

The Formation of Pirylium Ion Salts from Cyclopropanes

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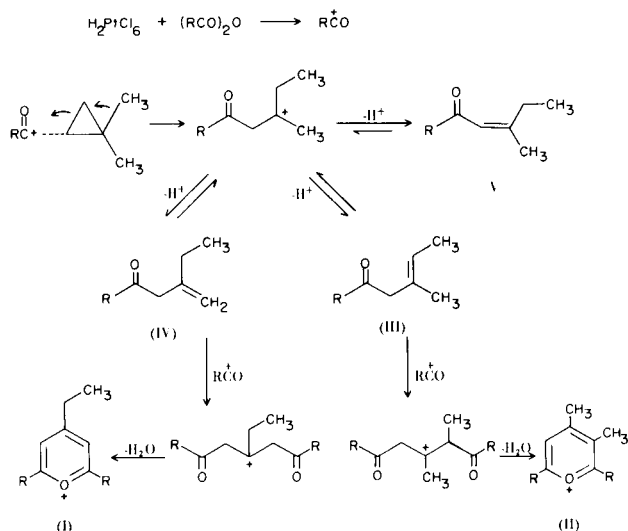
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Received August 26, 1974

Sir:

In 1955 Tipper (1) reported that the reaction of cyclopropane with chloroplatinic acid in acetic anhydride gave a compound of empirical composition $\text{PtCl}_2\text{C}_3\text{H}_6$, which he formulated as a complex containing cyclopropane π -bonded to platinum. Later work by Chatt (2) showed that the material is in fact a platinumocyclobutane—*e.g.*, the result of platinum insertion into a carbon-carbon ring bond. In order to determine the electronic and stereochemical course of this reaction, we began investigations of analogous reactions using substituted cyclopropanes.

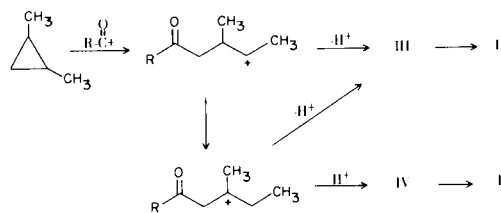
Surprisingly, the reaction between methyl-substituted cyclopropanes and chloroplatinic acid in anhydride solvents gives no product analogous to Tipper's complex. Contrary to our previous suggestion (3) of cyclobutenium ion formation, we have now established that the reaction proceeds *via* diacylation of the cyclopropane followed by dehydration and ring closure to produce pyrylium ion salts. Thus, 1,1-dimethylcyclopropane reacts over a period of three hours to produce a brown powder which may be crystallized from methanol or dichloromethane as orange crystals of composition $(\text{C}_9\text{H}_{13}\text{O}^+)_2\text{PtCl}_6^{2-}$ (4). The material is a 2:1 electrolyte in acetonitrile, and can be shown to contain the anion PtCl_6^{2-} . It has the infrared spectrum appropriate for a pyrylium ion (5), and can be shown by nmr in perdeuterioacetonitrile (τ 2.09 (2H), 6.93 (q, $J = 7.5$, 2H), 8.68 (t, $J = 7.5$, 3H), 7.12 (6H)) to contain the 2,6-dimethyl-4-ethylpyrylium ion (I) (6). The same ion, isolated as the perchlorate salt, is formed by the reaction of 1,1-dimethylcyclopropane and perchloric acid in acetic anhydride, indicating that the role of platinum, in the product at least, is merely that of counterion. The product of the reaction with chloroplatinic acid is commonly obtained as a mixture of the PtCl_6^{2-} salts of I and small but variable amounts of the isomeric 2,3,4,6-tetramethylpyrylium ion (II), which is the dominant product from the analogous reaction of 1,2-dimethylcyclopropane. The formation of both pyrylium ions in the reaction of 1,1-dimethylcyclopropane can be accounted for as in Scheme 1. (Ring closure of the carbonium ion derived from 1,5-pentanenediones to form pyrylium ion salts is a well-established reaction (7).) Although the conjugated olefin (V) is favored, it cannot lead to pyrylium ion products. The



Scheme 1: Proposed mechanism for the formation of pyrylium ions from 1,1-dimethylcyclopropane.

reversibility of its formation, or the general observation that α,β - and β,γ -unsaturated carbonyls are in equilibrium, allows for the formation of the observed products. The predominant formation of (I), rather than (II), in this reaction is presumed to be of steric origin. Consistent with this view is the formation of (I) as the sole pyrylium ion product when propanoic anhydride is used as the solvent. Several experiments rule out an alternative mechanistic possibility involving prior isomerization of the cyclopropane followed by diacylation of the resulting olefin.

The dominance of the tetramethylpyrylium ion (II) from either *cis*- or *trans*-1,2-dimethylcyclopropane is compatible with this scheme, since the precursor olefin (III) is formed directly upon acylation and proton loss, whereas the precursor to I (olefin IV) requires a hydride transfer prior to its formation:



Scheme 2: Proposed mechanism for the formation of pyrylium ions from 1,2-dimethylcyclopropane.

The reaction appears to be specific for methyl-substituted cyclopropanes, or olefins which may be derived from them. Isobutylene reacts under these conditions to produce the 2,4,6-trimethylpyrylium ion, whereas neither *cis*- nor *trans*-2-butene gives pyrylium ion products, presumably because the ions formed would be unsubstituted in the 4-position, and thus be relatively unstable.

In two cases the observed pyrylium ions are unexpected and as yet unexplained. Methylcyclopropane gives a product which is identical to that derived from 1,1-dimethylcyclopropane, and 1,1-dichlorocyclopropane gives a product identical to that derived from isobutylene. The full details of these and similar reactions will be reported in a subsequent publication.

Acknowledgement.

The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. Stephan P. B. Taylor for helpful suggestions.

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- (2) D. M. Adams, J. Chatt, R. G. Guy and N. Sheppard, *J. Chem. Soc.*, 738 (1961).
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- (4) In general, satisfactory analyses were obtained only for non-planar pyrylium ions. Thus, for the 2,6-dimethyl-4-ethylpyrylium hexachloroplatinate: Calculated (found) for $\text{PtCl}_6\text{C}_{18}\text{H}_{26}\text{O}_2$: Pt 28.60 (28.56), C 31.69 (31.70), H 3.84 (3.67), Cl 31.18 (31.04). Planar pyrylium ions tended to precipitate as mixtures of the PtCl_6^{2-} and planar $\text{Pt}_2\text{Cl}_6^{2-}$ salts, and consequently often gave poor analyses. In such cases, identification of the ion is based solely on nmr spectral data.
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