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NMR OF THIACHROMANS AND RELATED COMPOUNDS

M.M. Dhingra, G. Govil, C.L. Khetrapal and V.M. Vaidya†
Tata Institute of Fundamental Research, Bombay - 5 (INDIA)

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The present work on NMR studies of thiachromans and thiachromens was undertaken to study the reaction mechanism proposed by Tilak and Vaidya[1] for the new synthesis of 4-methylthiachromans published in the accompanying note. The spectra discussed in this work have been obtained on a Varian 60 Mc/s high resolution spectrometer and the shifts have been measured relative to cyclohexane as the external standard. All the samples used in this work were kindly provided by Prof. Tilak of the Department of Chemical Technology, Bombay and were diluted with carbon tetra chloride as they were viscous. The intensities of the various peaks were measured by finding the area under each peak. The accuracy in the measurement of intensities is of the order of 10%.

The NMR spectrum of 4-methylthiachromen obtained by dehydration of 4-methylthiachroman-4-ol (V)* by potassium hydrogen sulphate[1] is shown in fig.1. The spectrum consists of a multiplet

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† From Dept. of Chemical Technology, University of Bombay

1. B.D. Tilak and V.M. Vaidya (accompanying paper)

* The numbers in the present paper refer to those in the companion publication of Tilak and Vaidya.

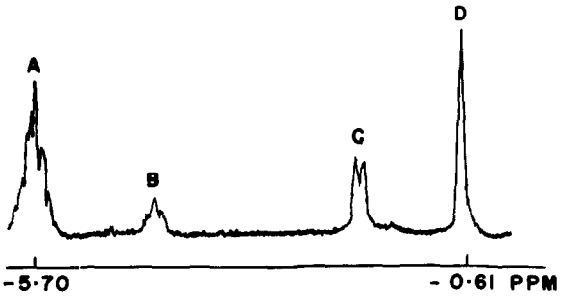
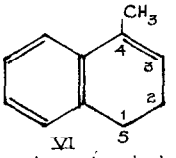


FIG. I : NMR SPECTRUM OF 4 METHYL THIOCHROMEN.

(marked A; shift $\delta \simeq -5.70$ ppm) due to aromatic protons, a triplet (marked B) due to ethylenic proton at position C-3 splitting being due to the two protons at position C-2 ($J \simeq 5.6$ c/s; $\delta \simeq -4.29$ ppm) a doublet due to protons at position C-2 (marked C; $\delta \simeq -1.82$ ppm) and a singlet due to methyl protons (marked D; $\delta \simeq -0.61$ ppm).



VI

The spectrum of the compound prepared by cyclodehydration of phenyl 3-oxobutyl sulphide (VII) by polyphosphoric acid PPA[1] (fig.2), however, did not resemble the spectrum of the thiachromen (VI) but was like the one expected from 4-methylthiachroman (VIII). In fact the spectrum of thiachroman (XVIII) prepared unambiguously by Parham and Koncos[2] is comparable to the spectrum of compound (VIII) except for the expected difference due to C-4 methyl group.

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

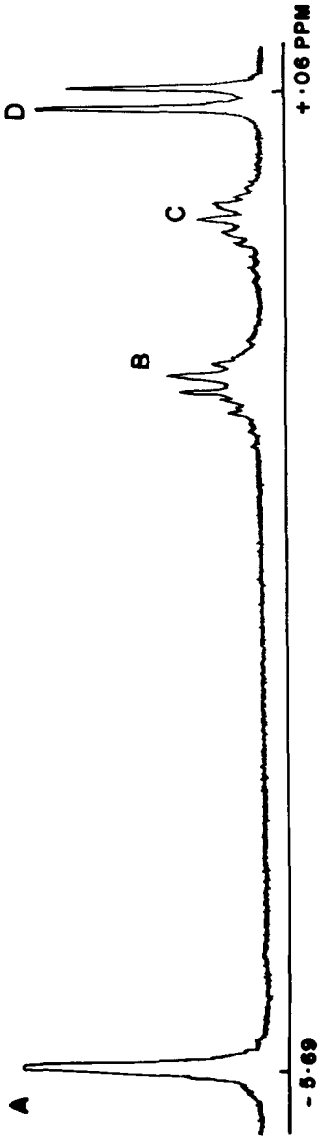

FIG. 2. SPECTRUM OF PRODUCT OBTAINED BY CYCLODEHYDRATION OF VII WITH PPA

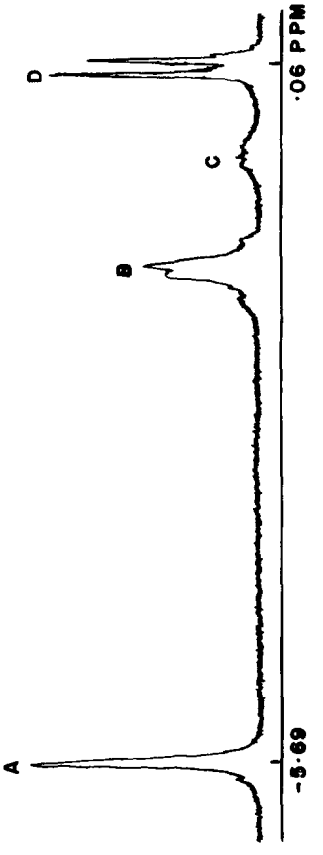

FIG. 3 : SPECTRUM OF THE PRODUCT OBTAINED BY CYCLODEHYDRATION OF VII WITH DEUTERATED PPA.

The NMR spectrum of 4-methylthiachroman prepared unambiguously by hydrogenation of 4-methyl- Δ^3 -thiachromen (vide Tilak and Vaidya) was also identical with that of the product obtained by cyclodehydration of (VII). This confirmed that the cyclodehydration product derived from (VII) was 4-methylthiachroman.

The shifts and relative intensities of different groups of lines are given in Table I and have been assigned to different protons in 4-methylthiachroman.

If the hydride ion transfer mechanism given by Tilak and Vaidya for cyclodehydration is correct, then one should obtain a deuterium replacement of one of the protons at C-3 if the reaction is conducted with deuterated PPA. While the doublet in the NMR spectrum due to methyl protons in the sample prepared by Tilak and Vaidya by the action of deuterated PPA on 4-methylthiachromen (VI) (fig.3) remains unaltered showing no deuteration of C-4 proton, the relative intensities do show a deuterium substitution at C-3. It may be further observed that the intensities of the lines A,C and D are less than expected. This is probably due to a preferential isotopic exchange of these protons with deuterated PPA during the synthesis. This has been confirmed by the NMR spectrum of a sample of 4-methylthiachroman treated with deuterated PPA under identical conditions. The relative intensities in the spectrum of this sample (last column of table I) do show a preferential exchange at these sites. The NMR spectrum of the 4-methylthiachroman obtained by cyclodehydration of (VII) with deutereo-PPA also is in general agreement with the spectrum of the product obtained by similar treatment of (VI). Thus the NMR results are in agreement with the hydride ion transfer mechanism suggested by Tilak and Vaidya.

Group	Assignment	Shift	Rel. intensities in sample prepared by cyclodehydration by PPA	Rel.intensities of deutero 4-methyl-thiachroman prepared by treatment of (VI) with deuterated PPA	Rel. intensities of 4-methylthiachroman treated with deuterated PPA
A	Phenyl protons	- 5.69 ppm	4	2.5	1
B	Protons at C-2 and proton at C-4	- 1.56 ppm	3	3	3
C	Protons at C-3	- 0.65 ppm	2	0.8	1.7
D	C-4-methyl protons	+ 0.06 ppm (doublet separation 7 c/s)	3	2.1	2

Table - I

The NMR spectrum of the compound formed by potassium hydrogen sulphate treatment of 2:4-dimethylthiachroman-4-ol (X) is shown in fig.4. It is obvious that the spectrum is in conformity with the structure, 2:4-dimethyl- Δ^3 -thiachromen proposed for the product. The spectrum of the compound obtained by the treatment of (X) with PPA (fig.5) though complicated for analysis is in line with the proposed structure (XII) for the product.

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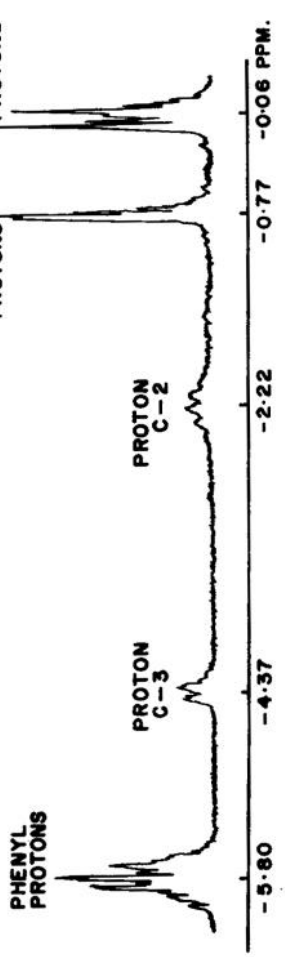

FIG. 4 : SPECTRUM OF THE PRODUCT FORMED BY $KHSO_4$ TREATMENT OF **X**.

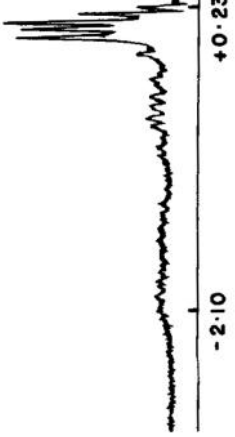

FIG. 5 : SPECTRUM OF THE PRODUCT FORMED BY PPA TREATMENT OF **X**.