Tetrahedron Letters No. 8, pp. 487-495, 1963. Pergamon Press Ltd.
Printed in Great Britain.

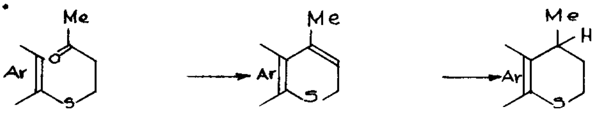
DISPROPORTIONATION OF THIACHROMENS TO THIACHROMANS AND THIANAPHTHALENIUM SALTS INVOLVING HYDRIDE TRANSFER

B.D. Tilak & V.M. Vaidya
Department of Chemical Technology,
University of Bombay,
Bombay 19, INDIA

(Received 8 January 1963)

The chemistry of thiachromans, thiachromens, aromatic thiachromens and thianaphthalenium salts has not been widely studied. A few examples of aromatic thiachromens have been reported by us earlier.[1,2,3.]

A new synthesis of 4-methylthiachromans involving cyclodehydration of aryl 3-oxo-butyl sulphides (I) is now reported. The latter were prepared in good yields (72 - 99%) by Michael addition of aryl mercaptans to methyl vinyl ketone (MVK) in presence of piperidine. Cyclodehydration of (I), with polyphosphoric acid (PPA) was expected to yield thiachromens (II) which would then lead to the desired thiachromans (III) by reduction.



(I) (II) (III)

Ar = aryl residue

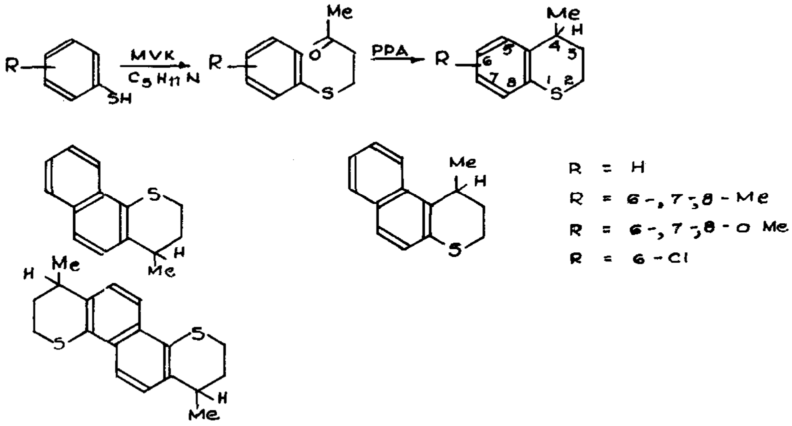
---

[1] B.D. Tilak, Proc. Ind. Acad. Sci. 33A, 71 (1951)

[2] B.D. Tilak, Tetrahedron 9, 84 (1960)

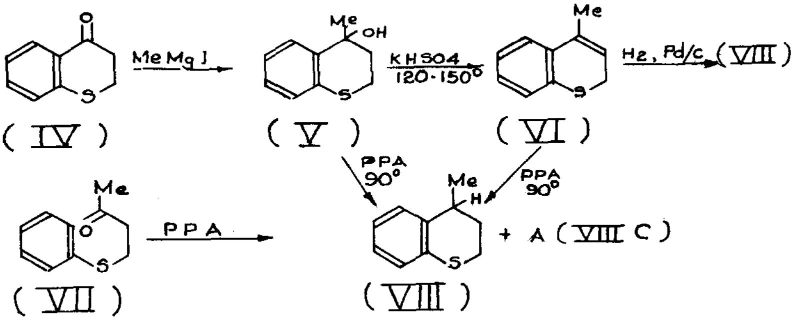
[3] H.S. Desai, Ph.D. thesis, Bombay University (1959)

However, when the keto-sulphides (I) were cyclised by treatment with PPA, we always obtained thiachromans (III) (yields $\ngtr$ 35%), directly, instead of the expected thiachromens (II). In addition a blue substance (A) was also formed. Starting from different aryl mercaptans, the following thiachromans were thus prepared:-



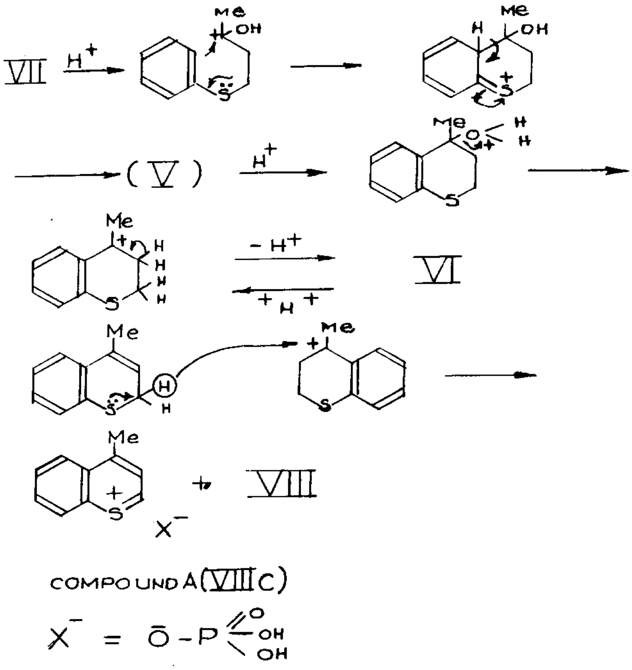
In each of the above cases, the thiachroman and <u>not</u> the thiachromen was invariably obtained.

The thiachromans (III) were also prepared from thiachroman-4-ones by the following alternative routes exemplified by the synthesis of 4-methylthiachroman (VIII):-



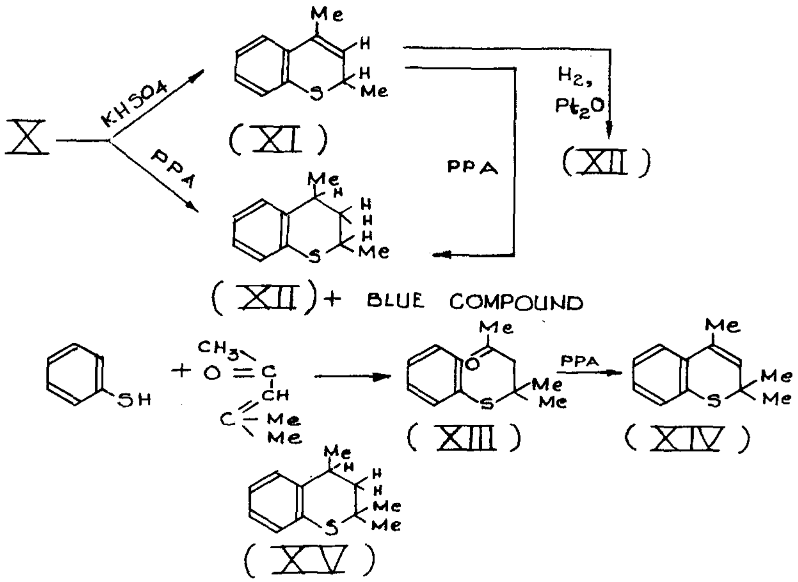
Since, (V) and (VI) gave (VIII), on treatment with PPA, the cyclodehydration of phenyl 3-oxobutyl sulphide (VII) with PPA to give (VIII) obviously proceeds through (V) and (VI).

Taking into account the above facts, the following mechanism may be suggested for the cyclodehydration of (VII) with PPA:-



The above mechanism is supported by the following reactions:-

(IX) (X)

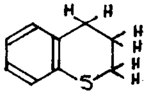


The fact that the thiachroman (XII) is obtained by treatment of (X) or (XI) with PPA, whereas cyclodehydration of (XIII) with PPA yields only the thiachromen (XIV), shows that a hydride transfer from the 2-position to the carbonium ion in the 4-position is involved. In the cyclodehydration of (XIII), neither 2,2,4-trimethylthiachroman (XV) nor a blue compound was formed.

In order to establish that a hydride shift is involved from C_2 to C_4 position in the PPA induced disproportionation of 4-methyl-Δ^3-thiachromen (VI) and the fact that protonation of the latter takes place at C_3 by PPA, we treated (VI) with deutero-polyphosphoric acid (D-PPA) (prepared by dissolving P_2O_5 in calculated amount of D_2O). Similarly (VII) was cyclised with D-PPA. In order to check the possibility of isotopic exchange 4-methylthiachroman was treated with D-PPA under similar conditions. The nmr spectra of 4-methylthiachroman thus obtained and the D-PPA treated 4-methylthiachroman (discussed in the accompanying paper) support the mechanism outlined above.

It is of interest at this stage to recall the work of Parham et al[4], who prepared Δ^3 -thiachromen (XVI) in high yield (91%), by dehydration of 4-thiachromanol (XVII) by heating it with potassium hydrogen sulphate at 120°.

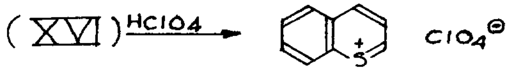
(XVII) (XVI)



(XVIII)

The u.v. spectrum of the product obtained by treatment of the thiachromanol (XVII) with PPA, revealed that it was a mixture of the thiachromen (XVI) and thiachroman (XVIII).

Further when the thiachromen (XVI), was treated with perchloric acid, thianaphthalenium perchlorate (XIX) was obtained in good yield. Since in the latter reaction, no thiachroman was isolated, perchloric acid must be acting as a dehydrogenating agent, involving hydride elimination from the thiachromen. In this

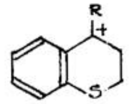


(XIX)

---

[4] W.E. Parham and R. Koncos, J. Am. Chem. Soc., 83, 4034 (1961)

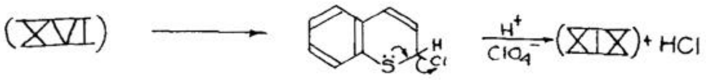
connection, the synthesis of (XIX), reported by Bronthone and Reid[5] from thiachromen (XVI) by interaction with triphenyl methyl perchlorate in acetic acid may be mentioned. Whereas, in the synthesis of (XIX), the above authors made use of triphenylmethyl carbonium ion for abstraction of hydride from the thiachromen (XVI), we have found that perchloric acid alone effects this conversion. In this conversion the carbonium ion (XX) does not play a significant role, since no thiachroman (XVIII) was isolated. The difference in the interaction of 4-methylthiachroman-4-ol (V), thiachroman-4-ol (XVIII) and thiachromen (XVI) with acids (polyphosphoric acid and perchloric acid) is obviously due to the relative ease of formation and stability of the relevant carbonium ions (XX) and (XXI) involved in these conversions.



(XX) R = H

(XXI) R = Me

Luttringhaus and Engelhard[6] prepared thianaphthalenium perchlorate (XIX) by the step-wise interaction of (XVI) with sulfuryl chloride and perchloric acid. It seems that (XVI) is converted to (XIX) by the following mechanism:-



However, as mentioned above, thiachromen (XVI) also directly gives (XIX), with even greater facility by treatment with perchloric

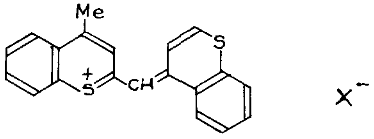
---

[5] W. Bonthrone and D.H. Reid, Chem. & Ind. 1192 (1960)

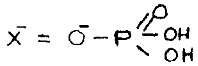
[6] A. Luttringhaus and N. Engelhard, Naturwissenschaften 44, 584 (1957)

acid alone.

We then turned our attention to the blue compound (A) obtained along with 4-methylthiachroman (VIII) in the cyclodehydration of (VII) with PPA. Compound (A) was insoluble in water, soluble in acetic acid, methylene chloride and chloroform and sparingly soluble in ethanol. Since the product was somewhat sticky, we employed perchloric acid for cyclodehydration of (VII). Here also, another blue compound (A_1) was obtained in higher yield. Compound (A_1) was repeatedly crystallised from CH_2Cl_2 and benzene until it gave constant absorbence ($\epsilon = 83,350$ at 628 mμ). Analysis of the blue product and its high absorbence compared to (XIX) lead us to suggest the structure (XXII A_1) for compound (A_1) which was found paramagnetic by electron magnetic resonance method.

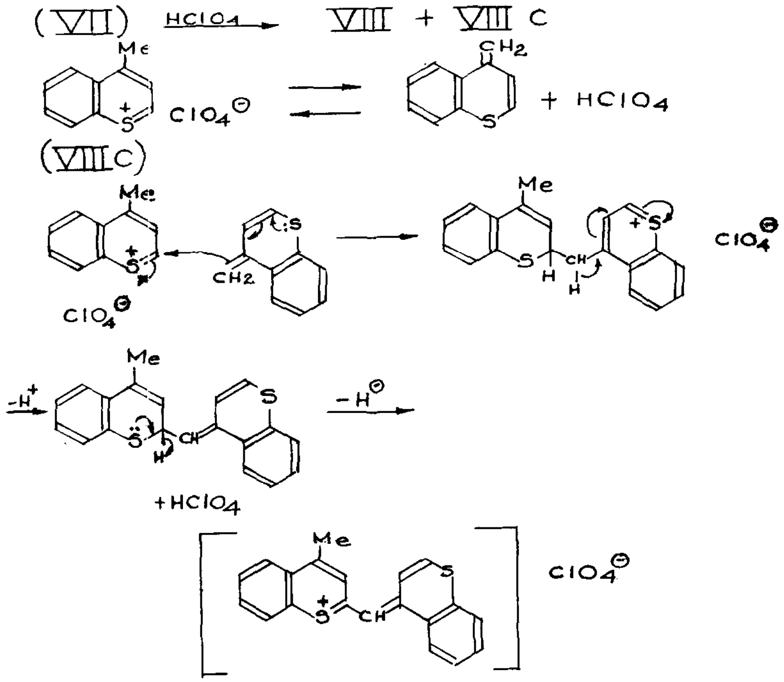


A_1 ; [XXII A_1], $X^- = ClO_4^{\ominus}$

A ; [XXII A],

$X^- = O^- - P(=O)(OH)OH$

The blue compound (A) obtained in the cyclodehydration of (VII) with PPA also gives an absorption spectrum closely similar to compound (A_1) and it contains the phosphate anion. Compound (A) is better represented by (XXII A) than by (VIII C), suggested earlier in the paper.

Whereas 4-methylthiachroman (VIII) when treated with perchloric remained unaffected, 4-methylthiachromen (VI) gave the blue compound (A_1). The formation of (XXII A_1) by cyclodehydration of (VII) may be visualised as proceeding through a compound such as (VIII C; X^- = ClO_4^-) according to the following scheme:-



A_1 3 (XII A_1)

When a solution of compound (A_1) in methylene chloride was treated with ethanolic sodium hydroxide, the blue solution changed its colour to red. Acidification of the alkaline solution with ethanolic hydrochloric acid, gave back the original blue colour with an absorption maximum at 628 mμ. Compound (A_1), which behaves like a cyanine dye, represents a new type in this group of dyes. Synthesis of other cyanine dyes containing thianaphthalenium ring systems is in progress.

Muljiani in this Laboratory has also observed a similar disproportionation in the dehydration of 4-hydroxy-4-methylchroman with PPA. In this reaction only 4-methylchroman was isolated. When, however, anhydrous copper sulphate was used for dehydration of the chromanol, the expected 4-methyl-Δ^3-chromen was obtained. It seems likely that cyclodehydration of 2-aryloxyethyl methyl ketones may also lead to 4-methylchromans by a mechanism similar to the above.

Further, cyclodehydration of methyl 2-phenylaminoethyl ketone (XXIII) with PPA has been shown by Ravindranathan of our Laboratory to give a mixture containing 1:2:3:4-tetrahydrolepidine and lepidine. The formation of these products is explicable by the mechanism postulated above.

Further work on the cyclodehydration of arylmercapto-, aryloxy- and arylamino-ethyl methyl (or aryl) ketones is in progress.

The U.V., I.R. and nmr spectra and analytical data for the compounds described in the paper are in conformity with the structures assigned and compare well with the spectral data for corresponding 4-des-methyl derivatives, reported by other workers. It is hoped that a full account of the work will be published shortly in Tetrahedron.

Acknowledgments:- This research was supported by a grant from the Petroleum Research Fund administered by American Chemical Society. Grateful acknowledgement is hereby made to the donors of the Fund. We are grateful to Prof. S.S. Dharmatti, et. al. for a study of magnetic resonance of the above compounds[*].

---

[*] The nmr studies of the compounds discussed in this paper are published in the companion publication.