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# ÉTARD REACTION—VI[1]

## OXIDATION OF *CIS* AND *TRANS*-DECALINE WITH CHROMYL CHLORIDE

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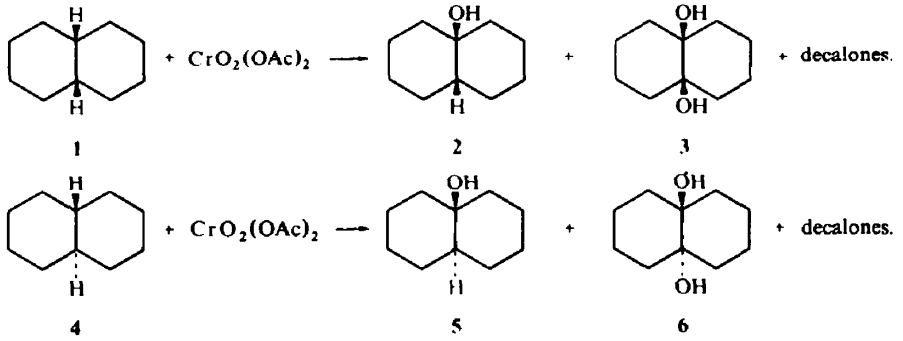
**Abstract**—Oxidation of *trans*-decaline with chromyl chloride yielded a mixture containing a small amount of *trans*-9-decalol and several ketones among which spiro [4.5]decan-6-one, *trans*-1-decalone, *cis*-1-decalone, 9,10-octal-1-one and 1-tetralone were identified. The main reaction product, spiro[4.5]-decan-6-one, for the first time is reported to appear among the products of decaline oxidation. Oxidation of *cis*-decaline with chromyl chloride yielded *cis*-9-decalol and a mixture of the same ketones as above, but in a slightly different ratio. The reaction mechanisms are discussed.

ALTHOUGH the oxidation of decalines with chromyl chloride has not been reported, their oxidation with chromic acid has been studied extensively.

In 1961, Rocek[2] studied kinetically the oxidation of *cis*- and *trans*-decaline (and a number of other alkanes and cycloalkanes) with chromic acid in acetic acid, in the presence of sulphuric acid, without identifying the reaction products.

In the same year, Schleyer *et al.*[3] observed that the oxidation of *cis*- and *trans*-decaline with chromyl acetate (chromic anhydride in acetic anhydride) is stereospecific. From *cis*-decaline (**1**), these authors obtained a mixture of *cis*-9-decalol (**2**; 32%), *cis*-9,10-decalin-diol (**3**; 5%) and decalones (4%). *trans*-Decaline (**4**), oxidized under the same conditions,[3] yielded a mixture of *trans*-9-decalol (**5**; 7%), *trans*-9,10-decalin-diol (**6**; 3%) and decalones (8%).




The oxidation of decalines with ozone[4] and oxygen[5] yields decaline-9-hydroperoxide, the reduction[7,8] and rearrangement[5–8] of which have been discussed in the literature.

The studies of Hickinbottom *et al.*[9] on the oxidation of alkanes with chromyl acetate show that the reaction is specific to a certain extent, the tertiary C atoms being attacked preferentially. The ratio[9] of the reaction rates in the series

$CH_3:CH_2:CH$ (prim:sec:tert) is about $1:10^2:10^3$. In the case of decalines the attack takes place at the tertiary C atoms, the major reaction products being the corresponding tertiary alcohols. The small amounts of decalones formed in this reaction, indicate that the secondary C atoms of decaline are also oxidized.

The Étard oxidations of other hydrocarbons[10] (and especially the oxidation of methylcyclohexane[11]), suggest that the decalones should be the oxidation product of octalines produced by primary oxidation of decalines. The epoxidic intermediates formed from octalines by oxidation would then rearrange[11, 12] to decalones. In order to check this hypothesis, all the ketones and other reaction products were identified and the ratio of the oxidation products of *cis*- and *trans*-decaline with chromyl chloride determined and compared with the products of chromic acid oxidation.

The complex of *trans*-decaline with chromyl chloride, prepared according to the usual method,[11] in carbon tetrachloride as a solvent, afforded on decomposition with water, at 0°, a mixture of reaction products. They were detected and isolated by preparative gas-chromatography and their IR spectra were compared with those of authentic samples. From Table 1 and Fig. 1, in which these results are shown, it can be seen that the major products obtained from *trans*-decaline are carbonyl compounds, namely: spiro[4.5]decan-6-one, *trans*- and *cis*-1-decalone, 9,10-octal-1-one and 1-tetralone. The product of the primary, stereospecific oxidation, *trans*-9-decalol, appeared only in a small amount (1·7%). In addition dehydrogenation/oxidation products naphthalene and 1-tetralone were produced in appreciable amounts (3·7% and 13·3%, respectively).

The oxidation of *trans*-decaline with chromic acid afforded *trans*-9-decalol as the major reaction product (71·8%), the ketones appearing only in small amounts (Table 1). The oxidation with chromic acid yielded spiro[4.5]decan-6-one only in a small amount, whereas in the oxidation with chromyl chloride it is a major product. This spiro-ketone was not observed by earlier workers.

From the complex of *cis*-decaline with chromyl chloride, reaction products similar to those obtained by oxidation of *trans*-decaline were isolated and identified. However, in this case the tertiary alcohol was *cis*-9-decalol, formed by stereospecific oxidation of *cis*-decaline, and the ketones, as shown in Table 1 and Fig. 1, appeared in ratios different from those observed in the oxidation of *trans*-decaline.

## DISCUSSION

The absence of 2-decalones (*cis* and *trans*) among the products of oxidation of decalines demonstrates that the carbonyl compounds formed in these reactions do not result from the competitive oxidation of the secondary C atoms of the hydrocarbons. On the other hand, the presence of spiro[4.5]decan-6-one (**8**) indicates the rearrangement of an epoxidic intermediate. In 1929, Hückel[13] hydrolysed 9,10-epoxi-decaline (**7**) with perchloric acid (0·02N) and obtained the glycol **6** which, in the presence of concentrated sulphuric acid, rearranged to spiro[4.5]decan-6-one (**8**):

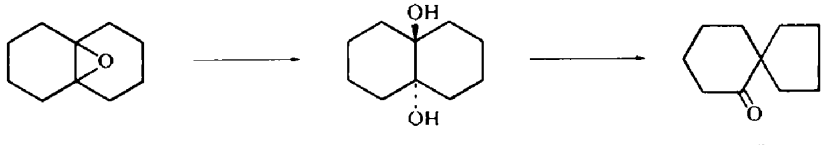



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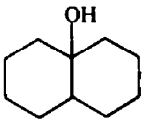
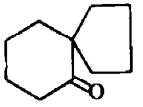
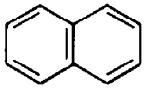
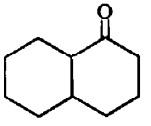
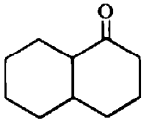
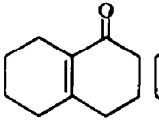
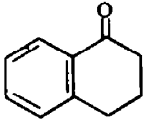
TABLE 1. THE PRODUCTS OF THE OXIDATION OF DECALINES WITH CHROMYL CHLORIDE AND CHROMIC ACID

| Starting material (oxidizer) \ Oxidation products (mole %) |  |  |  |  *trans* |  *cis* | |  |  |
|---|---|---|---|---|---|---|---|---|
| *trans*-Decaline[a] (Chromyl chloride) | 1·7 (*trans*) | 17·8 | 3·7 | 33·4 | 8·7 | 4·5 | 17·0 | 13·3 |
| *cis*-Decaline[b] (Chromyl chloride) | 11·6 (*cis*) | 26·5 | 1·3 | 16·0 | traces | 8·2 | 17·5 | 19·0 |
| *trans*-Decaline[c] (Chromic acid) | 71·8 (*trans*) | 1·9 | 1·4 | 13·5 | 9·6 | 0·8 | 1·0 | traces |

34% yield, based on the chromyl chloride used.

[b] 35% yield, based on the chromyl chloride used.

[c] Oxidation with $Na_2Cr_2O_7$—$H_2SO_4$, in 90% AcOH, at +8°; 66% yield. based on the *trans*-decaline consumed.

[d] This compound is not 2-decalone.

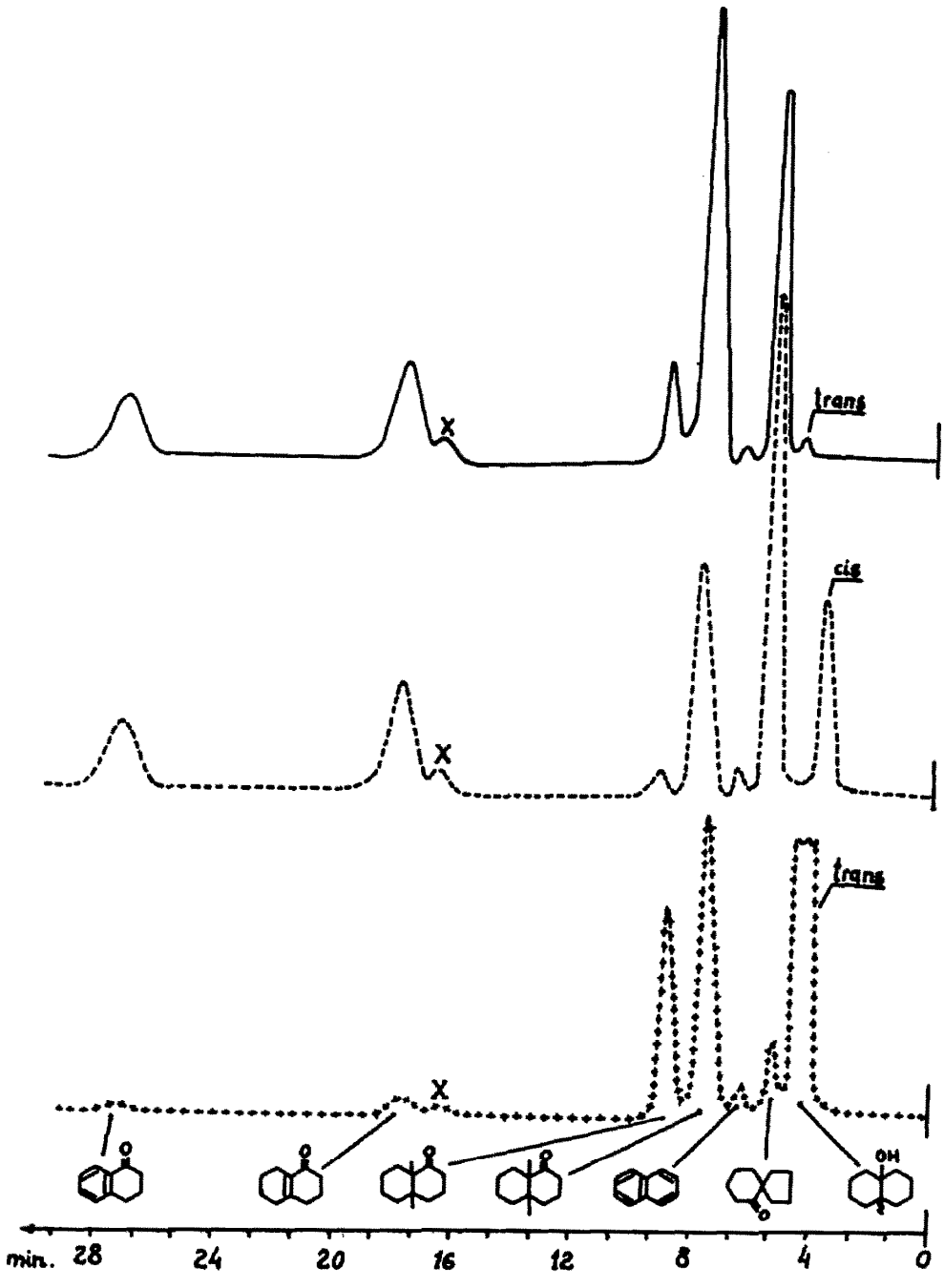
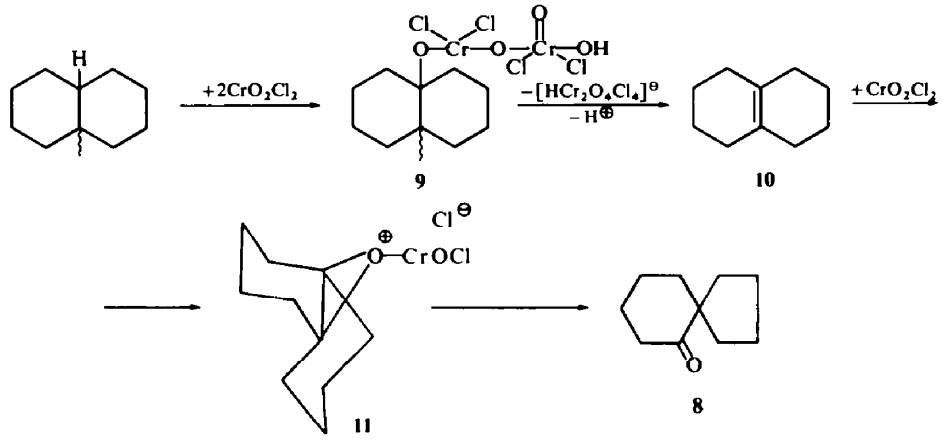
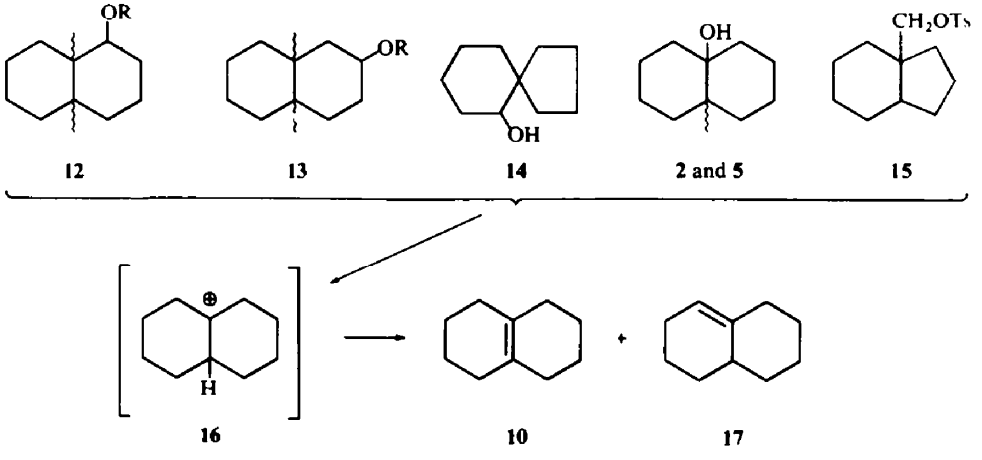



FIG. 1 Gas-chromatograms of the products of oxidation of *trans*-decaline (———) and *cis*-decaline (– – – –) with chromyl chloride, and of *trans*-decaline with chromic acid (+++++).

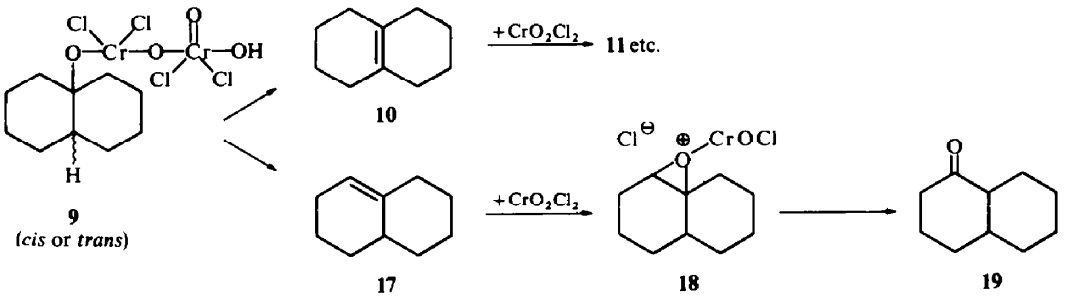
It can be assumed, by analogy with earlier observations,[14,15] that the initial complex of decalines with chromyl chloride (**9**) gives by elimination 9,10-octaline (**10**). The reaction of the latter with chromyl chloride would yield the epoxidic intermediate **11**, the rearrangement of which accounts for the formation of spiro-ketone **8**:




It is well known that the elimination of water from 1-decalol (**12**, R = H)[16] or 2-decalol (**13**, R = H),[17] as well as the solvolysis of the corresponding toluene-sulphonates (**12** and **13**, R = Ts)[18,19] yields a mixture of 9,10-octaline (**10**) and 1,9-octaline (**17**), in a ratio of about 4:1. These are the elimination products of the most stable carbonium ion **16**. This ion (**16**) is probably an intermediate in the dehydration of spiro[4.5]decan-6-ol (**14**)[20,21] and *cis*- and *trans*-9-decalol,[22] and of the solvolysis[23] of the toluene-sulphonate of octahydro-indenyl-8-carbinol (**15**):




It is thus likely that the elimination of the chromyl group from the Étard complexes of decalines results also in a mixture of 9,10- and 1,9-octaline. The reaction of the latter with chromyl chloride would give an epoxidic derivative **18**, the rearrangement of which (to 1-decalone **19**) could account for the presence of these ketones among the reaction products:




The difference in ketone ratio in the oxidation of *trans*-decaline and of *cis*-decaline is most probably due to the different ways by which the chromyl groups from the Étard complexes **9** (*cis* and *trans*) are eliminated.

In this context it is interesting to examine the configurational factors which govern eliminations from other 9-substituted derivatives of *cis*- and *trans*-decaline. Such a reaction, the deamination by nitrous acid of both *trans*- and *cis*-9-decalylamine was extensively studied by Hückel[24] and Dauben.[25] These authors obtained a mixture of 9-decalols (*cis* and *trans*) (20%), 9,10-octaline (70%) and 1,9-octaline (10%) from *trans*-9-decalylamine and a mixture of *cis*-9-decalol (40%), 9,10-octaline (10%) and 1,9-octaline (35%) from *cis*-9-decalylamine.

*trans*-9-Decalol is thermodynamically more stable than the *cis*-isomer (by about 2·4 kcal/mole[26]). On the other hand, the latter is less hindered[25] (by axial 1,3-interactions) in the close vicinity of the OH group. Therefore, one may assume that the favoured formation of *cis*-9-decalol in the deamination of *cis*-9-decalylamine is controlled by steric interactions and not by the overall thermodynamic stability of the products.[25]

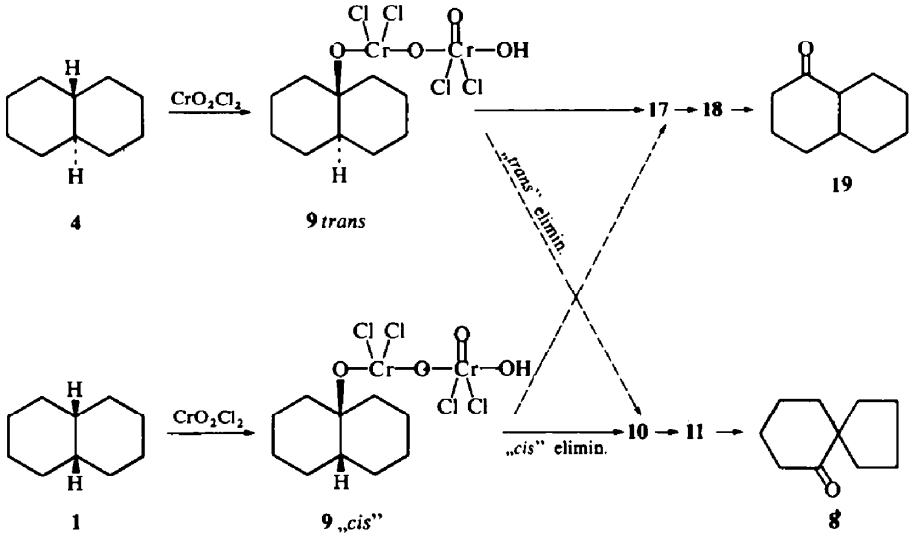
This could also explain the formation of the tertiary alcohol in greater amounts in the oxidation of *cis*-decaline with chromyl chloride (11·6%, Table 1) and with chromyl acetate[3] (32%), than in the oxidation of *trans*-decaline with chromyl chloride (1·7%, Table 1) or with chromyl acetate[3] (7%).

It should also be noted that the elimination accompanying the deamination of *trans*-9-decalylamine leads preferentially to 9,10-octaline (70% of **10**, as compared to 10% of **17**), whereas *cis*-9-decalylamine gives preferentially 1,9-octaline (35% of **17**, as compared to 10% of **10**).[24,25] Therefore in the eliminations accompanying the deamination of 9-decalylamines the "axial–axial" type of transition state is preferred ("*trans*" elimination).[27]

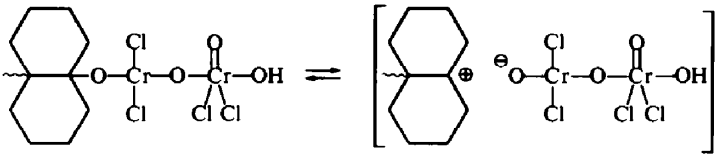
In the case of the oxidation of decalines this rule seems to be reversed. The product analysis (Table 1) suggests that the two Étard complexes, **9**-*cis* and **9**-*trans*, which resulted from *cis*- and *trans*-decaline, respectively, underwent "*cis*" elimination.

As a matter of fact, the major products of *trans*-decaline oxidation are 1-decalones which are formed by "*cis*" elimination from the *trans*-**9**-complex (the ratio decalones + 9,10-octal-1-one to spiro[4.5]decan-6-one is 3·3:1 in the oxidation with chromyl chloride and 12·6:1 in the oxidation with chromic acid). Likewise, the major product of the *cis*-decaline oxidation (which is the final product of a "*cis*" elimination from the *cis*-**9**-complex) is probably spiro[4.5]decan-6-one (the ratio decalones + 9,10-octal-1-one to spiro[4.5]decan-6-one is 1·2:1, Table 1). These results cannot be accounted for by an E1 elimination of the usual type, by which both decalines would

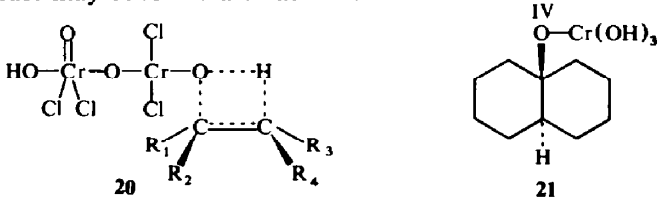
give the same 9,10-octaline, the product of a Saytzeff-type elimination. The latter would subsequently undergo oxidation and rearrangement to afford spiro[4.5]decan-6-one.




The following explanation may be viewed as far as "*cis*" elimination leading to 9,10-octaline (**10**) is concerned. As the carbon tetrachloride, the usual solvent of the Étard reaction, completely lacks basicity, we are bound to admit that the ion pair of **9a** type is not able to dissociate.




Therefore, the proton of the β-position which is eliminated can be accepted only by the chromyl "gegen-ion" ($HCr_2O_4Cl_4^-$). The transition state of this type of E1 elimination, studied by Skell[28] and Cram,[29] would lead to a "*cis*" elimination, which in the present case may be formulated as in **20**.




The *trans*-decaline oxidation with chromic acid in acetic acid, may proceed through an intermediate tetravalent chromium ester (**21**) similar to that assumed to occur primarily in the hydrocarbon oxidations with chromyl chloride.[14,30] Its

formation should be favoured by the reduced solvating power and basicity of the acetic acid. The rate of hydrolysis of ester **21** is obviously greater than the rate of elimination leading to alkenes. Consequently, the main product of this oxidation is *trans*-9-decalol (71·8%, Table 1).

The oxidation with chromic acid of primary or secondary alcohols, which proceeds through chromic esters,[31,32] is never accompanied by β-elimination.[33] However, the oxidation of branched alkanes and cycloalkanes and of arylalkanes, with chromyl chloride or chromic acid,[1,10–12,14,15] is always accompanied by elimination. We may suppose therefore that such eliminations leading to olefins occur preferentially in non-dissociated ion pairs, such as the assumed intermediates of the hydrocarbon oxidation.

## EXPERIMENTAL

*Starting materials*

trans-*Decaline* was prepared by isomerization of commercial decaline (Merck), with $AlCl_3$;[34] b.p.$_{760}$ 184·5–185·5°; 98% purity (VPC and NMR).

cis-*Decaline* was isolated preparatively, by VPC, from commercial decaline (Merck, containing 60% *trans*-decaline and 40% *cis*-decaline); 99·5% purity (VPC and NMR).

*Chromyl chloride* was prepared according to Sisler,[35] was used immediately after distillation.

*The Étard complex of* trans-*decaline*

In a 500 ml, 4-necked flask, provided with mechanical stirring, condenser (with $CaCl_2$ tube), thermometer, dropping funnel and inert gas (argon) inlet tube, the soln of 34·5 g (0·25 mole) *trans*-decaline in 70 ml dry $CCl_4$ was introduced. Then a soln of 62 g (0·4 mole; 32·4 ml) $CrO_2Cl_2$ in 65 ml dry $CCl_4$ was added dropwise, in the course of 4 hr, with stirring, in an inert gas atmosphere, at 38–39°. (Initially, external heating on a water bath was necessary, but after half of $CrO_2Cl_2$ was added the heat evolved maintained the required temp). The reaction mixture was allowed to stand for 3 days in an inert gas atmosphere, at room temp. The complex was then filtered under argon and washed with 250 ml dry $CCl_4$. The dry complex (71 g) was thus obtained, as a brown, insoluble, hygroscopic powder.

*The Étard complex of* cis-*decaline*

In a 25 ml, single necked flask, a soln of 1·5 g (0·0108 mole) *cis*-decaline in 3·5 ml dry $CCl_4$ was introduced. The flask was tightly stoppered (ground glass stopper) and cooled in an ice bath. A cold soln (0°) of 3·4 g (0·022 mole) $CrO_2Cl_2$ in 4 ml dry $CCl_4$ was then added at once. The flask was again stoppered and left in the ice-bath, with occasional shaking, until the ice melted, and afterwards for 3 days at room temp. After filtration and washing with $CCl_4$, 4·5 g dry complex was obtained as brown, insoluble, hygroscopic powder.

*Oxidation of* trans-*decaline with chromic acid*

In a 1·5 l, 4-necked flask, provided with mechanical stirring, dropping funnel, condenser and thermometer, a mixture of 450 ml glacial AcOH and 50 ml 2N $Na_2Cr_2O_7$[36,37] was added, and then, with stirring and cooling (in an ice-bath), 50 ml conc $H_2SO_4$.

When the mixture reached 8°, 6·9 g (0·05 mole) *trans*-decaline was added in a single portion, the ice-bath was removed and the reaction mixture allowed to reach 15°, with vigorous stirring (30 min were required). The mixture was then rapidly cooled at 0° (using an ice-salt bath), and a cold soln of 65 g NaOH in 600 ml water with ice was rapidly added. The crystalline $Na_2SO_4$ was filtered off and the filtrate extracted 5 times with 100 ml portions $CH_2Cl_2$. The ppt was also extracted with 100 ml $CH_2Cl_2$.

The combined extracts were washed with 5% $NaHCO_3$aq, dried over $K_2CO_3$ and yielded 5·4 g liquid residue after removal of solvent. On vacuum distillation (with a 30 cm column), two fractions were obtained: (1) b.p.$_5$ 45–50°, 2 g, consisting of *trans*-decaline; (2) b.p.$_5$ 75–135°, 3·2 g, containing the products of oxidation of *trans*-decaline. The second fraction was analyzed by VPC (Table 1).

*Analysis of the products of the oxidation reactions*

*The VPC analysis* of the reaction products obtained by decomposition with water of the Étard complexes of *cis*- and *trans*-decaline and by oxidation of *trans*-decaline with chromic acid, was performed on a LAC-728 column (20% on Chromosorb W, 1·5 m, at 160° and 20 ml $H_2$/min).

The qualitative and quantitative results are given in Table 1 and Fig. 1, so that only the identification of the main products is described.

trans-9-*Decalol* (**5**) obtained only by oxidation of *trans*-decaline with chromyl chloride and with chromic acid, was isolated by preparative VPC; m.p. 52° (lit.[21] 53–54°). Found C, 77·58; H, 11·77. Calc. for $C_{10}H_{18}O$: C, 77·86; H, 11·77%.

IR spectrum ($CCl_4$ and $CS_2$) identical with that recorded by Hückel.[19]

cis-9-*Decalol* (**2**) obtained only by oxidation of *cis*-decaline with chromyl chloride, was isolated by preparative VPC; m.p. 63° (lit.[21] 65·5°).

IR spectrum (in $CCl_4$ and $CS_2$) identical with that recorded by Hückel.[19]

*Spiro*[4.5]*decan-6-one* (**8**). The VPC retention time was identical with that of an authentic sample prepared according to Mousseron.[38] IR spectrum[39] (neat) identical with that of the authentic sample.

trans-1-*Decalone* (**19**-*trans*) was isolated by preparative VPC. IR spectrum (neat) identical with those recorded by Gutsche[40] and by Djerassi.[41]

cis-1-*Decalone* (**19**-*cis*) was isolated by preparative VPC. IR spectrum (neat) identical with those recorded by Gutsche[40] and by Djerassi.[41]

9,10-*Octal*-1-*one* isolated by preparative VPC from the Étard complex of *trans*-decaline. 2,4-Dinitrophenylhydrazone, dark-red needles, m.p. 268° (dec) from EtOH (lit.[42] 263° and[43] 264·5–265°).

IR spectrum (in $CCl_4$) identical with that recorded by House.[43]

*Naphthalene and* 1-*tetralone* were identified by VPC by comparing their retention times with those of an authentic sample.

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