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Reactions of Methylated Cyclopropanes and Olefins with Chloroplatinic Acid. I. Diacylation and Pyrylium Ion Formation

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Summary

In contrast to cyclopropane itself, simple methyl-substituted cyclopropanes do not produce platinum insertion products upon reaction with chloroplatinic acid in acetic anhydride. Instead, the major products are aromatic heterocyclic cations, the pyrylium ions, which are formed as the result of diacylation of the cyclopropane ring and subsequent dehydration and ring closure to the aromatic heterocycle. Similar products are formed from the diacylation of certain olefins in the presence of chloroplatinic acid in anhydride solvents. The combination of solvent and substrate variations has led to a proposed mechanism for these reactions which demonstrates the essential and unique role of platinum. In particular, the specific pyrylium ions produced are formed as a consequence of initial activation of the least-substituted cyclopropane ring bond by insertion of platinum, followed by acylation of platinum-bonded carbon, proton loss to a β,γ-unsaturated carbonyl, a second acylation, and, finally, ring closure.

Introduction

In 1955 Tipper (1) reported that the reaction of cyclopropane with chloroplatinic acid produced a stable product. This complex, of empirical

composition $PtCl_2(C_3H_6)$, was subsequently shown to be tetrameric (2), and to result from the insertion of platinum into the cyclopropane ring (3,4). Because this insertion represents direct activation of the carbon-carbon bond, a reaction with obvious importance, and because of its implications for the mechanisms of metal-catalyzed isomerizations of strained carbocyclic ring systems (5,6) it has generated much additional study. A large number of substituted analogs of Tipper's complex have been prepared (6-9), and similar materials have also been observed with iron (10) and platinum(0) (11-13), and implicated for rhodium (14-16).

Although Tipper's original work (1) involved the reaction between chloroplatinic acid and cyclopropane in acetic anhydride, the most convenient route to substituted analogs of Tipper's complex has been shown to be the metathetical reaction between Zeise's dimer, $[PtCl_2(C_2H_4)]_2$, and the substituted cyclopropane (7). Both the steric and electronic factors which influence this reaction have been probed in these studies. Although the failure of certain cyclopropanes to react is explicable on electronic grounds (9), others which are expected to react readily based on steric and electronic considerations give no insertion product with Zeise's salt. For example, complexes could not be obtained with cis-1-methyl-2-n-butylcyclopropane (9) or 1,1-dimethylcyclopropane (17), and cyclopropane itself gave, in addition to the expected insertion product, the complex derived from isomerization of cyclopropane, e.g., $[PtCl_2(CH_3CH{=}CH_2)]_2$ (17).

In part because of these observations, and also because of both the unusual specificity and stoichiometry of the reaction reported by Tipper, we began an investigation of the reactions of simple alkylated cyclopropanes under the conditions used by Tipper, i.e., reaction with chloroplatinic acid in acid anhydride solvents. Although several methylated cyclopropanes reacted readily under these conditions, it quickly became apparent that the products formed were not the result of simple insertion as had been observed for cyclopropane. In fact, when non-trivial solvent

variations are considered, at least five distinct platinum-containing complexes may be isolated. In acid anhydride solvents, however, the dominant products are found to be aromatic heterocyclic cations, the pyrylium ions, formed by the diacylation of cyclopropanes and subsequent ring closure. Attempts to decipher the course of this transformation led to the study of similar reactions with olefins, and this paper reports the results of our work on the diacylation reactions. The following paper (18) reports on the products formed by monoacylation of cyclopropanes and olefins. A preliminary account of this work has appeared (19).

Experimental Section

Materials. Cyclopropanes and 2-ethyl-1-butene (Chemical Samples Co.), 2-methyl-2-butene (Eastman Kodak Co.), and all gaseous olefins (Matheson Co.) were used as received. Mesityl oxide (Eastman Kodak Co.) was distilled before use. After it was determined that cis- and trans-1-2-dimethylcyclopropane gave identical products, mixtures of the two isomers were purchased from Columbia Organic Chemicals Co. Deuterated solvents for nmr measurements were purchased from Stohler Isotope Chemicals, Inc. Chloroplatinic acid, of nominal composition $H_2PtCl_6 \cdot 6H_2O$, was prepared from metallic platinum. This material was dried by gentle heating so that its actual water content, as determined by titrimetric molecular weight measurements, was approximately two waters of hydration.

Measurements. Proton nmr spectra were recorded on both the Jeol JNM-MH-100 100 MHz and the Jeol C-60HL High Resolution 60 MHz spectrometers. Infrared spectra in the range of 4000-250 cm^{-1} were obtained on the Beckman IR-20A spectrophotometer. Conductivity measurements were made at 25°C on an Industrial Instruments Model RC 1682 conductivity bridge using a cell calibrated with potassium chloride (0.1M).

Microanalyses were performed by Dornis and Kolbe (West Germany).

Reaction of Chloroplatinic Acid with 1,1-Dimethylcyclopropane in Acetic Anhydride. Chloroplatinic acid (0.69g, 1.3 mmole) was dissolved in acetic anhydride (25 ml) 1,1-dimethylcyclopropane (1.40g, 20.0 mmole) was quickly added and the reaction vessel was stoppered to prevent loss of the 1,1-dimethylcyclopropane. This mixture was stirred for approximately three hours in order to insure that the reaction was complete, although the reaction solution began to darken after three to five minutes. The reaction mixture was filtered, producing approximately 70 mg (0.103 mmole) of crude pyrylium ion product. This was recrystallized from methanol to give about 50 mg of orange crystals. Nmr spectra indicated that this product contained a mixture of the isomeric 2,3,4,6-tetramethyl pyrylium ion, (I), and the 2,6-dimethyl-4-ethyl-pyrylium ions, (II). Upon standing at 0°C for one day, a yellow material precipitated (50 mg, 0.132 mmole). This complex was found to be the $PtCl_2$ adduct of 2,3-dimethyl-1-pentene-4-one. (This complex, as well as analogous materials with other β,γ-unsaturated carbonyls, will be discussed in the next paper.) The formation of a mixture of pyrylium ions was common in this reaction. The use of more extensively hydrated chloroplatinic acid appeared to favor formation of II, and pure samples of II were formed occasionally.

Anal. Calcd. for $C_{18}H_{26}O_2PtCl_6$: C, 31.69; H, 3.84; Pt, 28.60; Cl, 31.18. Found: C, 31.70; H, 3.70; Pt, 28.56; Cl, 31.04.

A further complication in the preparation of analytically pure materials frequently arose in this reaction, as well as in the analogous reaction with 1,2-dimethylcyclopropane. Under conditions where the planar 2,3,4,6-tetramethylpyrylium ion (I) was formed, there was a tendency to precipitate the ion with the planar $Pt_2Cl_6^{2-}$ counterion. Although this frequently led to a mixture of counterions, on several occasions what appeared to be pure $(C_9H_{13}O)_2[Pt_2Cl_6]$, III, was formed.

Anal. Calcd. for $C_9H_{13}OPtCl_3$: C, 24.64; H, 2.99; Pt, 44.48; Cl, 24.25. Found: C, 25.69; H, 3.09; Pt, 42.92; Cl, 24.07.

The procedure for other reactions was comparable, and only significant variations will be detailed below.

Reaction of Chloroplatinic Acid with 1,1-Dimethylcyclopropane in Propanoic Anhydride. Chloroplatinic acid (0.70g, 1.36 mmole) was dissolved in propanoic anhydride (25 ml) and allowed to react with 1,1-dimethylcyclopropane (1.15g, 16.4 mmole). Recrystallization gave 65 mg (0.088 mmole) of 2,4,6-triethyl pyrylium hexachloroplatinate, IV.

Anal. Calcd. for $C_{22}H_{34}O_2PtCl_6$: C, 35.79; H, 4.64; Pt, 26.42; Cl, 28.81. Found: C, 36.09; H, 4.78; Pt, 25.64; Cl, 27.83.

Reaction of Chloroplatinic Acid with 1,2-Dimethylcyclopropane in Acetic Anhydride. Chloroplatinic acid (1.08g, 2.08 mmole) was dissolved in acetic anhydride (25 ml) and allowed to react with 1,2-dimethyl cyclopropane (2.75g, 39.2 mmole). Recrystallization gave 75 mg (0.11 mmole) of I.

Anal. Calcd. for $C_{18}H_{26}O_2PtCl_6$: C, 31.69; H, 3.84; Cl, 31.18. Found: C, 31.67; H, 4.03; Cl, 30.91.

Identical products were formed using either cis- or trans-1,2-dimethylcyclopropane or mixtures of both isomers.

Reaction of Chloroplatinic Acid with 1,2-Dimethylcyclopropane in Propanoic Anhydride. Chloroplatinic acid (0.75g, 1.46 mmole) was dissolved in 25 ml of propanoic anhydride and allowed to react with 1,2-dimethylcyclopropane. Recrystallization gave 70 mg (0.095 mmole) of IV.

Anal. Calcd. for $C_{22}H_{34}O_2PtCl_6$: C, 35.79; H, 4.64; Pt, 26.42; Cl, 28.81. Found: C, 34.68; H, 4.34; Pt, 28.10; Cl, 28.09.

Reaction of Chloroplatinic Acid with 1,1,2-Trimethylcyclopropane in Acetic Anhydride. Chloroplatinic acid (0.71g, 1.37 mmole) was dissolved in acetic anhydride (25 ml) and allowed to react with 1,1,2-trimethylcyclopropane (1.08g, 12.8 mmole). Recrystallization gave 75 mg (0.10 mmole) of the 2,6-dimethyl-4-isopropylpyrylium hexachloroplatinate, V.

Anal. Calcd. for $C_{20}H_{34}O_2PtCl_6$: C, 33.82; H, 4.26; Pt, 27.47; Cl, 29.95. Found: C, 33.80; H, 4.37; Pt, 27.40; Cl, 29.90.

Reaction of Chloroplatinic Acid with 1,1,2-Trimethylcyclopropane in Propanoic Anhydride. Chloroplatinic acid (0.65g, 1.28 mmole) was dissolved in propanoic anhydride (25 ml) and allowed to react with 1,1,2-trimethylcyclopropane (1.04g, 12.3 mmole). Following recrystallization, the product (60 mg, 0.08 mmole) was shown by nmr to contain a mixture of the isomeric 2,6-diethyl-3,4,5-trimethylpyrylium ion, VI, and the 2,4,6-triethyl-3-methylpyrylium ion, VII. All attempts to separate these two species by fractional crystallization were unsuccessful.

Anal. for a mixture of VI and VII. Calcd. for $C_{24}H_{38}O_2PtCl_6$: C, 37.61; H, 5.00; Pt, 25.46; Cl, 27.76. Found: C, 35.95; H, 4.71; Pt, 25.60; Cl, 27.52.

Reaction of Chloroplatinic Acid with 2-Methyl-1-butene in Acetic Anhydride. Chloroplatinic acid (0.77g, 1.48 mmole) was dissolved in acetic anhydride (25 ml) and allowed to react with 2-methyl-1-butene (1.00g, 14.3 mmole). Recrystallization gave 0.1g (0.15 mmole) of I.

Anal. Calcd. for $C_{18}H_{26}O_2PtCl_6$: C, 31.69; H, 3.84; Cl, 31.18. Found: C, 31.06; H, 3.40; Cl, 30.63.

Reaction of Chloroplatinic Acid with 2-Methyl-1-butene in Propanoic Anhydride. Chloroplatinic acid (0.76g, 1.47 mmole) was dissolved in propanoic anhydride (25 ml) and allowed to react with 2-methyl-1-butene (0.65g, 9.23 mmole). Recrystallization gave 161 mg (0.227 mmole) of IV.

Anal. Calcd. for $C_{22}H_{34}O_2PtCl_6$: C, 35.79; H, 4.64; Cl, 28.81. Found: C, 33.46; H, 4.54; Cl, 27.52.

Reaction of Chloroplatinic Acid with Isobutylene (2-methyl-1-propene) in Acetic Anhydride. Isobutylene was bubbled through a cooled solution of chloroplatinic acid (0.61g, 1.18 mmole) in acetic anhydride (25 ml). Re-

crystallization gave 143 mg (0.219 mmole) of 2,4,6-trimethylpyrylium hexachloroplatinate, VIII.

Anal. Calcd. for $C_{16}H_{22}O_2PtCl_6$: C, 29.38; H, 3.39; Pt, 29.82; Cl, 32.52. Found: C, 27.98; H, 3.63; Pt, 28.40; Cl, 30.93.

Reaction of Chloroplatinic Acid with Mesityl Oxide (2-methyl-2-pentene-4-one) in Acetic Anhydride. Chloroplatinic acid (1.15g, 2.22 mmole) was dissolved in acetic anhydride (25 ml) and allowed to react with mesityl oxide (10.0 ml, 102.9 mmole). Recrystallization gave 55 mg (0.15 mmole) of VIII.

Anal. Calcd. for $C_{16}H_{22}O_2PtCl_6$: C, 29.38; H, 3.39; Pt, 29.82; Cl, 32.52. Found: C, 29.73; H, 3.71; Pt, 29.03; Cl, 31.58.

Reaction of Chloroplatinic Acid with Isobutylene in Propanoic Anhydride. Isobutylene was bubbled through a cooled solution of chloroplatinic acid (1.20g, 2.32 mmole) in propanoic anhydride (25 ml). Recrystallization gave 85 mg (0.12 mmole) of 2,6-diethyl-4-methylpyrylium hexachloroplatinate, IX.

Anal. Calcd. for $C_{20}H_{30}O_2PtCl_6$: C, 33.82; H, 4.26; Pt, 27.46; Cl, 29.95. Found: C, 33.76; H, 4.41; Pt, 27.61; Cl, 29.74.

Reaction of Chloroplatinic Acid with 2-ethyl-1-butene in Acetic Anhydride. Chloroplatinic acid (1.15g, 3.38 mmole) was dissolved in acetic anhydride (25 ml) and allowed to react with 2-ethyl-1-butene (1.90g, 22.6 mmole). Recrystallization gave 100 mg (0.14 mmole) of 2,3,6-trimethyl-4-ethylpyrylium hexachloroplatinate, X.

Anal. Calcd. for $C_{20}H_{30}O_2PtCl_6$: C, 33.82; H, 4.26; Cl, 29.95. Found: C, 33.72; H, 4.40; Cl, 29.72.

Reaction of 1,1-Dimethylcyclopropane with Perchloric Acid in Acetic Anhydride. 10.0 ml of 70% perchloric acid was added dropwise, with cooling, to a solution of 1,1-dimethylcyclopropane (7.00g, 100 mmole) in acetic anhydride (50 ml). The solution was allowed to warm to room temperature and stirred until a reaction was observed. The reaction mixture finally

darkened completely after seventy-two hours, producing 75 mg (0.317 mmole) of the 2,6-dimethyl-4-ethyl pyrylium perchlorate, XI. This material was identical to a genuine sample of this ion prepared by literature methods (20).

Anal. Calcd. for $C_9H_{13}O_5Cl$: C, 45.68; H, 5.45; Cl, 14.98.
Found: C, 47.16; H, 5.68; Cl, 15.46.

Preparation of the Trichlorocarbonylplatinate (II) Ion.

The tetra(t-butyl)ammonium salt of $(Pt(CO)Cl_3)^-$ was prepared by a reaction similar to that used by Bardarenko et al. (21), whose work involved dimethylformamide rather than acetic anhydride.

0.715g (1.74 mmole) of chloroplatinic acid was refluxed with 20 ml of acetic anhydride for one hour. The mixture was placed in a nitrogen filled glove bag, and aqueous tetra(t-butyl)ammonium bromide was added to hydrolyze excess reagents. The mixture was filtered under nitrogen, and an infrared spectrum of the air stable product thus obtained was identical to that prepared from dimethylformamide. The yield was 0.200g (0.378 mmole) of crude product.

Other Reactions. Based on the observation of an intense infrared absorption at 1630 cm^{-1}, pyrylium ions were formed in a number of other reactions. Because either pure materials were not readily obtained, or because their importance did not warrant extensive investigations, such reactions were not pursued further. Nonetheless, our evidence suggests that pyrylium ions are formed in the following reactions: chloroplatinic acid plus 1,1-dimethylcyclopropane in butanoic anhydride; chloroplatinic acid plus acetylacetone; chloroplatinic acid plus methylenecyclohexane in acetic anhydride; and perchloric acid plus 1,1-dimethylcyclopropane in propanoic anhydride. In addition, pyrylium ions were formed in certain reactions of methylcyclopropane and 1,1-dichlorocyclopropane. However, in order to account for the

products observed in these later reactions, a mechanism requiring fragmentation pathways is required, and our investigations involving these materials will be the subject of a separate communication.

Results

Although the reactions of methylated cyclopropanes and chloroplatinic acid in acid anhydride solvents lead directly to poorly soluble precipitates similar in appearance to that formed in the reaction with cyclopropane itself, the products are clearly different. In particular, the materials formed here differ from Tipper's complex in their spectral properties (ir and nmr), conductivity, analyses, and failure to produce a pyridine di-adduct. Because there was no precedent for the formation of pyrylium ions from cyclopropanes, the most difficult barrier in these investigations was the initial recognition of this general structure. Thus, although a species of empirical composition $PtCl_2C_5H_{10}$ was expected from the reaction with 1,1-dimethylcyclopropane, the major product actually formed had the composition $PtCl_6C_{18}H_{26}O_2$, (I). This result suggests extensive solvent participation and structural reorganization. These materials are found to be 2:1 electrolytes in both acetonitrile and dichloromethane (for II in CH_3CN, Λ_o = 178 Ω^{-1} cm^{-1} at C = 1.0 x 10^{-2} M, Λ_o = 266 Ω^{-1} cm^{-1} at C = 2.0 x 10^{-3} M), and the precipitation of $Pt(NH_3)_4PtCl_6$ from aqueous methanolic solutions of II and $Pt(NH_3)_4Cl_2$ establishes $PtCl_6^{2-}$ as the anion. Thus the cation in II must be an ion of formulation $C_9H_{13}O^+$. This data, as well as the absence of observable ^{195}Pt-^1H coupling in the proton nmr spectra also demonstrate that the only role of platinum, in the product, is that of counterion.

Once these materials are established as pyrylium ions, their structural determination follows readily from infrared and nmr spectra. Table I gives significant spectral data for these materials, as well as literature data for a typical pyrylium ion salt for comparison. Several features in the infrared spectra are characteristic for these materials. Invariably the

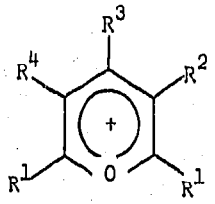

Table I. Spectral Data for Pyrylium Ions[a,b]

Compound	R^1	δR^1	R^2	δR^2	R^3	δR^3	Aromatic Protons	Characteristic Infrared Frequencies (cm^{-1})
(I)	$-CH_3$	2.84 2.87	$-CH_3$	2.40	$-CH_3$	2.63	8.02	3060, 1640, 1532, 878, 315
(II)	$-CH_3$	2.96	--	--	$-CH_2CH_3$	1.32(t) 3.02(q) (J=7.6)	7.99	3060, 1638, 1530, 875, 315
(IV)	$-CH_2CH_3$	1.41(t) 3.20(q) (J=7.5)	--	--	$-CH_2CH_3$	1.36(t) 3.10(q) (J=7.5)	8.00	3065, 1638, 1532, 870,320
(V)	$-CH_3$	2.95	--	--	$-CH(CH_3)_2$	1.43(d) 3.43(m) (J=6.8)	7.93	3050, 1638, 1529, 895,303
(VI)[c]	$-CH_2CH_3$	1.50(t) 3.32(q) (J=7.5)	$-CH_3$	1.67	$-CH_3$	2.58	--	3070, 1638, 1532, 872, 310
(VII)[c]	$-CH_2CH_3$	1.50(t) 3.32(q) (J=7.5)	$-CH_3$	2.08	$-CH_2CH_3$	1.50(t) 3.32(q) (J=7.5)	8.06	

(VIII)	$-CH_3$	2.70	--	--	$-CH_3$	2.90	7.93	3065, 1632, 1535, 855, 310
(IX)	$-CH_2CH_3$	1.40(t) 3.23(q) (J=8.0)	--	--	$-CH_3$	2.78	7.99	3060, 1635, 1532, 863, 311
(X)	$-CH_3$	2.90	$-CH_3$	2.42	$-CH_2CH_3$	1.27(t) 3.01(q) (J=8.0)	7.90	3055, 1635, 1496, 863, 310
(XI)	$-CH_3$	2.84	--	--	$-CH_2CH_3$	1.39(t) 3.09(q) (J=7.5)	7.80[22]	3065, 1645, 1542[20]

[a] All nmr spectra were obtained using solutions in acetonitrile $-d_3$. Infrared spectra were obtained using KBr pellets.

[b] Except for XI, which is the perchlorate salt, all ions have $PtCl_6^{2-}$ as counterion.

[c] Assignments for the individual species VI and VII and are based on an analysis of the spectrum of a mixture of the two.

most intense spectral band is centered near 1635 cm^{-1}, a band assigned to a ring stretching mode, and the presence of absorption in this region may generally be taken as indicating the presence of pyrylium ions (20). A sharp C-H mode near 3060 cm^{-1}, a ring mode near 1530 cm^{-1}, and an absorption near 870 cm^{-1} are also characteristic, as is a single Pt-Cl stretching mode near 315 cm^{-1} in the chloroplatinate salts.

All structures reported here have been assigned on the basis of nmr spectra. Absorption in the aromatic region (ca. 8δ) is characteristic of the ring-bound protons, and mixtures of pyrylium ions are most readily diagnosed by multiple absorptions in this region. Structural assignment is generally straightforward from the nmr data (22), but in ambiguous cases exchange reactions may be used to advantage, since protons on substituents at the 4-position exchange rapidly with D_2O whereas those at the 2,6-positions do so more slowly, and those at the 3,5-positions do not exchange at all (23).

Solvent variation was also valuable as both a mechanistic probe and for the determination of structures and assignment of spectra. In particular, analogous reactions carried out in acetic and propanoic anhydride allowed the assignment of particular nmr absorptions to substituents in the 2,6-positions because of the particular mechanistic role of the anhydride. Furthermore, reactions in propanoic anhydride generally lead to more tractable materials and appeared to follow more clearly defined pathways. For example, 1,1-dimethylcyclopropane reacted in acetic anhydride to form both the 2,3,4,6-tetramethylpyrylium ion and the 2,6-dimethyl-4-ethylpyrylium ion, whereas in propanoic anhydride it gave only the 2,4,6-triethylpyrylium ion. The role of the solvent is seen as being predominantly that of a source of acyl cations, rather than as exhibiting more extensive participation. This is also demonstrated by the following observations: First, pyrylium ions may also be obtained from the reactions of cyclopropanes, chloroplatinic acid, and acetyl chloride in both ethyl acetate and acetic acid-ethyl

acetate mixtures; and, second, the solid product obtained upon reaction of chloroplatinic acid with acetyl chloride reacts with cyclopropanes in a variety of solvents to form acylation products. Not surprisingly, the monoacylation products are dominant under these conditions.

Yields of crude pyrylium ions on the order of 50% of the theoretical value could be obtained consistently, and occasionally were as high as 70%. However, for the reactions as detailed in the experimental section yields given are typically on the order of 10%. Although there are several reasons for this discrepancy, the predominant factor is the attempt to carry out the reactions under conditions where product resolution, or purity, was maximized at the expense of yield. When prepared under conditions where yields were maximized the pyrylium ions obtained were invariably contaminated with the (β,γ-unsaturated carbonyl) platinum dichloride complexes. Since purification by recrystallization is a difficult and low-yield process, attempts were made to produce pure materials directly in order to circumvent this problem. Of course, the diversity of reaction pathways which are possible in these systems will invariably lead to reduced yields of any particular component.

Discussion

Although pyrylium ions have been prepared by a variety of routes (23), the two most common, and those relevant to the reactions observed here, are from the diacylation of olefins and the monoacylation of unsaturated ketones. Figure 1 shows these general pathways. Of particular importance to these reactions, and potentially the rate-limiting step in each, is the formation of the β,γ-unsaturated ketone, which is a necessary prerequisite to the subsequent formation of the 1,5-dione system. The equilibrium between α,β- and β,γ-unsaturated ketones is only slowly established in the absence of catalysts, and proton loss following acylation of an olefin would be expected to favor the conjugated, α,β-unsaturated product. For this reason, cyclopropanes would appear to be a desirable starting material for the preparation of pyrylium ion, since acylation and ring opening

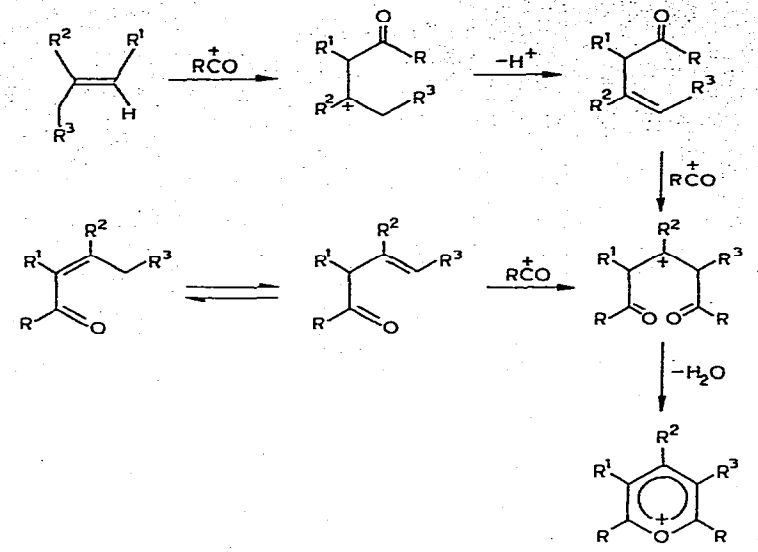

Figure 1. Formation of Pyrylium Ions from Olefins and Unsaturated Ketones.

would be expected to lead directly to positive charge on the γ-carbon, with subsequent direct formation of the β,γ-unsaturated carbonyl. It is perhaps surprising, then, that there have been no reports of the formation of pyrylium ions from cyclopropanes. One report (24), however, mentions the formation of an "unidentified polymeric material" upon acylation of 1,1-dimethylcyclopropane, and it is possible that this material is in fact a pyrylium ion.

Although a priori, several routes to these materials are possible, a variety of experimental evidence allows us to eliminate all except one. In particular, we believe that the reaction proceeds by initial insertion of platinum into the least hindered cyclopropane ring bond, followed by acylation at a platinum-bound carbon atom. Rearrangement and proton-loss to form a β,γ-unsaturated ketone, followed by a second acylation and subsequent ring closure leads to the observed product. In the discussion which follows we present the evidence which leads to the proposed mechanism. Since platinum is involved in the products only as the counterion, evidence for its participation in the reaction is necessarily indirect. However, several lines of evidence do suggest a specific role for the metal.

The substrate studied in greatest detail in this work was 1,1-dimethylcyclopropane. Since its reactions are representative of those observed for analogous species, detailed consideration of its reactions will be given. In acetic anhydride, 1,1-dimethylcyclopropane reacts with chloroplatinic acid to form both the 2,3,4,6-tetramethyl- and 2,6-dimethyl-4-ethyl-pyrylium ions, and any reaction scheme proposed must be compatible with the formation of both products. It is assumed that the initial step in all of these reactions is that between chloroplatinic acid and the anhydride solvent to generate the active electrophilic reagent, the acyl cation (25).

Since the route to pyrylium ions ultimately involves acylation of β,γ-unsaturated ketones, certain specific β,γ-unsaturated ketones must be formed as a result of the initial cyclopropane acylation. Those necessary for the formation of the pyrylium ions formed from 1,1-dimethylcyclopropane are shown in Figure 2.

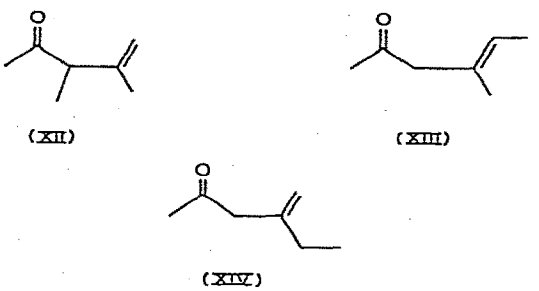

Figure 2. β,γ-unsaturated Ketone Intermediates Possible in the Formation of Pyrylium Ions from 1,1-dimethylcyclopropane.

The 2,3,4,6-tetramethylpyrylium ion (I) can be formed by acylation of either 2,3 dimethyl-1-pentene-4-one (XII) or 3-methyl-2-hexene-5-one (XIII). The other product, the 2,6-dimethyl-4-ethylpyrylium ion (II) can be formed only by acylati of 2-ethyl-1-pentene-4-one (XIV). Reaction of 1,1-dimethylcyclopropane, then, must be able to lead to XIV and either XII or XIII.

On the basis of both steric and electronic factors, direct acylation of 1,1-dimethylcyclopropane is expected to occur at C_2, with cleavage of the C_1-C_2 bond. This would involve attack at a sterically unhindered site and lead to a stable, tertiary carbonium ion. However, such cleavage is not able to produce any of the necessary β,γ-unsaturated ketone intermediates. The converse situation - acylation at C_1 with cleavage of the C_1-C_2 bond - is unfavorable both sterically and electronically, and once again cannot yield the necessary intermediates.

The path which we believe to be correct is shown in Figure 3. Although cleavage of the C_2-C_3 cyclopropane ring bond is unlikely in the absence of the platinum, insertion of the metal into this particular bond is expected from

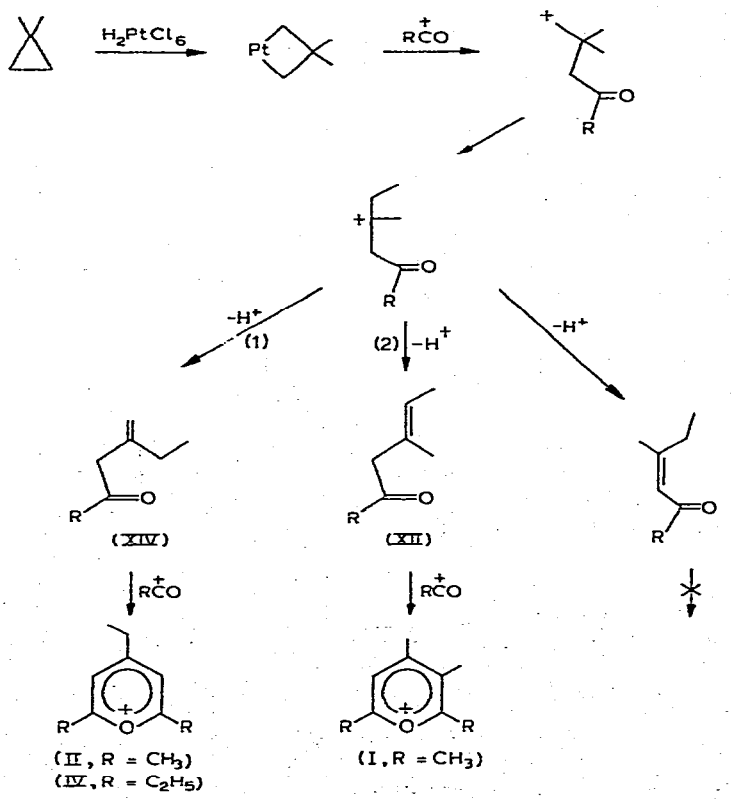

Figure 3. Probable Reaction Mechanisms for 1,1-dimethylcyclopropane.

steric considerations. Following acylation and cleavage of the carbon-platinum bond, methyl migration and proton loss can lead to the β,γ-unsaturated ketones XII and XIV. Although both of the initial acylation products in Figure 3 have been written as the free species, it is possible that they actually exist as the platinum-stabilized carbonium ions, and interconvert via proton loss and a platinum-olefin intermediate. There is, however, no evidence which bears directly on this question.

In propanoic anhydride, only the single pyrylium ion, IV, is formed. Apparently, path 2 becomes relatively much slower, possibly because of inhibition of attack at the internal olefin by the sterically more demanding propionyl group, or because of steric interactions which would be present in the resulting 2-ethyl 3-methyl substituted product.

The reactions of other methyl-substituted cyclopropanes are compatible with

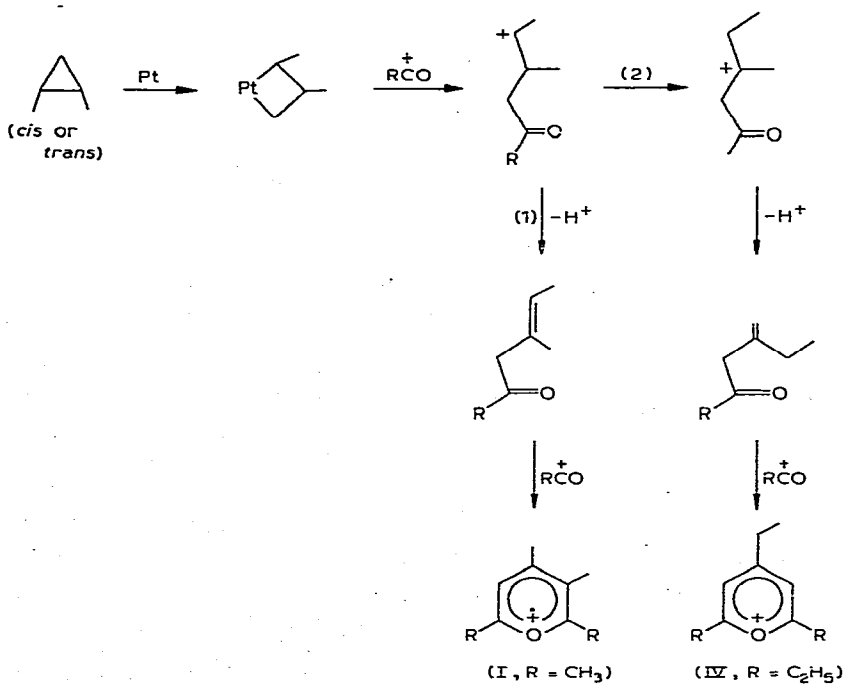

Figure 4. Reaction Mechanisms for 1,2-dimethylcyclopropane

the results obtained for 1,1-dimethylcyclopropane. 1,2-Dimethylcyclopropane reacts as in Figure 4, there being no difference in the products obtained with the cis or trans isomers, since stereochemistry is lost following ring-opening. In acetic anhydride, only a single product, I, is formed. Path 2, which requires a proton migration prior to olefin formation, is apparently much slower than path 1, which leads directly to the β,γ-unsaturated ketone. In contrast, the reaction in propanoic anhydride apparently occurs exclusively by path 2 in spite of the required proton transfer, presumably for the steric reasons mentioned above. In acetic anhydride 1,1,2-trimethylcyclopropane reacts rapidly as in Figure 5, giving the

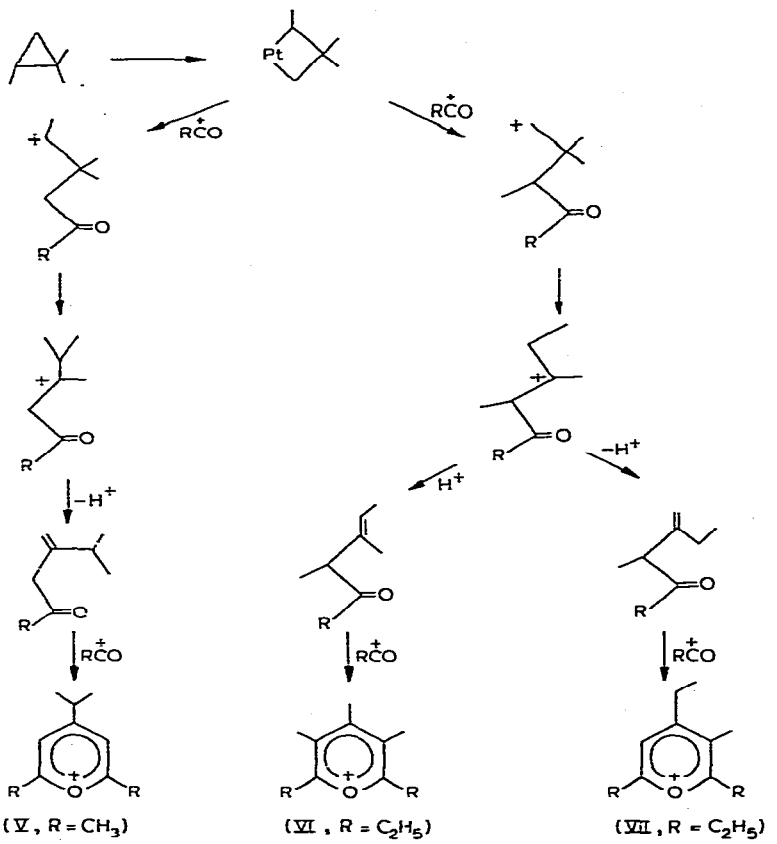

Figure 5. Reaction Mechanisms for 1,1,2-trimethylcyclopropane.

2,6-dimethyl-4-isopropyl pyrylium ion. In propanoic annydride, although the initial cleavage still occurs at C_2-C_3, the acyl group attaches to C_2. This leads to an inseparable mixture of isomers VI and VII, which can be readily identified by nmr. The failure of 1,1,2,2-tetramethylcyclopropane to give any pyrylium ion product, as well as the lack of facile pyrylium ion formation with methylcyclopropane, is explicable. In acetic anhydride methylcyclopropane would be expected to react by cleavage of the C_2-C_3 bond followed by rapid methyl migration, leading eventually to the 2,3,6-trimethylpyrylium ion. Since pyrylium ions unsubstituted in the 4-position are unstable, no isolable product is expected. Cleavage of C_2-C_3 in 1,1,2,2-tetramethylcyclopropane would produce a tertiary carbonium ion which is unable to form a β,γ-unsaturated ketone. Although cleavage of C_1-C_2 would allow formation of a β,γ-unsaturated ketone, it would be unable to proceed to a pyrylium ion.

The specific role of platinum in these reactions is difficult to define unambiguously. Recently there have been two reports of reactions involving metals which lead to pyrylium ions. Oldham and Ketteringham reported (26) that reaction of $PtCl_4$ with acetylacetone produced 2,4,6-trimethyl-3-acetylpyrylium hexachloroplatinate, a reaction which we have reproduced using chloroplatinic acid. This transformation presumably takes place <u>via</u> an aldol condensation of acetylacetone to give 3-acetylhept-3-ene-2,6-dione, which then cyclizes to the pyrylium ion. Surprisingly, Tl(I)acetylacetonate reacts with dimethylsilicondichloride in dichloromethane to produce an iscmeric form of this same pyrylium ion, the 2,4-dimethyl-6-(2-hydroxyprop-1-enyl)pyrylium ion (27). The formation of this ion is explicable only in terms of an aldol condensation involving the primary, terminal, carbanion. In neither of these studies, however, has there been any evidence for specific involvement of the metal. It is, then, possible that in the reactions of chloroplatinic acid with cyclopropanes the role of platinum is non-specific--e.g., that chloroplatinic acid serves only as a source of acid for generation of the acetyl cation, and as a counterion for precipitation of the product. We believe that the role of platinum is more important, and although no exact documentation

exists, we offer the following evidence in support of this belief. Cyclopropane itself is known to react with chloroplatinic acid in acetic anhydride, and the result--insertion--represents a process derived from activation of the cyclopropane ring bonds. Although insertion products have not been observed in the reactions of methylsubstituted cyclopropanes in acetic anhydride, we have managed to isolate such products from ethyl acetate (28). It is likely that the initial step in the reactions observed here is also insertion, or at least incipient "π"-complex formation. The substituted cyclopropanes, once activated in this fashion, are more susceptible to electrophilic attack than is cyclopropane itself, so that acylation and subsequent pyrylium ion formation becomes more favorable than formation and precipitation of the tetrameric insertion product. This step is supported by the rate enhancement for pyrylium ion formation observed with platinum. Upon adding 1,1-dimethylcyclopropane to a solution of chloroplatinic acid in acetic anhydride, a color change begins immediately, and precipitation of the product commences after approximately ten minutes. In contrast, the reaction using perchloric acid is much slower, with no sign of complex formation until approximately two days have passed. This difference in times reflects the actual reaction rates, rather than rates of precipitation, since the perchlorate salts have lower solubility in acetic anhydride, and by contrast the reactions with olefins are much faster with perchloric acid. Activation of the cyclopropane ring by platinum is more strongly supported by the specific mode of reaction. As mentioned previously, 1,1-dimethylcyclopropane must cleave at the C_2-C_3 bond in its reaction with chloroplatinic acid, whereas acylation in the absence of platinum is expected to lead to cleavage of C_1-C_2. In fact, acylation of 1,1-dimethylcyclopropane using $AlCl_3$ was found to proceed entirely by C_1-C_2 cleavage and rearrangement (29). The unexpected cleavage at C_2-C_3 which is involved in the formation of pyrylium ions using chloroplatinic acid is completely consistent with initial formation of a platinum insertion complex, because the product isolated from the reaction of 1,1-dimethylcyclopropane and

chloroplatinic acid in ethyl acetate is specifically the result of insertion of platinum into the C_2-C_3 bond (28). The same result holds for the other cyclopropanes examined, since in each case the bond cleaved is that with which platinum reacts in the genuine insertion product. This observation, combined with the mixture of products observed with chloroplatinic acid compared to the single products obtained with perchloric acid, dictates extensive involvement of platinum in the reaction.

It is also possible that the acetyl group is coordinated to platinum at some point in this reaction. Reaction of chloroplatinic acid with acetic anhydride at elevated temperatures led to the isolation of the trichlorocarbonylplatinate(II) ion, $[PtCl_3(CO)]^-$. This ion probably arises by methyl migration from an acetyl complex, and suggests that platinumacetyl formation in the reaction solutions is feasible. Thus, the actual acylation step may be intramolecular, again consistent with the enhanced rates of pyrylium ion formation using chloroplatinic acid.

Because of the possibility (vide infra) that these reactions proceed through the intermediate formation of olefinic rearrangement products of the cyclopropanes, we examined the reactions of several olefins, chosen because of the possibility that they could be derived from the methylcyclopropanes investigated, with chloroplatinic acid in acid anhydride solvents. Although, as discussed previously, the formation of pyrylium ions by the diacylation of olefins is a well-known phenomenon, these reactions have not been observed using chloroplatinic acid as the acid catalyst. These reactions differ both from the perchloric acid catalyzed reactions, and also from the reactions of cyclopropanes. All of the olefins examined are known to produce pyrylium ions with perchloric acid, whereas in these reactions only those with certain structural features do so. Similarly, with the exception of isobutylene, all of the olefins give only a single product--either a single pyrylium ion or a specific β,γ-unsaturated carbonyl complex of platinum (or, in the case of cis-2-butene, the simple olefin complex). This may

be contrasted with the reactions of 1,1-dimethylcyclopropane and 1,1,2-trimethylcyclopropane, which give both a mixture of pyrylium ions and a β,γ-unsaturated carbonyl complex. Thus, 2-methyl-1-butene and 2-ethyl-1-butene give exclusively pyrylium ion products, isobutylene gives both pyrylium ion and β,γ-unsaturated carbonyl complexes, and 2-methyl-2-butene and trans-2-butene give exclusively β,γ-unsaturated carbonyl complexes. It is assumed that the initial reaction is acylation of the olefin and formation of the β,γ-unsaturated carbonyl. The type of product observed is then dependent upon the relative reactivity of the unsaturated carbonyl toward either further acylation or complex formation. Two factors appear to be important. First, when the α-carbon bears an alkyl substituent, only complex formation is observed, probably because of steric considerations which force a conformation which either favors complex formation or renders further acylation unlikely. Second, platinum complexes are formed only when the β,γ-unsaturated carbonyl complex contains a terminal olefin. This result is reasonable in terms of both the destabilization of metal-olefin bonding by alkyl substitution and also enhanced reactivity toward further electrophilic attack, with subsequent pyrylium ion formation, in the internal olefins. The β,γ-unsaturated carbonyl which would be formed from isobutylene contains both these features--a terminal olefin and no α-substituent--and it is thus reasonable that both types of complex are formed.

Since there is little prior precedent for direct acylation of cyclopropanes, and since the acid-catalyzed isomerization of cyclopropanes is well documented, the possibility that these reactions proceed via prior isomerization to olefins must be considered. Figure 6 includes acid-catalyzed pathways to the observed pyrylium ions, but all such routes can be ruled out by the experimental evidence. Path 1 involves formation of 2-methyl-2-butene, the most likely isomerization product of 1,1-dimethylcyclopropane. This path can be ruled out as the exclusive route because only the single pyrylium ion, I, could be formed. Reaction via this path is eliminated entirely by the observation that under the same conditions 2-methyl-2-butene does not react to form any pyrylium ion products. However, 2-methyl-1-

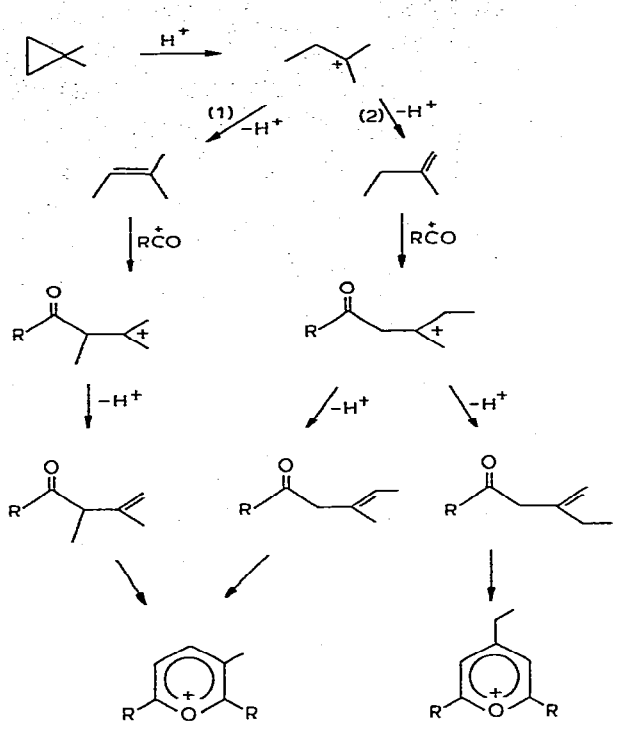

Figure 6. Possible Acid-catalyzed Pathways to Pyrylium Ions.

butene (path 2) does react to form the pyrylium ion I. Path 2 can nonetheless be ruled out by labeling experiments. Reaction <u>via</u> path 2 to form II using 1,1-di-(methyl-d_3)cyclopropane would lead to deuterium incorporation only in the 3,5-positions of the pyrylium ion. Experimentally, however, deuterium is found to be incorporated not only there but also in the methyl group of the 4-ethyl substituent. Similarly, reaction <u>via</u> path 2 to form II using $D_2PtCl_6 \cdot 6D_2O$ would lead to incorporation of deuterium specifically in the methyl group of the 4-ethyl substituent. Experimentally, no deuterium incorporation is observed in this reaction. The results of both of these labeling studies are compatible with the mechanism in Figure 3, and it must be concluded that ring-opening promoted by insertion of platinum represents the actual course of these reactions.

These studies have demonstrated a new route to the synthesis of pyrylium ions. Although for obvious reasons of costs of materials and yields these reactions do not have general synthetic utility; in certain cases the specificity of cleavage involved may allow the formation of pyrylium ions not accessible by other routes. Several details of the mechanism remain obscure, but several lines of evidence demonstrate that the initial acylation involves cyclopropanes activated by insertion of platinum into the least sterically hindered carbon-carbon ring bond.

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