylphenylmethane (benzylcyclopropane, V) was purchased from Aldrich Chemical Co., Inc.; it was found to be greater than 98% pure and was used without further purification. All synthesized compounds were purified by preparative gas–liquid chromatography (glc); the purity obtained for all was in excess of 98%.

Analyses. All nuclear magnetic resonance (NMR) spectra were recorded with a Varian A60-D spectrometer as the neat liquids or in solution with chloroform-d_1 (Diaprep, Inc., Atlanta, GA) or carbon tetrachloride (Matheson, Coleman, and Bell, spectroscopic grade). Chemical shifts were recorded in ppm (δ) from tetramethylsilane ($\delta = 0.00$).

Both synthetic and isomerization reaction mixtures were analyzed and/or purified by glc, employing a Varian-Aerograph 90-P with thermal conductivity detectors, in conjunction with a Sargent SRG recorder. A 6 ft, 0.25 in. o.d. column packed with 10% SE-30 on 60/80 Chromosorb P was used throughout.

Reactions. The isomerization reactions were performed in degassed deuterochloroform (Diaprep. Inc., Atlanta, GA; minimum isotopic purity: 99.8%) as solvent as described previously (*1*). All solutions were prepared and handled in a nitrogen-filled dry-box (Hamilton Manufacturing Co.). A stock solution of rhodium dicarbonyl chloride dimer, $[Rh(CO)_2Cl]_2$ (Strem Chemical Co., Inc.), was prepared by adding 20.0 ml of chloroform-d_1 to 10.0 mg of rhodium dimer, resulting in a solution of 1.29×10^{-3} molar concentration. An NMR sample tube was then charged with 0.50 ml of the compound to be isomerized and 1.00 ml of catalyst stock solution was added resulting in a 8.60×10^{-4} *M* catalyst solution. (All liquids and solutions were degassed before use and flushed with nitrogen throughout the preparation of the solutions.) The sample tube was then emersed in a dry ice isopropyl alcohol slurry. A positive pressure of nitrogen was then applied to the dry-box, an NMR tube cap was placed on the sample tube, the dry ice slurry (with sample still emersed) was removed from the dry-box, and the tube was immediately sealed with a torch (tube cap still in place). The NMR spectrum of this solution was then obtained. It had previously been determined that the isomerization reaction was quite slow at room temperature (*1*), so that the initial NMR spectrum was assumed to represent the isomerization mixture upon mixing, or $t = 0.00$ for the kinetic run.

To initiate the reaction, the NMR sample tube was emersed in an oil bath maintained at 90 ± 1°C. The tube was periodically removed and the NMR spectrum of the mixture was recorded. Rates were calculated directly from the decrease in the integral of the characteristic cyclopropyl protons' resonance signal (0.00–1.00δ) compared to the constant integral of the phenyl protons' signal. At the conclusion of the kinetic run, the sample tube was opened and the products were first analyzed and then preparatively separated by glc. The structures of the purified isomerization products were then determined by interpretation of the corresponding NMR spectra and, when readily feasible, by comparison of glc retention times with authentic standards.

RESULTS

The isomerization reaction was examined in two respects: reaction rate and product identity. A variety of products were formed at rates which markedly depended on the structural features of the reactants.

Rates. The mole ratios of compounds to catalyst were adjusted to about 3000:1 to ensure that the reaction being observed was truly catalytic in nature. Under these conditions, the reaction is pseudo-zero order in the cyclopropyl compounds, although first order under more nearly equal molar conditions (*1*); the reaction had previously been shown to be first order with respect to the catalyst. The rate of reaction for phenylcyclopropane (I) is illustrated in Fig. 1; the nonlinear portion of the plot near the end of the reaction indicates a rate dependency on the concentration of I. The rates for the isomerizations of I–V are given in Table 1; the values are those determined from the first half of the reaction.

A pronounced structural influence on the rate of reaction is evident from examination of Table 1. Of the three structural methylphenylcyclopropane isomers, the order of reactivity was found to be *trans* > *cis* >> *gem*; the rate of isomerization of phenylcyclopropane (I) fell within this series rather than at either end, such that III > I > IV >> II; benzylcyclopropane (V), like the *gem* compound (II), did not react detectably after several

TABLE 1
RATES OF ISOMERIZATION OF PHENYLCYCLOPROPANES[a]

Compound	Relative rate[b]
trans-2-Methyl-1-phenylcyclopropane (III)	13.5
Phenylcyclopropane (I)	(1.00)[b]
cis-2-Methyl-1-phenylcyclopropane (IV)	0.38
1-Methyl-1-phenylcyclopropane (II)	0.00
Cyclopropylphenylmethane (V)	0.00

[a] Initial rates, measured as the rate of disappearance of the cyclopropyl proton NMR signal vs total phenyl proton signal; reactions performed in deuterochloroform at 90 ± 1°C with compound: catalyst ratio of about 3000:1 and catalyst concentration at $8.6 \times 10^{-4} M$.

[b] Relative rate values for the zero-order reaction compared to Compound I (relative rate defined as 1.00); the actual rate for I was 7.01×10^{-3} mmoles/day. The values are the averages of at least two kinetic runs for each compound.

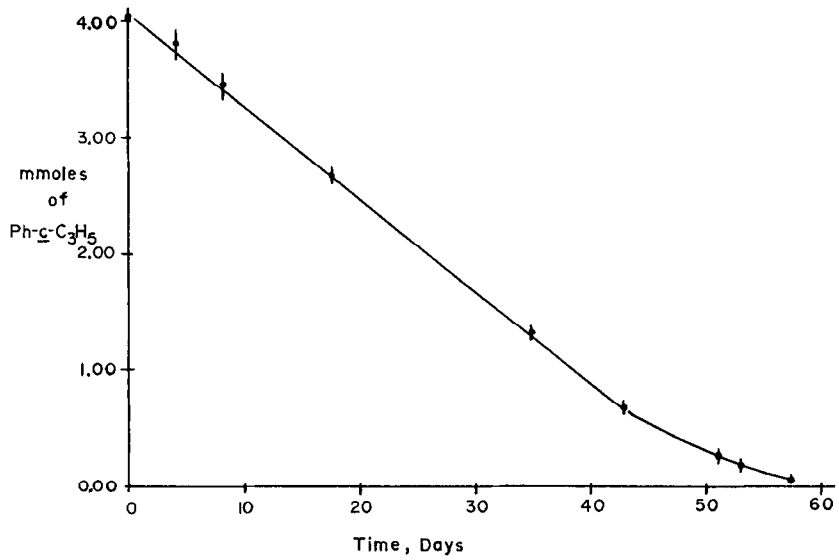


FIG. 1. Rate of reaction of phenylcyclopropane.

weeks under the reaction conditions. This structural influence is very similar to that observed for substituted vinylcyclopropanes (*1*).

Product conjugation. All the reaction products' propenyl side-chains were conjugated with a phenyl group (Table 2). This result, like the rate trend, is directly analogous to that found for vinylcyclopropanes, from which all the main products obtained were conjugated dienes (*1*). While ring-opening was found to be always adjacent to phenyl, it was also mainly across the ring from methyl substituents.

Most noteworthy was the failure of II and V to react. Also, the products from III and IV, although formed at much different rates, appeared to be identical not only in geometry but in the relative amounts of the two major isomers 1-phenyl-2-methylpropene (70%) and 2-phenyl-2-butene (20%). The products from III were thoroughly analyzed by NMR and glc; since the NMR spectrum of the mixture produced from IV appeared to be identical in all respects, especially in the characteristic vinyl region of the spectrum, glc separation and individual analyses of the purified components were not performed.

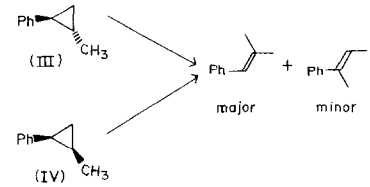
TABLE 2
ISOMERIZATION PRODUCTS

Compound	Products (% yield)[a]
I, Ph-cyclopropyl	Ph-allyl (50.0) + Ph-propenyl[b] (30) + Ph-isobutenyl (20)
III, Ph, CH$_3$	Ph-propenyl (70.0) + Ph-isobutenyl (20) + other (10)
IV, Ph, CH$_3$	Ph-propenyl (major)[c] + Ph-isobutenyl (minor)[c] + other (small)[c]

[a] Determined by glc, unless otherwise stated; values are ±0.1%.

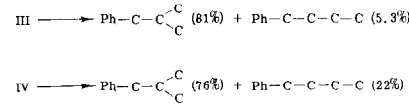
[b] Determined by a combination of NMR integration and glc: *cis*-1-phenylpropene and 2-phenylpropene had identical retention times with several glc columns tested; the values shown correct those reported in Ref. (*1*) as 70% *cis*-1-phenylpropene and 30% 2-phenylpropene; these values are ±2%.

[c] Determined from NMR spectrum alone, but very similar to the amounts for III.



(3)

The mode of ring-opening observed for I, III, and IV is not only similar to that observed for vinylcyclopropanes, but is distinctly reminiscent of that found for the heterogeneous hydrogenolyses of these same phenylcyclopropanes over palladium-on-silica (*3,14,15*):



(4)

Another similarity to the hydrogenolysis reaction is the poor reactivity of V, which could only be converted to 3.5% hydrogenolyzed products under conditions where II, III, and IV were all nearly completely transformed over palladium. That II reacted as smoothly as III and IV in the surface reaction is an obvious dissimilarity to the present study, however.

DISCUSSION

Conformation. In the case of vinylcyclopropanes, the conformation of the vinyl group with respect to the cyclopropyl group was found to have a pronounced effect on the rate of reaction (*1*). This was interpreted to mean that conjugation of the unsaturated double bond with cyclopropyl "pi-character" (*8*) or "strained" sigma (*6*) orbitals is crucial during the slow step of the reaction. A "bisected" conformation, similar to that found for the cyclopropylcarbinyl cation (*10,11,16,20*), was deduced to be the most favorable (Fig. 2).

A very similar conclusion is indicated by the results reported here. No detectable

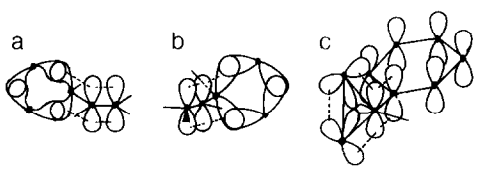


FIG. 2. "Bisected" conformation of conjugated cyclopropanes. (a) "Bent-bond" model of vinylcyclopropane; (b) "sp^5" model of vinylcyclopropane; (c) "Walsh" model of phenylcyclopropane.

reaction was observed for V, which may not conjugate due to the intervention of a CH_2 group between phenyl and cyclopropyl, illustrating again the requirement for activation of the cyclopropyl group by C–C pi-bonds.

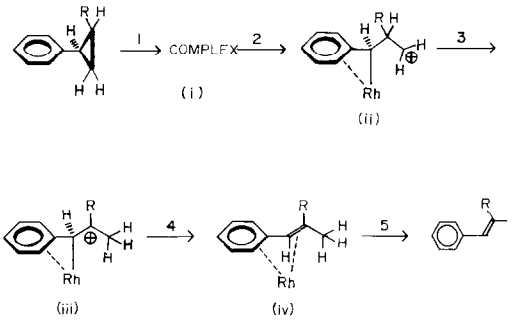
More interesting is the case of II which also did not react in any observable way. This is the most striking example of the requirement of not only the adjacency of C–C unsaturation but also the ability of the unsaturated group to conjugate with the cyclopropyl ring orbitals; this is possible only when favored by an appropriate conformation of phenyl with respect to cyclopropyl. In the case of II, the *gem* methyl group prevents phenyl from readily assuming the bisected conformation, as judged from models (17). Also IV (*cis*) possesses a methyl group which interferes with the bisected conformation, but not as seriously as does the methyl in II. Of the three phenylmethyl isomers, III (*trans*) appears to have the least steric inhibition to assumption of the bisected conformation by phenyl; in fact, other conformations appear to be less favored in this compound than in the unmethylated case (I). The relative reaction rate sequence matches this qualitative assessment of steric inhibition quite well. As in the case of the vinylcyclopropanes, phenylcyclopropanes apparently undergo isomerization most readily when the compounds can easily assume the bisected conformation through rotation about the phenyl-cyclopropyl C–C bond.

This reaction preference for the bisected rotational form is clearly analogous to a variety of previously reported results besides the vinylcyclopropane case (*10,11,16,17*). Those previous reports have ascribed this preference to the conjugation of pi-bond *p*-type orbitals with the bonds of cyclopropane. Whether one employs the models of cyclopropane of Walsh (*18*), Coulson-Moffitt (*19*), Burnett (*7*), Buenker–Peryerimhoff (*6*), or Pasto *et al.* (*9*), a similar conclusion is reached: the most favorable conformation for conjugated cyclopropyl systems is that described above as "bisected" (Fig. 2), such that an adjacent *p*-orbital may overlap best when it is coplanar [or nearly so (*7*)] with the cyclopropyl ring, as in the case of the cyclopropylcarbinyl cation (*8,17,18*).

Product distribution. The products formed from the isomerization of I, III, and IV were all conjugated phenylalkenes, with the *trans* isomer forming the major component in the case of I. Also, ring-opening occurred predominately across the ring from methyl but adjacent to phenyl, probably reflecting the coordination preference for the relatively large rhodium complex. Multiple products were formed in all cases where isomerization occurred and this variety certainly suggests the formation of a freely rotating intermediate, free of the stereospecific constraints imposed by a concerted, orbital-symmetry-regulated isomerization process. Also, the near identity of the results achieved with III and IV strongly indicates a common intermediate for the isomerization of this pair. However, since III and IV react at significantly different rates, it must be assumed that the rate-controlling step must occur along the reaction path leading to the common intermediate. As discussed above, the rate differential appears to be related to conformational preference of the starting materials, perhaps related to the initial coordination step.

Mechanism. The rate information, product distributions, and the precedents derived from the analogous vinylcyclo-

propane study [and other studies cited (*19*)] all suggest a reaction sequence which should contain the following features: (a) a multiple process, involving at least one intermediate [probably a carbocation (*2,5,10,19*)] (b) conjugative assistance to the reaction in steps both prior and subsequent to intermediate formation; (c) regioselectivity due to steric and conjugative effects, probably at the rhodium coordination stage; (d) a hydrogen migration step, either concerted with or subsequent to ring-opening.



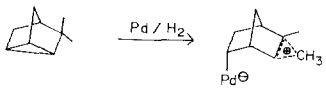
(5)

Intermediates *ii* and *iii* are related by a hydride migration step common to carbocations; steps (2) and (3) could, however, occur simultaneously, as in the protolytic and metal ion catalyzed reactions of unsubstituted cyclopropanes. In both theoretical treatment and experimental solvolytic studies, the hydrogen migration has been interpreted as both concerted (*21*) and stepwise (*4,22*).

The "complex" shown in the mechanism may reflect the requirement for the bisected conformation by aligning the pi-bonds of phenyl with the reactive orbitals of cyclopropyl. The complex could either be an intermediate formed in a preequilibrium prior to ring-opening or the complex could simply be a transition state molecule if ring-opening and metal coordination are concerted processes (*3–5,19*).

There is substantial precedent for photolytic diradical ring-opening of both alkyl and phenyl substituted cyclopropanes (*23,24*). A similar mechanism to the one shown above, employing radical intermediates, represents an alternate mode of ring-opening but seems less likely when the data and precedents taken as a whole, are considered.

Heterogeneous catalysis analogue. As mentioned above, the isomerization reaction, both in its overall descriptive features (mode of ring-opening and isomer distribution) and in the proposed mechanism, bears some striking similarities (and some dissimilarities) to the supported-palladium metal catalyzed hydrogenolysis of cyclopropanes. Both reactions favor adjacent-to-phenyl and across-from-methyl regioselectivity; both are subject to conjugative and steric effects to approximately the same degree; both have been deduced to involve a benzyl carbon coordinated to the catalyst atom(s) in key mechanistic steps [this latter feature has other catalytic precedents (*25*)]. These analogies do not, of course, dictate that the intermediates or mechanisms of the two reactions must be the same, but certainly they appear to be closely related if not essentially the same. It has recently been proposed that a palladium–carbocation intermediate is important for the heterogeneous isomerization–hydrogenolysis of a cyclopropyl derivative (*26*):



(6)

In this case, a methyl group migrates from a neighboring position rather than a hydrogen from the bridgehead, presumably due to Bredt's rule, but other important features are directly analogous: carbocation formation upon coordination of the cyclopropyl ring with either concurrent or subsequent rearrangement to form the more stable cation. In the present instance, the more stable cation yields the stable, conjugated product.

ACKNOWLEDGMENTS

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