*Tetrahedron.* Vol. 25, pp. 1939 to 1946. Pergamon Press 1969. Printed in Great Britain

# STEREOCHEMISTRY OF HYDRIDE TRANSFER IN ACID INDUCED DISPROPORTIONATION OF THIACHROMENES AND CHROMENES*

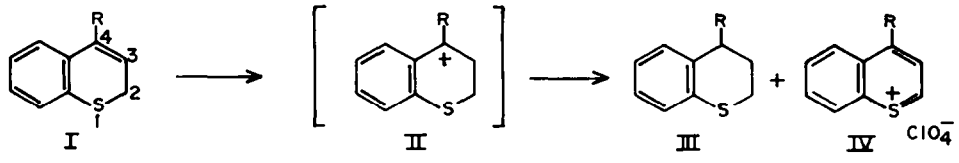
B. D. TILAK, R. B. MITRA and Z. MULJIANI
National Chemical Laboratory, Poona-8, India

(*Received in the UK* 25 *October* 1968; *Accepted for publication* 4 *December* 1968)

**Abstract**—Acid catalysed disproportionation of 3,4-dimethyl-$\Delta^3$-thiachromene (V) involves stereoselective intermolecular hydride transfer to give 85% *cis*-isomer (VIIA) and 15% *trans*-isomer (VIIB) of 3,4-dimethylthiachroman. In contrast, the oxygen analogue shows no stereospecificity, giving an equal mixture of *cis/trans* isomers of 3,4-dimethylchroman (XX). The intermediacy of a bridged sulfonium ion A with a predictable steric configuration has been proposed.

In the tricyclic series the difference between the thia- and oxa-series is less pronounced presumably because of additional steric factors imposed due to the rigidity of the fused ring system.

EARLIER reports[1-3] from this laboratory have shown that the acid catalysed disproportionation of thiachromenes (I) to give thiachromans (III) and thiapyrilium salts (IV) involves an intermolecular transfer of hydride from the 2-position of one molecule of thiachromene to the 4-position of its conjugate acid (II).




Since the hydride addition could occur from either face of the planar carbonium ion (II), in cases where the thiachromene is 3,4-disubstituted, *cis/trans* isomerism in the resulting thiachroman (II) would occur depending on the steric course of hydride attack.

In this communication we wish to report that the hydride transfer during the disproportionation of 3,4-disubstituted thiachromenes proceeds stereoselectively leading predominantly to the *cis*-isomer. Thus the bicyclic 3,4-dimethylthiachroman[2,4] (VII) obtained by treatment of 3,4-dimethyl-$\Delta^3$-thiachromene (V), with perchloric acid was found to be a mixture of 85% of *cis*-isomer VIIA and 15% *trans*-isomer VIIB. In contrast, we recently observed[5] that in the oxa-series, bicyclic 3,4-dimethylchroman (XX) is formed from its corresponding $\Delta^3$-chromene as only a 50:50 mixture of *cis/trans* isomers showing no steric preference for hydride transfer.

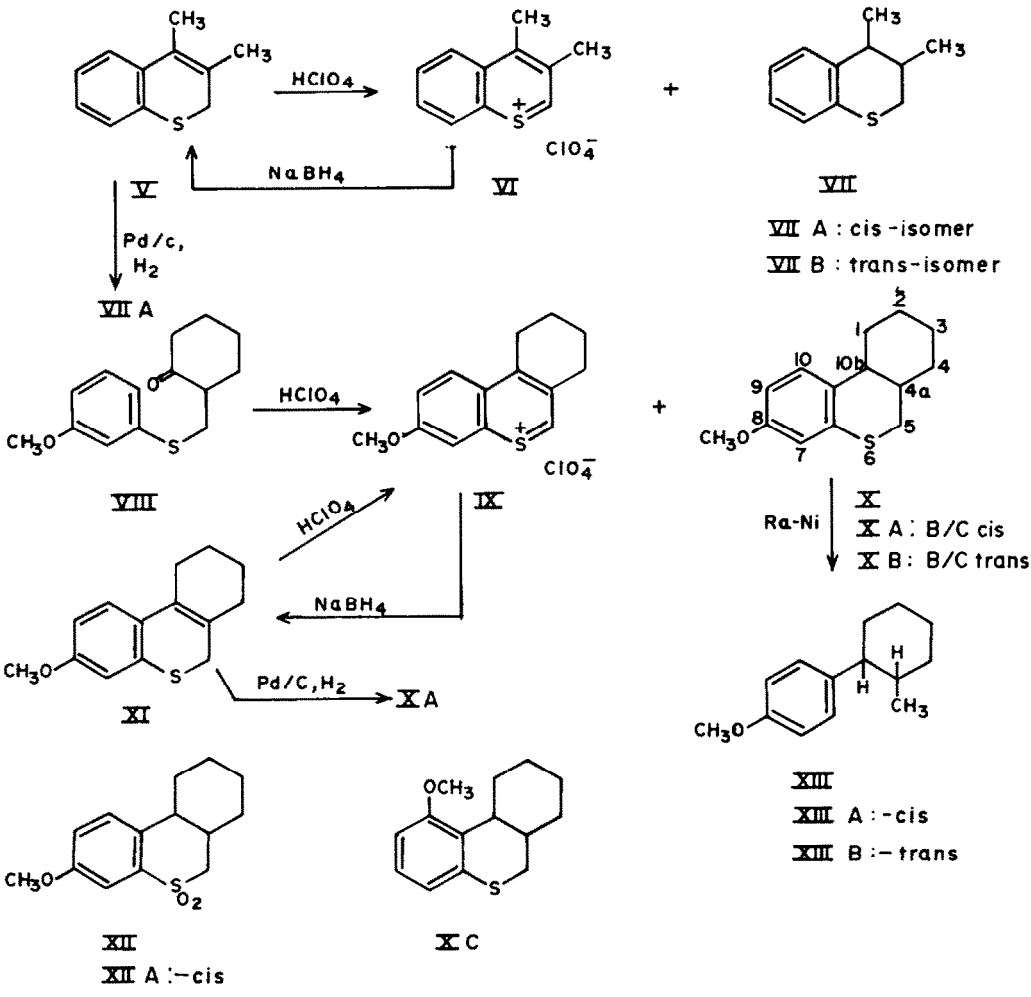
In the tricyclic series, the situation is more complicated because of the further steric effects imposed due to the greater rigidity of the tricyclic system. Thus, disproportionation of the thiachromene XI gave 77% of the ring B/C *cis*-isomer (XA) of thiachroman (X), whereas the chroman (XIV) of the oxa-series was formed from its

* NCL Communication No. 1282.

corresponding chromene (XIX) as a mixture of about 65% ring B/C *cis*-isomer (XIVA) and 35% *trans*-isomer (XIVB).

Chart 1 describes the synthetic scheme followed in the thia-series.

CHART 1




3,4-Dimethylthianaphthalenium perchlorate[2] (VI) on reduction with sodium borohydride gave 3,4-dimethyl-$\Delta^3$-thiachromene (V) which on catalytic hydrogenation gave *cis*-3,4-dimethylthiachroman (VIIA).[2,4] Disproportionation of V by treatment with perchloric acid gave VI and a mixture of VIIA and *trans*-3,4-dimethyl thiachroman (VIIB). The percentage of *cis* and *trans*-isomers in VII was determined by VPC. Pure *cis*-VIIA showed a single peak with retention time 4·4 min. Under the same conditions VII showed 2 peaks, one (85%) identical with the *cis*-isomer with retention time of 4·4 min. and another (15%) with a retention time of 3·3 min for the *trans*-isomer VIIB.

Reaction of *m*-methoxythiophenol with the Mannich base, 2-dimethylaminomethylcyclohexanone[6] gave 2-(*m*-methoxyphenylmercaptomethyl)cyclohexanone (VIII). Cyclodehydration of VIII with $HClO_4$ gave 8-methoxy-1,2,3,4-tetrahydro-6-thiaphenanthrenium perchlorate (IX) and 8-methoxy-1,2,3,4,4a,5,6,10b-octahydro-6-thiaphenanthrene (X). Reduction of the perchlorate IX with $NaBH_4$ furnished the 8-methoxy-1,2,3,4,5,6-hexahydro-6-thiaphenanthrene (XI). Catalytic hydrogenation of XI gave the B/C *cis* thiachroman XA. Disproportionation of the thiachromene (XI) also gave the thiachroman (X) and the perchlorate (IX). The thiachroman (X) was a mixture of isomers as indicated by its conversion to the sulphone XII with a m.p. range of 127–145° whereas the *cis* thiachroman (XA) gave a sharp melting sulphone (XIIA), m.p. 151–152°.

Both XII and XIIA ran as a single spot on TLC with the same $R_f$ value in the following solvent systems: benzene–ethyl acetate (1:3, 2:3, 1:1, 9:1); petroleum ether–acetone (3:1); benzene–methanol–ACOH (45:8:4). The original thiachromans likewise showed a single spot on TLC with the same $R_f$ values in the solvent system: benzene–petroleum ether (1:3, 1:1, 3:1). The TLC studies thus precluded the presence of any *ortho*-cyclized isomer XC in the disproportionation product X which was further confirmed by the NMR of the desulphurized thiachromans which showed the typical $A_2B_2$ pattern of a *para* disubstituted phenyl group.

The percentage of *cis* and *trans* isomers in X was determined by VPC. Pure *cis*-thachroman (XA) appeared as a single peak with retention time 67·3 min. Under the same condition X showed two peaks, one (77%) corresponding to the *cis* isomer with retention time of 67 min and another peak (23%) with a retention time of 74 min for the *trans* isomer XB. The peak at 67 min was identical with the *cis* isomer at 67·3 min as shown by the gas chromatography of a mixture of X and XA.

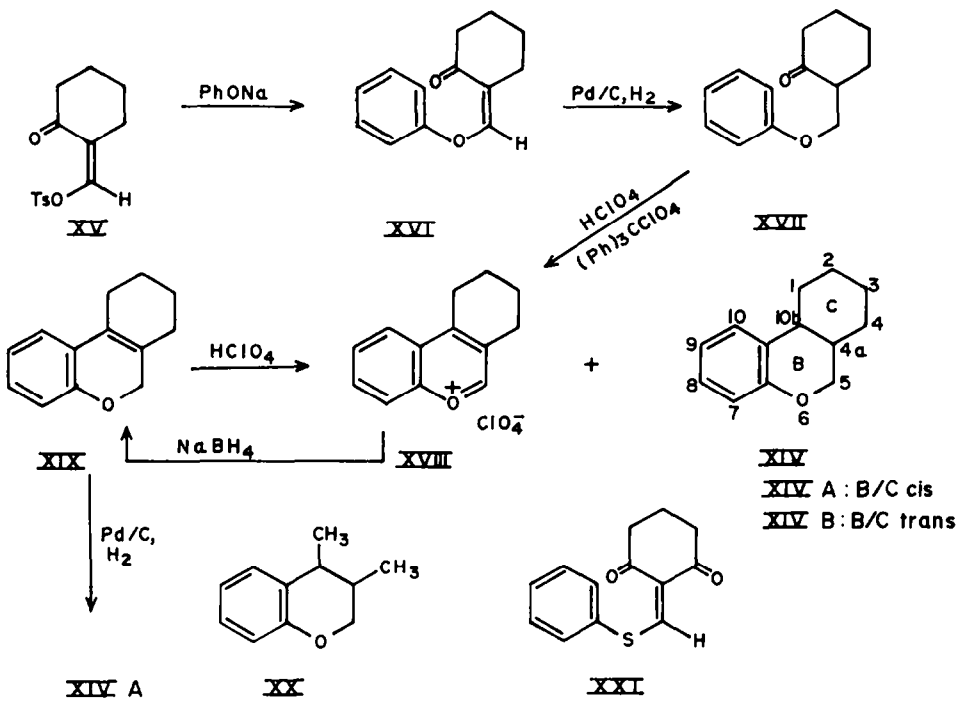
The above VPC results were further confirmed by Raney nickel desulphurization of X and XA to give 1-methyl-2-p-methoxyphenylcyclohexanes (XIII and XIIIA). The VPC study of these was carried out under the same conditions as above. Compound XIIIA appeared as a single peak with retention time of 16·2 min, whereas XIII was shown to be a mixture of 72% *cis* isomer (XIIIA) with retention time 16·2 min and 28% of *trans* isomer (XIIIB) with retention time 13 min.

A careful comparison of the NMR spectra of X and XA showed differences in the aromatic region. In the spectrum of XA, the C-10 aromatic proton appeared as a doublet at $\delta$ 6·93 ($J$ = 9·5 c/s) whereas in the spectrum of X, apart from this doublet, another doublet of weaker intensity (ratio ca. 80:20 by integration) was visible slightly downfield at $\delta$ 7·15 ($J$ = 9·5 c/s). This doublet was assigned to the C-10 proton of the *trans* isomer XB present in X, based on the recent work by Nagata *et al.*[7]

In the oxa series, the tricyclic chroman XIV and its pure *cis* isomer XIVA were synthesized according to the scheme outlined in Chart 2.

2-Tosyloxymethylenecyclohexanone (XV), prepared from 2-hydroxymethylenecyclohexanone was a *cis* compound (the tosyloxy and keto groups on the same side of the double bond) as revealed by its NMR. The olefinic hydrogen appeared at $\delta$ 7·3. This is in agreement with the chemical shifts of $\delta$ 7·2–7·4 for the olefinic protons of *cis*-isomers of alkoxymethylenecyclohexanones.[8] In the *trans* series of isomers, the olefinic proton, being on the same side as the keto group would fall within the deshielding zone of the carbonyl and would thus be expected to appear at lower fields. This is borne out by our work on 2-phenylmercaptomethylene-cyclohexane-1,3-

CHART 2



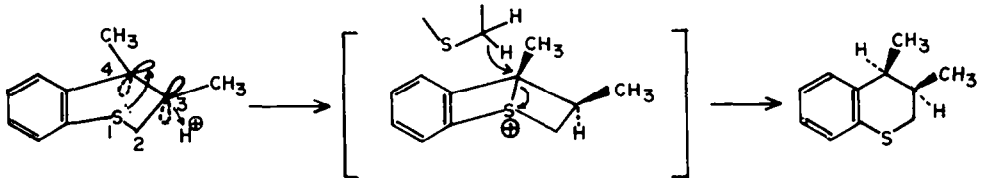

dione (XXI) the olefinic proton of which appears at $\delta$ 8·7. Interaction of XV with sodium phenate gave 2-phenoxymethylenecyclohexanone XVI which was also found to be a *cis*-isomer, the vinyl proton appearing at $\delta$ 7·6 in the NMR spectrum. The *cis* geometry of XVI is confirmed by further work done in this laboratory with derivatives of cyclohexane-1,3-dione to be published later.

The conversion of XV to XVI by nucleophilic displacement with the phenolate anion proceeds with retention of configuration. This is in agreement with the general observation[9] of retention of configuration in the reaction of nucleophiles with vinyl halides activated by electron-withdrawing groups. Lately, nucleophilic substitutions of activated ethylenic halides have become the object of increasing interest.[9] However, further work needs to be done in order to elucidate the exact mechanism of such substitutions. In our laboratory work is in progress along these lines with a variety of substrates and considerable data has accumulated which will soon be published elsewhere.

Catalytic hydrogenation of XVI gave 2-phenoxymethylcyclohexanone (XVII). Cyclization of XVII with 70% perchloric acid in the presence of trityl perchlorate gave 1,2,3,4-tetrahydro-6-oxaphenanthrenium perchlorate (XVIII). Sodium borohydride reduction of XVIII gave 1,2,3,4,5,6-hexahydro-6-oxaphenanthrene (XIX). Disproportionation of XIX with 70% perchloric acid gave the chroman 1,2,3,4,4a,5,6,10b-octahydro-6-oxaphenanthrene (XIV) and the perchlorate (XVIII). Catalytic hydrogenation of XIX gave the pure *cis*-oxaphenanthrene (XIVA). Compound XIV was a mixture of isomers XIVA and XIVB as shown by VPC. Pure *cis*-chroman (XIVA) appeared as a single peak with retention time of 6·4 min. Under the same conditions

XIV showed two peaks, one (65%) identical with the *cis*-isomer (XIVA) with a retention time of 6·4 min and the other (35%) with a retention time of 7·5 min for the *trans*-isomer (XIVB).

In order to elucidate the mechanism of the stereo-selective hydride transfer in the thia-series, further work is in progress with appropriately substituted model substrates. It is known that steric factors play a major role in the transition states of such intermolecular hydride transfers. For example, Kramer[10] has shown that in the hydride transfer between t-butyl carbonium ions and several paraffin donors in concentrated $H_2SO_4$ the reaction is first order in ion and donor concentrations and proceeds through a bimolecular transition state with large steric requirements. The question then arises as to nature of the steric control operating in the thia-series. In view of the fact that in the oxa-series, the bicyclic 3,4-dimethylchroman (XX) is formed as only an equal mixture of *cis/trans* isomers, it appears that the substituents at C-3 and C-4 of such systems are not the only stereochemically controlling factors for hydride transfer. Rather, some other mechanism seems to be operating in the thia-series. One possibility is the participation by the S-atom in the carbonium ion formed by protonation of the thiachromenes to give an intermediate sulfonium ion such as A shown below.




V A VII A

Protonation of V at C-3 would occur with overlap of the π-orbital of the double bond with the proton from one face of the molecule (α-side shown in diagram) synchronously with overlap from the opposite face of the S- lone pair with the now released p-orbital at C-4, the benzylic position. This would lead to the stereochemistry of the sulfonium ion A as shown, with the two $CH_3$-groups *cis* to each other. Attack by hydride from the donor molecule would then occur at C-4 from the side opposite to the newly formed C—S bridge leading to VIIA. It will be seen from the scheme formulated above that the stereochemistry of the end-product is dependent primarily on the stereochemistry of protonation of the thiachromene leading to intermediate A with definite steric configurations at C-3 and C-4.

## EXPERIMENTAL

cis- *and* trans-3,4-*Dimethylthiachromans* (VIIA and VIIB). The $\Delta^3$-thiachromene V (0·72 g), obtained by the reduction of VI, was dissolved in EtOAc (10 ml) and hydrogenated at atm press with 30% Pd/C (0·3 g) at 30°. After the absorption of theoretical amount of $H_2$, the mixture was filtered to remove the catalyst. The residue obtained after removal of solvent gave, on distillation *in vacuo*, the pure *cis*-VIIA, 0·6 g, (yield 85%) as a colourless liquid, b.p. 110–115°/5 mm.

Disproportionation of V by treatment with perchloric acid gave a mixture of VIIA and VIIB as described earlier.[2] The proportion of the two isomers in this mixture was determined by VPC. Using a 6 ft × ¼ in

diam column of 20% polyester on firebrick at 200° and $H_2$ flow-rate of 60 ml/min, pure *cis*-VIIA as described showed a single peak with retention time of 4·4 min. Under similar conditions, the mixture obtained by disproportionation showed two peaks, one (85%) identical with VIIA and another (15%), with a retention time of 3·3 min for the *trans*-VIIB.

2-(m-*Methoxyphenylmercaptomethyl)cyclohexanone* (VIII). A mixture of *m*-methoxythiophenol (3·6 g) and 2-(dimethylaminomethyl)cyclohexanone[6] (3·875 g) was heated at 130–135° for ½ hr under a stream of $N_2$. The reaction mixture was diluted with ether, washed with dil NaOHaq and dil HClaq. The ether layer was dried over $Na_2SO_4$ and ether removed yielding VIII, 5·319 g (yield, 83%), b.p. 137–138°/0·009 mm. (Found: C, 67·2; H, 7·3; S, 12·9. $C_{14}H_{18}O_2S$ required: C, 67·3; H, 7·5; S, 13·1%).

8-*Methoxy*-1,2,3,4-*tetrahydro*-6-*thiaphenanthrenium perchlorate* (IX) *and* 8-methoxy-1,2,3,4,4a,5,6,10b-*octahydro*-6-*thiaphenanthrene* (X). Compound VIII (1·5 g) was stirred with 60% $HClO_4$ for 2 hr at 50–60°. The reaction mixture was extracted with pet ether (60–80°). The extract was washed with $NaHCO_3$aq and water, dried ($Na_2SO_4$) and solvent removed leaving a thick liquid (0·69 g). This was chromatographed over alumina (Brockman grade I) using pet ether (60–80°) as eluent. The major fraction gave a liquid which on distillation gave X, 0·412 g, (yield, 29%) b.p. 120–125°/0·001 mm; $\lambda_{max}$ EtOH (log $\varepsilon$) 221 (4·45), 257 (3·96), 291 (3·47), and 299 (3·40); NMR: ppm, 3·73 (3H s, —OMe), 6·53 ($C_9$H q, $J$ = 9·5 and 3 c/s), 6·55 ($C_7$H d, $J$ = 3 c/s), 6·93 ($C_{10}$H d $J$ = 9·5 c/s) 7·15 ($C_{10}$H of *trans*-isomer, low intensity doublet, $J$ = 9·5 c/s). (Found: C, 71·9; H, 7·6; S, 13·2. $C_{14}H_{18}OS$ requires: C, 71·7; H, 7·74; S, 13·6%). Separation of isomers was done by VPC using a 16 ft × ¼ in diam column of 0·25% $Me_2SiCl_2$ and 20% Apiezon L on 60–80 mesh chromosorb at column temp 285°, He flow-rate 60 ml/min.

The $HClO_4$ layer from the reaction after removal of X was cooled in an ice bath and saturated with ether yielding IX as yellow needles m.p. 172–173°, 0·78 g, (yield, 39%); $\lambda_{max}$ (ACOH + $HClO_4$) (log $\varepsilon$) 273 (4·60), 340 (3·66), 420 (3·86). (Found: S, 9·9; Cl, 10·6. $C_{14}H_{15}O_5ClS$ requires: S, 9·6; Cl, 10·7%).

8-*Methoxy*-1,2,3,4,5,6-*hexahydro*-6-*thiaphenanthrene* (XI). The perchlorate IX (3·324 g) was dissolved in methylene chloride (25 ml). A saturated soln of $NaBH_4$ in EtOH was added dropwise till the soln became colorless. A few drops of AcOH was added to decompose excess $NaBH_4$. The reaction mixture was diluted with water and washed with $NaHCO_3$aq. The methylene chloride (dried over $Na_2SO_4$) was evaporated under reduced press and the residual liquid distilled immediately to give XI, 2·08 g; (yield, 89%), b.p. 140–160° air bath 0·01–0·009 mm; $\lambda_{max}$ EtOH (log $\varepsilon$): 256 (4·14), 330 (3·05): NMR: ppm, 1·70 (4H on $C_2$, $C_3$ m), 2·25 (4H on $C_1$, $C_4$ m), 3·07 (2H broad s —$SCH_2$—), 3·70 (3H s, OMe), 6·5–8·5 (3H aromatic m). (Found: C, 72·1; H, 6·8; S, 14·0. $C_{14}H_{16}OS$ requires: C, 72·39; H, 6·94; S, 13·7%).

*Disproportionation of* XI. Compound XI (3·38 g) was stirred with 60% $HClO_4$ (20 ml) for 2 hr at 60°. The reaction mixture was worked up as in the cyclodehydration of VIII to give X (yield 38%) and IX (yield 34%).

cis-8-*Methoxy*-1,2,3,4,4a,5,6-10b-*octahydro*-6-*thiaphenanthrene* (XA). The perchlorate IX (2·67 g) was reduced with $NaBH_4$ as above, the residual liquid after removal of methylene chloride was dissolved in EtOAc and hydrogenated with 10% Pd/C (0·8 g) at 45 lb/sq in for 23 hr. After removal of solvent the residual oil was distilled to give XA; 1·7 g (yield, 90%) b.p. 130–135°/0·001 mm. (Found: C, 71·5; H, 7·9; S, 13·5. $C_{14}H_{18}OS$ requires: C, 71·7; H, 7·74; S, 13·6%). The NMR spectrum of XA was identical with that of XV except for the absence of the low intensity doublet at $\delta$ 7·15. The gas chromatography of XA was carried out under the same conditions as for X.

8-*Methoxy*-1,2,3,4,4a,5,6,10b-*octahydro*-6-*thiaphenanthrene*-6,6-*dioxide* (XII). A mixture of X (0·380 g), ACOH (3 ml) and 30% $H_2O_2$ (4 ml) was stirred for ½ hr at room temp and the mixture left overnight. 30% $H_2O_2$ (0·5 ml) was added and the reaction mixture left at room temp for a further period of 24 hr, after which it was cooled. The white crystalline ppt was filtered off and washed with dil ACOH to give XII 0·40 g, (yield 93%), m.p. 127–145°. Crystallization from dilute ACOH, gave colourless needles, m.p. 127–141°. (Found: C, 63·1; H, 6·9; S, 12·3. $C_{14}H_{18}O_3S$ requires: C, 63·1; H, 6·8; S, 12·0%).

cis-8-*Methoxy*-1,2,3,4,4a,5,6,10b-*octahydro*-6-*thiaphenanthrene*-6,6-*dioxide* (XIIA). Oxidation of XA (0·475 g) as above gave XIIA (0·485 g; yield 91%) m.p. 150–152°. On crystallization from dil AcOH thick white needles m.p. 151–152° of XIIA was obtained. (Found: C, 62·2; H, 6·8; S, 11·9. $C_{14}H_{18}O_3S$ requires: C, 63·1; H, 6·8; S, 12·0%).

*Desulphurization of* X *and* XA. The thiachroman X or XA (0·105 g) was refluxed in EtOH (15 ml) under stirring with Raney Ni (1·1 g) for ½ hr. The reaction mixture was filtered and washed with EtOH. Alcohol was evaporated under reduced press and the residual liquid distilled to give XIII or XIIIA (0·085 g) b.p. 80–100° air bath/0·25 mm. NMR of XIIIA; ppm, 0·67 ($CH_3$ d, $J$ = 7 c/s), 1·62 (9H alicyclic m) 2·76 (1H benzylic, m), 3·73 (3H s, OMe) 6·87 (4H aromatic AB q, $J$ = 9 c/s).

*2-Tosyloxymethylenecyclohexanone* (XV). A soln of 2-hydroxymethlenecyclohexanone[11] (13 g) in methylene chloride (50 ml) and pyridine (10 ml) was cooled to −10°. To the above cooled soln was added during ½ hr a soln of *p*-toluenesulphonyl chloride (20 g) in methylene chloride (50 ml) and pyridine (6 ml). The reaction mixture was stirred for 3 hr maintaining the temp at 0° to −5°. Ice cold water was then added to the reaction mixture and the methylene chloride layer washed thoroughly with water (8–10 times). Removal of methylene chloride under reduced press gave XV as a white solid, 23 g, (yield 80%). Compound XV is stable in soln but decomposes in the solid state; $\nu_{max}$ ($CCl_4$); 1185 $cm^{-1}$ and 1378 $cm^{-1}$ (—O—$SO_2$—), 1680 $cm^{-1}$ (conjugated C=O); NMR: 7·3 ppm (1H olefinic, tr, $J$ = 2 c/s).

*2-Phenoxymethylenecyclohexanone* (XVI). To sodium phenate [from phenol (2·35 g) and NaH (1·2 g, 50% suspension in oil)] was added a soln of XV (7 g) in benzene (100 ml) and the reaction mixture stirred for 2 hr and left overnight. The mixture was filtered and the filtrate washed with water, dried ($Na_2SO_4$) and benzene removed to give XVI, 4·12 g, (yield 82%). The product was purified by passing over neutral $Al_2O_3$, Grade IV, and eluting with pet. ether (60–80°). The product from the major fraction on distillation gave XVI as a colourless oil, b.p. 120–140° air-bath/0·2 mm; $\nu_{max}$ ($CCl_4$); 1690 $cm^{-1}$ (C=O), 1620 $cm^{-1}$ (—C=C—); NMR: 7·6 ppm (1 H, olefinic, tr, $J$ = 2 c/s). (Found: C, 76·9; H, 7·3. $C_{13}H_{14}O_2$ requires: C, 77·2; H, 6·9%).

*2-Phenoxymethylcyclohexanone* (XVII). Compound XVI (2·786 g) was hydrogenated at atm press in EtOAc in presence of 5% Pd/C (0·50 g) till $H_2$ absorption ceased (6 hr). The reaction mixture was filtered and the solvent removed. The residue was dissolved in ether and the soln washed with 1% NaOH aq, water, dried ($Na_2SO_4$) and ether removed. The residue on distillation gave XVII, 2·42 g (yield 86%) b.p. 120°/0·1 mm; $\nu_{max}$: 1710 $cm^{-1}$ (C=O). (Found: C, 76·0; H, 8·0. $C_{13}H_{16}O_2$ requires: C, 76·4; H, 7·8%).

1,2,3,4-*Tetrahydro-6-oxaphenanthrenium perchlorate* (XVIII). To trityl perchlorate (3·645 g) suspended in 70% $HClO_4$ (8 ml) and cooled in an ice bath was added the ketone XVII (2·171 g). The reaction mixture was stirred for 1 hr at room temp, after which it was cooled in an ice salt bath and saturated with ether. The pale yellow crystalline ppt was filtered off and washed with ether to give XVIII 1·554 g (yield, 51%), m.p. 200–202°; $\lambda_{max}$ ($HClO_4$) (log ε): 240 (4·33), 262 (3·45), 324 (3·99). Found: Cl, 12·9. $C_{13}H_{13}ClO_5$ requires: Cl, 12·5%).

1,2,3,4,5,6-*Hexahydro-6-oxaphenanthrene* (XIX) The perchlorate XVIII (115 mg) was reduced with $NaBH_4$ as described above. The liquid obtained was distilled immediately to give XIX, 60 mg; (yield, 80%) as a colourless liquid b.p. 100–120°/0·1 mm; $\lambda^{max}$ EtOH (log ε): 305 (3·71), 266 (3·78); NMR: ppm, centred at 2·0 (8H m, methylene protons), 4·51 (2H, m —$OCH_2$—), 6·85 (4H, aromatic), no olefinic protons.

cis-1,2,3,4,4a,5,6,10b-*Octahydro-6-oxaphenanthrene* (XIVA). The perchlorate XVIII (300 mg) was reduced with $NaBH_4$ as above and the liquid obtained on removal of methylene chloride was dissolved in EtOAc (10 ml) and hydrogenated at atm press in the presence of 5% Pd/C (50 mg) for 3 hr. The mixture was filtered, EtOAc removed by distillation and the residual liquid distilled to give XIVA 160 mg (yield 81%) as a colourless liquid b.p. 100°/0·1 mm. (Found: C, 83·2; H, 8·6. $C_{13}H_{16}O$ requires: C, 82·9; H, 8·5%). VPC on a 2 ft × ¼ in diam tung oil column (column temp 185° $H_2$ flow rate 100 ml/min) gave retention time 6·4 min.

*Disproportionation of* XIX. The perchlorate XVIII (187 mg) was reduced with $NaBH_4$ as above and the liquid obtained treated with 70% $HClO_4$ (1 ml) in the cold. The reaction mixture was kept at room temp for 1 hr and worked up as usual to give the chroman XIV, 52 mg (yield, 35%) b.p. 100°/0·1 mm. (Found: C, 82·9; H, 8·4. $C_{13}H_{16}O$ requires: C, 83·0; H, 8·5%). VPC was carried out under the conditions used for XIVA. From the $HClO_4$ layer was obtained the perchlorate XVIII, 97 mg (yield, 34%).

*Acknowledgement*—We are grateful to Professors R. H. Martin and G. Van Binst, University of Brussels, for their help in VPC analyses of the above compounds and to Dr. Madhavan Nair and Professor C. N. R. Rao for determination of NMR spectra.

## REFERENCES

[1] B. D. Tilak and V. M. Vaidya, *Tetrahedron Letters* 487 (1963).
[2] B. D. Tilak, H. S. Desai, C. V. Deshpande, S. K. Jain and V. M. Vaidya, *Tetrahedron* **22**, 7 (1966).
[3] B. D. Tilak and S. K. Jain, Communicated to the *Indian J. Chem.*
[4] C. V. Deshpande, Ph.D. Thesis, Bombay University, 78 (1965).
[5] B. D. Tilak and Z. Muljiani, *Tetrahedron* **24**, 949 (1968).
[6] R. L. Frank and R. C. Pierle, *J. Am. Chem. Soc.* **73**, 724 (1951).

[7] W. Nagata, T. Tarasawa and K. Tori, *Ibid.* **86**, 3746 (1964).
[8] L. Bardon, J. Elguero and R. Jacquier, *Bull. Soc. Chim. Fr.* 297 (1967).
[9] G. Marchese, G. Modena and F. Naso, *Tetrahedron* **24**, 663 (1968).
[10] G. K. Kramer, *J. Org. Chem.* **30**, 2671 (1965).
[11] Pl. A. Plattner, P. Treadwell and C. Scholz, *Helv. Chim. Acta* **28**, 771 (1945).