THIAPYRYLIUM SALTS (REVIEW)

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The literature data touching upon the synthesis of thiapyrylium salts and the stability of the thiapyrylium cation as compared with its isoelectronic analogs, as well as the nucleophilic, oxidation, anion-exchange, and other reactions of the salts with substituted and unsubstituted thiapyrylium cations are examined in this review.

Thiapyrylium salts became accessible almost a half century later than, and up to now have been less extensively studied than their isoelectronic analogs, pyrylium salts.

The thiapyrylium cation, like the pyrylium cation, is described as a resonance hybrid of a thionium and three carbonium structures [1-5].

The limiting structures reflect the principal properties of the thiapyrylium cation — its aromatic character and its ability to react with nucleophilic reagents (H₂O, H₂S, amines, Grignard reagents, etc.) to give 2-, 4- or 6-substituted thiopyrans and also with organolithium compounds to give 1-substituted 1-thiabenzenes [6-12].

It should be noted that the electron densities and bond orders had been calculated and conclusions regarding the direction of nucleophilic reactions had been drawn [3, 4] for the unsubstituted thiapyrylium cation prior to its synthesis. In the opinion of Kontecky and Zahradnik, the relatively high delocalization energy (46 kcal/mole) and the bond orders [4] indicate the aromatic character of the thiapyrylium cation.

SYNTHESIS OF THIAPYRYLIUM SALTS

From Pyrylium Salts

In 1954, Wizinger and Ulrich [13, 14] established the possibility of conversion of pyrylium perchlorates to thiapyrylium perchlorates by the successive action of sodium sulfide and perchloric acid:

Pyrylium salts are also capable of undergoing similar transformations with other anions (Cl⁻, BF₄⁻, etc.) [15]. The Wizinger reaction was one of the important methods for the preparation of salts with a thiapyrylium cation [6-12, 16-19]; however, it is evidently not a general reaction [13, 14, 20].

From Thiophene

An unsubstituted thiapyrylium cation was synthesized for the first time by expansion of the thiophene ring [21].
From 3,5-Diketotetrahydrothiopyran

The same thiapyrylium salts are also formed as a result of a number of transformations of 3,5-diketotetrahydrothiopyran [2]:

From Thiopyrans and 1,5-Diketones. Disproportionation of Thiopyrans

The formation of thiapyrylium salts from 2H- and 4H-thiopyrans is possible by means of splitting out of a hydride ion. Just as in the salt formation of 1,5-diketones, the problem of hydride-ion acceptors during the salt formation of thiopyrans seems of great interest and has a common solution. The formation of pyrylium salts by reaction of 1,5-diketones with protic and aprotic acids (perchloric acid, sulfuric acid, ferric chloride, stannic chloride, and phosphorus oxychloride) has been considered to be (for example, see [23, 24]) a redox process in which the acid acts as an oxidizing agent. However, it was found that pyrylium salts can also be generated by the action of polyphosphoric acid, to which the role of an oxidizing agent cannot be ascribed, on 1,5-diketones. It was later found that the yields of salts are lower in acetic acid or in ether than in acetic anhydride. It was found that acetic anhydride reacts with perchloric acid to give acetyl perchlorate (CH₃CO- ClO₄), which acts not only as an anion donor but also as a hydride-ion acceptor (for example, see [25-27]). The role of the acetyl cation as a hydride-ion acceptor is confirmed by the detection of acetaldehyde in the reaction mixture [25]. Chalcones, which are added to the reaction mixture in the preparation of salts from 1,5-diketones, pyrans, and thiopyrans [27-29], also may act as hydride-ion acceptors. It is assumed that in this case the carbonyl group of the chalcone is protonated to give a stable hydroxyallyl cation, which acts as a hydride-ion acceptor [27]:

\[
\text{RCH=CH-C-C₆H₅} \xrightarrow{\text{HClO₄}} \text{RCH=CH-C-C₆H₅} \xrightarrow{\text{HClO₄}} \text{RCH=CH-C-C₆H₅} \xrightarrow{\text{HO}} \text{RCH=CH-C-C₆H₅} \xrightarrow{\text{ClO₄}^{-}} \text{RCH=CH-C-C₆H₅} \xrightarrow{\text{OH}}
\]

The yields of pyrylium salts reach 95% in the reaction of perchloric acid [27] or boron trifluoride [28] with 1,5-diketones when an equimolecular amount of the chalcone is present, whereas the yields do not exceed 40% when the chalcone is absent.

Triphenylmethyl perchlorate [29-33] and tert-butyl chloride [27], which readily give carbonium ions that act as hydride-ion acceptors, are widely used as reagents to obtain pyrylium and thiapyrylium salts from diketones [28-33], pyrans, and thiopyrans [24, 34-36].

\[
\text{R''''} \xrightarrow{(\text{C₆H₅})₂\text{CCIO₄}} \text{R''''} \xrightarrow{(\text{C₆H₅})₂\text{CCIO₄}} \text{R''''}
\]

Trityl perchlorate is not only a hydride-ion acceptor but also a strong dehydrating agent, as evidenced by its ability to convert thiacyclohexanes to thiapyrylium salts [20].