for the NO_2 radical which may indicate association with the π bonds of the solvent. The equilibrium constant in benzene deviates from the correlation line in the opposite sense. This deviation may be indicative of a differential complexation effect with the N_2O_4 forming a better π complex than NO_2.

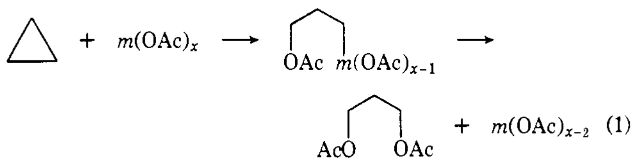
Oxidation by Palladium(II). II.[1] Products of the Oxidation and Isomerization of Phenylcyclopropane by Palladium(II)[2]

Robert J. Ouellette* and Charles Levin[3]

Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210. Received June 6, 1970

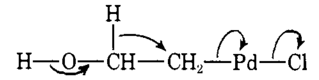
Abstract: The products of the oxidation of phenylcyclopropane by Na_2PdCl_4 in 2:1 glyme–water by volume are propiophenone and phenylacetone; the relative amount of each substance is controlled by the ratio of phenylcyclopropane to Na_2PdCl_4. At low ratios of phenylcyclopropane/Pd(II) a direct oxidation product, propiophenone, is favored whereas at high ratios an isomerization process to *trans*-propenylbenzene occurs which is followed by oxidation to phenylacetone. Oxidation to propiophenone in glyme–D_2O occurs without deuterium incorporation. Oxidation of phenylcyclopropane-*1-d* in glyme–water yields propiophenone-*2-d*, a product consistent only with consecutive hydride and deuteride shifts in a proposed 1,3-oxypalladium intermediate. Exchange of palladium for mercury in an 1,3-oxymercury adduct of phenylcyclopropane rapidly results in the formation of propiophenone.

To date most studies of cyclopropane cleavage by heavy metal salts have involved species Hg(II),[4,5] Tl(III),[6] and Pb(IV)[7] which have filled d subshells. The mechanism of the oxidative cleavages by such metals are regarded as qualitatively similar. For the general reagent $m(\mathrm{OAc})_x$ the cleavage reaction proceeds as given in eq 1. It was of interest, therefore, to investigate the corresponding reaction with transition metals where vacant d orbitals and the attendant variety of coordination numbers and geometries might lead to interesting new reactions. The reactions of Hg(II), Tl(III), and Pb(IV) with olefins have been known for many years;[8] moreover, it was the well-documented similarity in the behavior of cyclopropanes and olefins toward electrophiles which prompted studies of cyclopropane oxidations by these metals originally.[9] It seemed plausible that in looking for a suitable transition metal to again consider the analogous olefin reactions.



Palladium chloride reacts with olefins to give carbonyl products.[10] The oxidation of ethylene to acetaldehyde by platinum group metals was known as early as 1894.[11] Today the reaction is the basis for the commercial production of acetaldehyde, the so-called Wacker process.[12]

The mechanism of palladium(II) oxidation of ethylene has been established on the basis of both product and kinetic studies.[13] A coordination complex in which both ethylene and hydroxide are bound to palladium is formed by a series of equilibrium steps. In the rate-determining step collapse of the coordination complex to a σ-bonded intermediate (**1**) occurs. A fast subsequent step involves reduction of palladium to its metallic state as it serves as a leaving group. The occurrence of a concomitant 1,2 hydride shift is supported by the facts that ethylene in D_2O yields acetaldehyde and ethylene-d_4 in H_2O yields acetaldehyde-d_4.[10]



1

The similarity of the chemistry of cyclopropanes and olefins in their reactions with Hg(II), Tl(III), and Pb-

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* To whom correspondence should be addressed.

(1) R. J. Ouellette and C. Levin [*J. Amer. Chem. Soc.*, **90**, 6889 (1968)] should be considered as the first report in this series.

(2) The authors acknowledge Grant 4765-ACl from the Petroleum Research Fund of the American Chemical Society in support of this research.

(3) Sinclair Oil Fellow 1967–1968.

(4) R. Ya. Levina, V. N. Kostin, P. A. Gembitski, and A. D. Vinogrador, *Vestn. Mosk. Univ. Khim.*, **16**, 67 (1961); R. Ya. Levina and V. N. Kostin, *Zh. Obshch. Khim.*, **28**, 3307 (1958); R. Ya. Levina, D. G. Kim, and T. K. Ustynyuk, *ibid.*, **29**, 1956 (1959); R. Ya. Levina, V. N. Kostin, and M. S. Shanazorov, *ibid.*, **29**, 40 (1959); R. Ya. Levina, V. N. Kostin, and V. A. Tartakovskii, *ibid.*, **23**, 1054 (1953); **26**, 2998 (1956); **27**, 881 (1957); R. Ya. Levina, V. N. Kostin, and T. K. Ustynyuk, *ibid.*, **30**, 359 (1960).

(5) R. J. Ouellette, R. D. Robins, and A. South, Jr., *J. Amer. Chem. Soc.*, **90**, 1619 (1968).

(6) R. J. Ouellette, D. L. Shaw, and A. South, Jr., *ibid.*, **86**, 2744 (1964); R. J. Ouellette, A. South, Jr., and D. L. Shaw, *ibid.*, **87**, 2602 (1965); A. South, Jr., and R. J. Ouellette, *ibid.*, **90**, 7064 (1968).

(7) R. J. Ouellette and D. L. Shaw, *ibid.*, **86**, 1651 (1964); R. J. Ouellette, D. Miller, A. South, Jr., and R. D. Robins, *ibid.*, **91**, 971 (1969).

(8) (a) P. M. Henry, *ibid.*, **88**, 1597 (1966); (b) C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 606 (1963); (c) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968; (d) K. B. Wiberg, "Oxidation in Organic Chemistry," Academic Press, New York, N. Y., 1965.

(9) M. Yu. Lukina, *Russ. Chem. Rev.* **31**, 419 (1962).

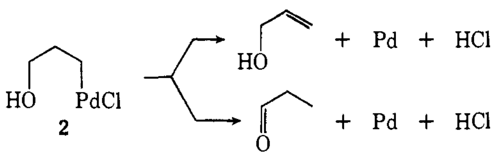
(10) (a) A. Aguiló, *Advan. Organomet. Chem.*, **5**, 321 (1967); (b) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., Chapter 4.

(11) J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Ruttinger, and H. Kojer, *Angew. Chem.*, **71**, 182 (1959).

(12) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, and A. Sabel, *Angew. Chem., Int. Ed. Engl.*, **1**, 80 (1962).

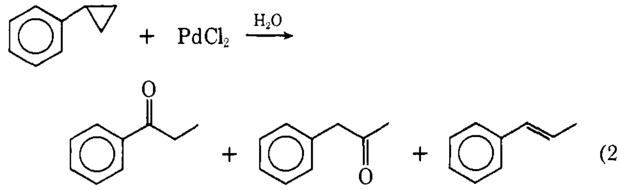
(13) (a) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964); (b) *ibid.*, **88**, 1595 (1966).

(IV) makes it seem likely that a 1,3-oxypalladium intermediate (**2**) would be formed in reaction of Pd(II) with cyclopropanes. The chemistry of such an intermediate could involve formation of allylic alcohols if an elimination occurs. Alternatively a carbonyl could result from a single 1,3-hydride shift or two 1,2-hydride shifts both of which are without precedent. As reported in an earlier communication carbonyl products are formed in the cleavage of phenylcyclopropane.



Results

Products and Mass Law Effects. Phenylcyclopropane (2 equiv) and Na_2PdCl_4 (1 equiv) react in 2:1 glyme–water at 75° for 2 hr to give propiophenone (**3**), phenylacetone (**4**), and *trans*-propenylbenzene (**5**) as indicated by eq 2. The crude products after conventional work-up were identified by the nmr spectrum of the reaction mixture since the aliphatic protons of each compound appear in a unique area of the spectrum. A three-proton triplet at τ 8.8 and a two-proton quartet at 7.2 identify the propiophenone. A three-proton singlet at 8.1 and two-proton singlet at 6.5 are consistent with phenylacetone, while a three-proton doublet at 8.2 together with a complex multiplet centered at 3.9 correspond to the *trans*-propenylbenzene. An nmr spectrum of commercial samples of the reaction products in the same ratio as observed above is identical in every way with that of the original reaction mixture. In addition the retention times of the substances on vpc were identical with authentic samples. No other products were observed. Both ketones were collected from the vpc column and their nmr redetermined and compared with authentic samples.



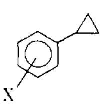
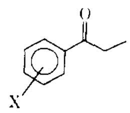
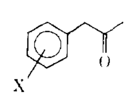
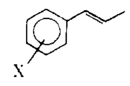
(2)

3, 65% **4**, 30% **5**, 5%

Although detailed studies were not carried out for other arylcyclopropanes, *p*-methoxy- and *p*-methylphenylcyclopropane react more quickly than the parent hydrocarbon as evidenced by visual observation of the rate of deposition of elemental palladium from the solution. On the other hand, *m*-chlorophenylcyclopropane does not react at all under the same reaction conditions. Only at 100° does this substrate slowly react after 10 hr. Only the nmr spectra of reaction mixtures of the activated cyclopropanes after conventional work-up were determined. The product distributions for the cyclopropane oxidations are summarized in Table I.

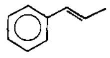
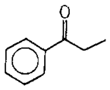
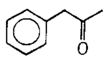
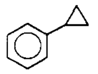
Experiments in which 2 equiv of phenylcyclopropane/equiv of Pd(II) were carried out in order to determine if an altered product distribution would result from a deficiency of the oxidizing agent.[14] These studies as a function of reaction times are summarized in Table II. It should be noted that the reaction is not complete in 2 hr and that the two ketones are ultimately formed in essentially equal quantities.

Table I. Product Distribution of 1:1 Experiments as a Function of Substituent[a]

X				
p-CH_3O		25	25	50
p-CH_3		31	26	43
H	<5	65	30	<5
m-Cl[b]	79	16	5	

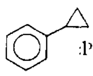
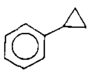
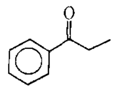
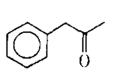
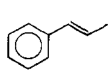
[a] Reaction conditions, 75° for 2 hr. [b] Reaction conditions, 100° for 10 hr.

Table II. Product Distribution of 2:1 Experiments as a Function of Time (Per Cent)

	45 min	2 hr	9 hr	2 days
	4.8	14.5	13.2	4.2
	12.7	15.9	18.4	22.9
	11.7	11.6	19.7	22.1
	71.8	58.0	48.7	50.8

The observation that the product distribution is affected by reactant stoichiometry led to additional experiments in which new reactant ratios were employed. When the metal to cyclopropane ratio is 4:1, propiophenone is obtained in quantitative yield within a reaction time of 2 hr. On the other hand, when this ratio is 1:4, the sole product, in about 15% yield, is *trans*-propenylbenzene under the same reaction conditions. These data are summarized in Table III.

Table III. Product Distribution as a Function of Reactant Stoichiometry (Per Cent)[a]

 :$PdCl_2$				
1:1	>5	65	30	>5
2:1	58	12	16	14
4:1	85			15
1:4		100		

[a] Reaction conditions, 2 hr at 75°.

The Oxypalladium Intermediate. Although a mechanism for the oxidation of phenylcyclopropane involving an oxypalladium intermediate has been proposed,[1] no

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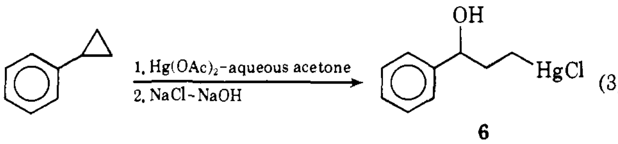
(14) These studies were prompted by the results obtained in attempted competitive relative rate studies as determined by nmr analysis of the products. It was startling to find that the products were not the composites expected on the basis of studies with individual aryl cyclopropanes. The competitive rate studies involved a stoichiometric excess of mixtures of cyclopropanes. Therefore, individual cyclopropanes were examined to determine how the products formed were functions of reactant ratios.

definitive evidence for its existence had been put forth. The first consideration was to actually isolate such a species or synthesize it independently. However, the instability of organopalladium compounds containing β-hydrogens has been well established;[15] such moieties rapidly eliminate H–Pd–Cl and are thus not isolable. However, a number of workers have succeeded in generating organopalladium compounds transiently.[10,15] The method most commonly employed has been to make the corresponding organomercuric chloride and then exchange it with palladium chloride.[10] Therefore, one would expect that the oxymercury analog of the proposed oxypalladium intermediate should give propiophenone quite readily when the former is allowed to react with Pd(II).

The desired oxymercury compound (**6**) was synthesized as outlined in eq 3. The method is an application of that of Traylor, *et al.*,[16] for the preparation of oxymercury compounds from olefins and is discussed in greater detail in the Experimental Section. In contrast to the 3-aryl-3-acetoxypropylmercuric acetates formed in earlier studies,[5] the 3-phenyl-3-hydroxypropylmercuric chloride (**6**) could not be induced to crystallize. No elemental analysis was obtained. However, the nmr of the substance as described in the Experimental Section was consistent with that observed for similar cyclopropane adducts.[5] When the highly viscous, clear organomercuric alcohol is treated with Pd(II) at 75°, propiophenone is formed quantitatively in a matter of a few minutes. This observation is strong evidence for the presence of the oxypalladium intermediate.



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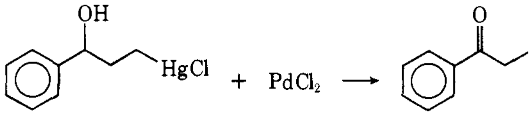
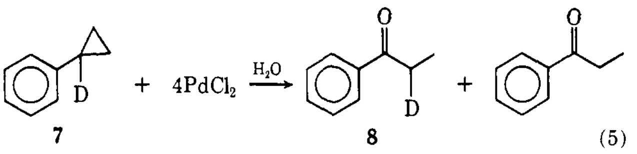
(3)



(4)

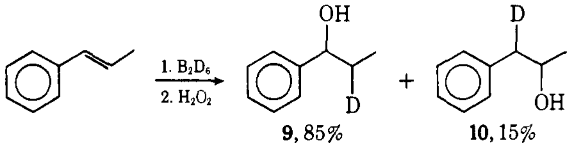
Isotope Labeling. The phenylcyclopropane oxidation was carried out in glyme–D_2O as solvent under conditions favoring propiophenone formation. Incorporation of deuterium at either the 2 or 3 position could be easily detected by nmr. However, both the intensity and multiplicity of the τ 8.8 resonance indicated the absence of deuterium at the 3 position. Furthermore, while the τ 7.2 resonance appeared to differ slightly from the expected absorption for the methylene protons of propiophenone the quantity of propiophenone-*2-d* present results from exchange with the solvent. Therefore the propiophenone is formed retaining all of the protons originally contained in phenylcyclopropane.

Phenylcyclopropane-*1-d* (**7**) was prepared as detailed in the Experimental Section. Reaction of the phenylcyclopropane-*1-d* with 4 equiv of Pd(II) followed by conventional work-up and collection of the product from the vapor phase chromatograph yielded a mixture of 80% propiophenone-*2-d* (**8**) and 20% propiophenone. The analysis is based on the nmr spectrum. The methyl group resonance integrated for three protons relative to the five aromatic proton resonance. However, the characteristic methyl triplet had become a mixture of 20% of the usual triplet and 80% of a 1:1 doublet exhibiting considerable line broadening. The propiophenone observed arises through exchange of propiophenone-*2-d* with the solvent. Prolonged contact of the product with the solvent results in increased percentages of propiophenone.



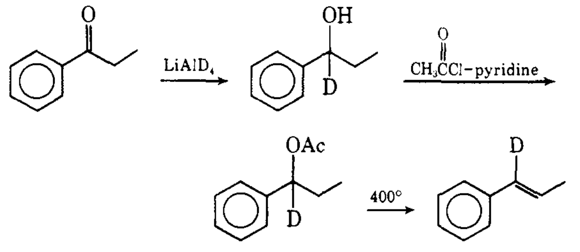
(5)

Propiophenone-*2-d* was synthesized independently by a hydroboration procedure. Brown[17] has reported a similar product distribution with B_2H_6. Palladium(II) oxidation of 1-phenylpropanol-*2-d* (**9**) gives a mixture of 80% propiophenone-*2-d* and 20% propiophenone. Examination of the nmr resonance of the methyl group on a 50-Hz sweep width unequivocally demonstrated the presence of a one to one doublet split into barely discernible triplets, and the usual methyl triplet. The ratio of the integrated areas was 4:1. Interestingly, the 20% of the propiophenone formed in the oxidation of the alcohol is identical with the amount of the protio ketone formed in the oxidation of phenylcyclopropane-*1-d*. These observations indicate that the propiophenone arises from slow exchange of propiophenone-*2*-d with the solvent. Prolonged contact of the product with the reaction medium increases the percentage of propiophenone.



(6)

The position of deuterium in the phenylacetone and *trans*-propenylbenzene was determined by studies using 4 equiv of phenylcyclopropane-*1-d* and 1 equiv of palladium(II). The olefin observed is *trans*-propenylbenzene-*1-d* (**11**) as established from nmr analysis, and by comparison of the nmr so obtained with that of an authentic sample of the deuterioolefin. The deuterioolefin was synthesized in a straightforward manner given by eq 7.



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(7)

Attention was turned to location of deuterium in phenylacetone. This ketone presents a problem in that its methylene group is particularly labile due to the presence of the α-phenyl substituent in addition to the carbonyl group. Hence, exchange of the methylene protons complicates locating the deuterium in phenylacetone. Since it has been shown that phenylacetone

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(15) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).

(16) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963).

(17) H. C. Brown and W. J. Hammer, *ibid.*, **89**, 1552 (1967).

arises from oxidation of *trans*-propenylbenzene, one would predict the deuterium to be on the same carbon in this ketone as in its olefin precursor, *i.e.*, C-1.

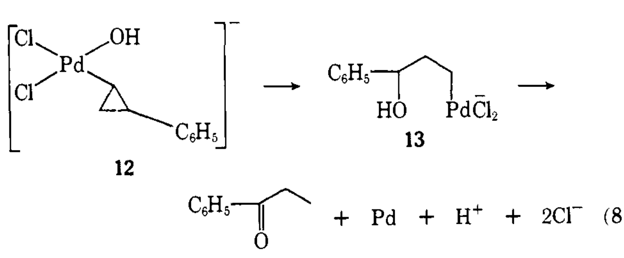
Qualitatively, the nmr spectrum of the phenylacetone derived from phenylcyclopropane-*1-d* strongly suggests that deuterium is present at the methylene position. The τ 6.5 resonance is considerably distorted by broadening and some elements of splitting by deuterium. Furthermore, the ratio of methyl to methylene protons is 3:1.5 instead of 3:2. Thus the product is most reasonably phenylacetone-*1-d* containing phenylacetone which results from exchange with the solvent.

Olefin Reactions. When 1 equiv each of *trans*-propenylbenzene and Pd(II) are allowed to react under the same conditions as for the phenylcyclopropane oxidation phenylacetone is the only product obtained. Both nmr of the reaction product and vpc analysis establish this fact.

Reaction of 1 equiv each of allylbenzene and Pd(II) yields phenylacetone containing approximately 5% *trans*-propenylbenzene. In a manner reminiscent of the observations of phenylcyclopropane oxidative cleavage, reaction of 2 equiv of allylbenzene with Pd(II) yields *trans*-propenylbenzene in quantitative yield. The conversion was monitored by nmr as the isomeric olefins exhibit markedly different olefinic proton resonances. No deuterium incorporation is observed in the isomerization of allylbenzene to *trans*-propenylbenzene in D_2O.

Discussion

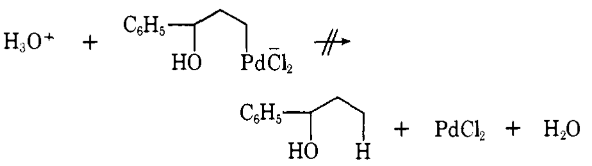
Mechanism of Oxidative Cleavage. The observation that 3-phenyl-3-hydroxypropylmercuric chloride is converted to propiophenone by palladium(II) indicates that a 3-phenyl-3-hydroxypropylpalladium salt is an intermediate in the cleavage of phenylcyclopropane by palladium(II). Therefore, the oxidative cleavage of cyclopropanes probably proceeds in a manner entirely analogous to the oxidation of olefins by palladium(II). Kinetics studies which are necessary to determine the elements present in the transition state will be reported in a subsequent paper. On the basis of the kinetic evidence[18] the palladium contains two chlorine atoms, a hydroxyl group, and a phenylcyclopropane unit. Thus the rate-determining step is most likely conversion of the complex ion (**12**) into a σ-bonded 1,3-oxypalladium adduct (**13**) which undergoes rapid subsequent reactions.



(8)

The decomposition of the organopalladium intermediate involves two specific consecutive 1,2-hydride shifts. The isotope labeling studies clearly eliminate the alternative 1,3-hydride shift which could also result in propiophenone formation. The predicted product of such a shift in phenylcyclopropane-*1-d* is propiophenone-*3-d* and could have easily been detected if formed.

Another *a priori* mechanistic possibility which is ruled out by the deuterium-labeling studies and the experiment in which propiophenone is formed in D_2O without deuterium incorporation is the protolysis of the 1,3-organopalladium adduct followed by oxidation of 1-phenyl-1-propanol which yields propiophenone.



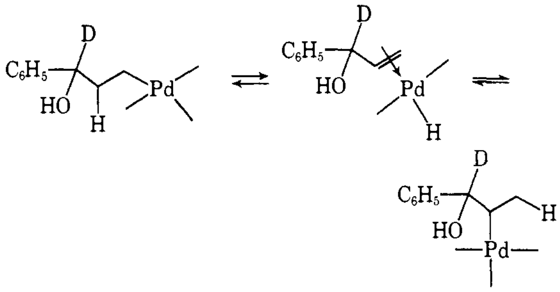
(9)

It should be noted that the 1,3-organopalladium intermediate does not undergo an elimination characteristic of palladium compounds[16] to yield 1-phenylallyl alcohol. The absence of the alcohol in the product mixture as ascertained by vpc analysis and the fact that 1-phenylallyl alcohol did not give rise to propiophenone in control studies indicates the presence of a hydroxyl group in the oxypalladium intermediate strongly control its chemistry.

Oxidation studies with *trans*-propenylbenzene clearly eliminate an isomerization reaction of phenylcyclopropane followed by oxidation as the source of propiophenone. However, the olefin does give the phenylacetone obtained in the reaction.

Although the majority of the work reported involves phenylcyclopropane it is clear from the observations made on the reactivity of arylcyclopropanes that ring substituents strongly control the reaction rate.[19] Electron donating substituents increase the rate of reaction. Therefore palladium(II) is electrophilic and in formal sense reacts with cyclopropanes in the same manner as do Hg(II), Tl(III), and Pb(IV). Of course, in detail there are substantial differences in the character of the carbon–metal bonds.

One possible mechanism accounting for the observed hydride shifts involves a conversion of an σ-bonded palladium intermediate to a π-bonded intermediate followed by conversion to an isomeric σ-bonded intermediate.[20,21] The 1,2-oxypalladium intermediate is similar in structure to the proposed intermediates in olefin oxidations and should yield propiophenone. Of interest is the fact that the intermediate is isomeric with the intermediate expected in the oxidation of *trans*-



(10)

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(18) C. Levin, Ph.D. Thesis, The Ohio State University (1970).

(19) The competitive reactions of oxidation and isomerization exhibit different substituent dependence as reflected by the data given in Table I. Electron-donating substituents increase the yield of products resulting from isomerization.

(20) There is some precedent[21] for isomerization of oxypalladium intermediates by either metal hydride or π-allylic intermediates.

(21) P. M. Henry, *J. Org. Chem.*, **32**, 2575 (1967); R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966); J. F. Harrod and A. J. Chalk, *ibid.*, **88**, 3491 (1966).

propenylbenzene which leads to formation of phenylacetone.

Another possible mechanism which cannot be distinguished from the σ- to π-bonded conversion mechanism on the basis of available experimental data involves a molecular reorganization in which two hydride shifts occur while in the vicinity of the metal.

Mass Law Effects. The reaction of phenylcyclopropane with Pd(II) involves two competing processes: a direct oxidation to propiophenone and an isomerization followed by oxidation to phenylacetone. The partitioning of the reactant into the two reactions is controlled in an interesting manner by the ratio of phenylcyclopropane to Pd(II).

To rationalize the mass law effects it is necessary to make the following hypothesis. A prerequisite for oxidation to occur is that water or hydroxide ion be bound to metal. This does not seem an unreasonable proposition in view of Henry's kinetic results for the Pd(II) oxidation of olefins[13] in which he concluded that the palladium species involved in the rate-determining step of ethylene oxidation contains bound hydroxide ion.

Assuming the necessity of bound water or hydroxide in the oxidation process, the fact that no oxidation is observed when the metal to cyclopropane ratio is 1:4 might be explained by postulating that under such circumstances cyclopropane complexation with palladium excludes water from the metal coordination sphere. As a result no oxidation to propiophenone would take place and the alternate pathway, isomerization to olefin, occurs by default. The fact that olefin, once formed in the reaction, is not rapidly oxidized to the phenylacetone is rationalized in the same way. In fact, olefins are known to complex more strongly with Pd(II) than cyclopropanes[22] and this suggests that the presence of olefin is even more likely to exclude water from the metal coordination sphere.

The experiments summarized in Table III in which the metal to substrate ratio is 2:1 is consistent with the water bound to metal hypothesis. With phenylcyclopropane and Pd(II) in a ratio of 2:1 the chances of completely excluding water from the coordination sphere of the metal are smaller than in the 4:1 experiment, although still quite favorable. Thus, isomerization would still be expected to predominate; however, the olefin, once formed, would be expected to oxidize much more rapidly than the cyclopropane. This is in agreement with the results of Table III where it is seen that the phenylacetone is produced in greater yield than the isomeric ketone.

The exclusive isomerization of allylbenzene to *trans*-propenylbenzene when the olefin to Pd(II) ratio is 2:1 is in keeping with the results of the phenylcyclopropane mass law experiments in which isomerization is favored by increasing the ratio of substrate to metal of 2:1 or greater leads to an effective saturation of metal's coordination sphere with the result that water is excluded and oxidation repressed. Since olefins complex more strongly than cyclopropanes with Pd(II), it does not seem unreasonable that 2 equiv of allylbenzene could exclude water from the metal coordination sphere. In the absence of oxidation allylbenzene is isomerized to *trans*-propenylbenzene and the latter also prevents water from binding to Pd(II).

Experimental Section

Commercial samples[23] of phenylacetone, propiophenone, allylbenzene, *trans*-propenylbenzene, *cis*-propenylbenzene, and 3-phenyl-1-propanol were used in this research.

1-Hydroxy-1-phenyl-3-propylmercuric Chloride. A mixture of 1.18 g (0.010 mol) of phenylcyclopropane, 2.20 g (0.007 mol) of mercuric acetate, 45 ml of acetone, and 45 ml of water was heated at 50° for 9 hr. The initially bright yellow solution turned completely colorless after 5 hr, and after 9 hr the reaction mixture was cooled to room temperature. To the cooled reaction mixture was added 9 ml of 1 *N* sodium hydroxide (0.009 mol) and 80 g (0.020 mol) of solid sodium chloride. The solvent was removed on the rotary evaporator until one-fourth of the original volume remained. A viscous clear material precipitated out of solution and the remaining solvent was removed by decantation. The viscous material was then dried under vacuum for 48 hr after which time it had turned slightly opaque. A sample was dissolved in pyridine and exhibited resonances at approximately τ 8.5 (two-proton 1:1 doublet), 8.15 (two-proton multiplet), and 5.5 (one-proton 1:2:1 triplet).

Benzaldehyde-*1-d* was prepared by a series of reactions involving formation of 2-phenyl-1,3-dithiane, exchange of the 2-proton by a deuteron, and decomposition of the dithiane with mercuric oxide as outlined by other workers.[24] The nmr spectrum of the aldehyde showed no aldehyde proton.

Ethyl cinnamate-*1-d* was prepared from benzaldehyde-*1-d* by the method of Marvel and King[25] as outlined for ethyl cinnamate. The nmr spectrum obtained in carbon tetrachloride exhibited absorption at τ 8.77 (three-proton triplet), 5.90 (two-proton quartet), 3.74 (one-proton triplet—1:1:1, J_{HD} = 2 Hz), and aromatic resonances.

Phenylcyclopropane-*1-d* was prepared from ethyl cinnamate-*1-d* by the method of Jorgenson and Friend[26] as outlined for phenylcyclopropane and as utilized in our earlier work.[5] The nmr spectrum exhibited a considerably simplified four-proton multiplet centered at τ 9.25 as compared to phenylcyclopropane. The τ 8.25 region which contains a one-proton multiplet absorption in phenylcyclopropane was blank.

1-Phenyl-1-propanol-*2-d*. In a dry three-necked 250-ml flask equipped with reflux condenser, thermometer, and pressure equilibrating dropping funnel was placed 5.9 g (0.050 mol) of *trans*-propenylbenzene and 28 ml (0.014 mol) of 0.5 *M* sodium borodeuteride in diglyme. The flask was immersed in a water bath at 20° and 2.3 ml (18.8 mmol) of boron trifluoride etherate was transferred by syringe to the dropping funnel which had been fitted with a septum at its mouth. The boron trifluoride etherate–diglyme mixture was added to the olefin over a 30-min period. After an additional 1 hr at 20° the flask was immersed in an ice bath and cooled to 5°. Water (5 ml) was added to destroy residual hydride and then 5.4 ml of 3 *N* sodium hydroxide followed by 5.3 ml of 30% hydrogen peroxide added over a 15-min period.

The reaction mixture was poured into 50 ml of water, extracted with ether, and the combined ether layers were washed with saturated sodium bicarbonate solution. After drying over anhydrous magnesium sulfate the ethereal solution was filtered and the ether removed on the rotary evaporator. The nmr spectrum of the distilled product, bp 93–95° (9 mm), exhibited resonances at τ 9.25 (three-proton broadened doublet), 8.50 (one-proton multiplet), 6.38 (hydroxyl proton, sharp singlet), and 5.67 (one-proton broadened doublet).

1-Phenyl-1-propanol-*1-d*. To a slurry of 1.0 g (0.026 mol) of lithium aluminum deuteride in 150 ml of ether was added 12.9 g (0.096 mol) of propiophenone in 20 ml of ether. The reaction mixture was stirred for 24 hr at room temperature and then hydrolyzed. The nmr spectrum of the distilled product, bp 79–80° (5 mm), exhibited resonances at τ 9.23 (three-proton triplet), 8.50 (two-proton quartet), and 6.10 (hydroxyl proton-broadened singlet).

1-Acetoxy-1-phenylpropane-*1-d*. To a solution of 7.2 g (0.080 mol) of 1-phenyl-1-propanol-*1-d* and 8.7 ml of pyridine in 120 ml of

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[22] W. J. Irwin and F. J. McQuillin, *Tetrahedron Lett.*, 1937 (1968).

[23] Chemical Samples, Columbus, Ohio.

[24] D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966).

[25] C. S. Marvel and W. B. King in "Organic Syntheses," Coll. Vol. I, H. Gilman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1943, p 252.

[26] M. J. Jorgenson and A. W. Friend, *J. Amer. Chem. Soc.*, **87**, 1815 (1965).

ether was added 6.4 ml (0.080 mol) of acetyl chloride. An ice bath was used to cool the reaction mixture during the addition. The solution was stirred at room temperature for 24 hr; the pyridinium hydrochloride was filtered off and the solution was washed with 5% HCl, water, saturated sodium bicarbonate solution, saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. After filtration of the magnesium sulfate, the solvent was removed by rotary evaporation and the product was distilled, bp 90–93° (5 mm).

***trans*-Propenylbenzene-*1-d*.** A solution of 7.0 g (0.039 mol) of 1-acetoxy-1-phenylpropane-*1-d* in 50 ml of ether was passed through a column of glass beads at 400° at the rate of 5 drops/min. The pyrolysis was conducted under a stream of dry nitrogen and the product dropped into a collection vessel which had been cooled to −70° in a Dry Ice–isopropyl alcohol bath. The crude olefin was dissolved in ether and washed with saturated sodium bicarbonate solution until no more CO_2 evolved. The ethereal solution was then dried over magnesium sulfate, filtered, and the solvent removed by rotary evaporation. The relative areas of 1 to 3 for the vinyl and methyl proton resonance, the absence of allylic coupling in the methyl resonance the simplified splitting of the vinyl resonance and the absence of the low-field portion of the vinyl resonance as compared to *trans*-propenylbenzene all confirm the structure of the *trans*-propenyl-*1-d*.

Product Studies. The molar concentrations of reactants employed in this work were varied in order to achieve desired ratios of reactants and to ensure solubility. In a typical experiment utilizing a 1:1 ratio of reactants, 0.27 g of Na_2PdCl_4, 0.12 g of phenylcyclopropane, and 6 ml of 2:1 glyme–water were placed in a flask fitted with a reflux condenser. The flask was maintained at 75° for 2 hr during which time palladium precipitation was observed. After cooling the flask to room temperature, the contents were removed with 40 ml of water and the organic product was extracted with two 20-ml portions of ether. After drying the solution with magnesium sulfate the ether solvent was removed to the extent necessary to allow for the analysis desired, *i.e.*, either vpc, nmr, or ir.

Controls were designed to determine if the products and reactants were stable to the finely divided palladium which is produced in the reaction. Palladium was obtained from one reaction by filtration and used in examining the stability of each organic substance under the reaction condition. Of importance to this study is the absence of isomerization of phenylcyclopropane to *trans*-propenylbenzene under the reaction conditions.

Thiirene Dioxides. Synthesis, Characterization, and Reactivity[1]

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Abstract: The synthesis of 2,3-diphenylthiirene 1,1-dioxide (**12**) by a modified Ramberg–Bäcklund reaction is described. α,α'-Dibromodibenzyl sulfone (**11**) was obtained by (a) bromination of dibenzyl sulfide followed by oxidation or (b) brominative decarboxylation of α,α'-diphenylsulfodiacetic acid (**13**). Without separation of the mixture of diastereomeric dibromides, treatment with triethylamine in refluxing methylene dichloride gave **12**. The structure of **12** was established by reduction to the corresponding dihydro derivative, *cis*-2,3-diphenylthiirane 1,1-dioxide (**21**), by means of aluminum amalgam in wet ether. Reaction of **12** with phenyldiazomethane gave α-diazobenzyl 1,2-diphenylvinyl sulfone (**19**). Three alkyl-substituted thiirene dioxides were obtained by a general method which involves generation of a sulfene from an α-bromoalkanesulfonyl chloride and triethylamine in the presence of a diazoalkane. Interaction of the sulfene and diazo compound leads to a bromoepisulfone which is dehydrobrominated by means of triethylamine or a stronger base. The method was applied to the synthesis of the monomethyl (**32**), dimethyl (**38**), and 2-methyl-3-phenyl (**39**) derivatives. The most unusual property of the thiirene dioxides is their marked stability relative to their saturated analogs, a fact which is suggestive of special conjugative effects.

Previously the only stable, isolable compounds incorporating a heteroatom in a cyclopropene ring system were derivatives of the 1-azirine[2] and 1-diazirine[3] systems (**1** and **2**, respectively). Furthermore


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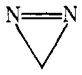
2


3

not a single compound of this type had been synthesized with the heteroatom substituted at position 3 as in **3** (M = O, NH, S, etc.) although several such compounds have been postulated as transient intermediates.[4] In fact special instability has been suggested for those species in this class which bear an unshared electron pair on the heteroatom.[4a,b,e,5]

As part of a general survey of the synthesis of such 3-heteracyclopropenes we have now succeeded in pre-

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(1) (a) Abstracted in part from the Ph.D. Theses of Louis V. McAdams, III, 1966, and John W. Spiewak, 1969, University of Massachusetts; (b) a portion of this work has appeared in preliminary form: L. A. Carpino and L. V. McAdams, III, *J. Amer. Chem. Soc.*, **87**, 5804 (1965); L. A. Carpino and R. H. Rynbrandt, *ibid.*, **88**, 5682 (1966).

(2) For a brief review, see A. Hassner and F. W. Fowler, *ibid.*, **90**, 2869 (1968).

(3) E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, Berlin, 1967.

(4) (a) R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, **86**, 4866 (1964); (b) J. K. Stille and D. D. Whitehurst, *ibid.*, **86**, 4871 (1964); (c) J. Meinwald and D. H. Aue, *ibid.*, **88**, 2849 (1966); (d) R. Huisgen and H. Blaschke, *Chem. Ber.*, **98**, 2985 (1965); (e) D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Commun.*, 147 (1969); (f) J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 5091 (1966); (g) O. P. Strauss, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 4805 (1967); (h) O. M. Nefedow and M. N. Manakow, *Angew. Chem.*, **78**, 1039 (1966).

(5) (a) D. T. Clark, *Theor. Chim. Acta*, **15**, 225 (1969). (b) For a review of the concept of anti-aromaticity as applied to hydrocarbons, see R. Breslow, *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968).