# ÉTARD REACTION—III<sup>1</sup> OXIDATION OF N-PROPYLBENZENE AND METHYLCYCLOHEXANE WITH CHROMYL CHLORIDE

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Abstract—Étard oxidation of n-propylbenzene yields a number of products among which benzaldehyde, methyl benzyl ketone, propiophenone, 1-chloro-1-phenylpropane, 1-phenylpropan-1-ol, 1-phenyl-1-chloropropan-2-one and 1-phenyl-2-chloropropan-1-one were identified. The same products were obtained by treatment of 1-phenylpropene and 1,2-epoxy-1-phenylpropane with chromyl chloride. Presumably all these compounds result from a common intermediate possessing an epoxide like structure. The oxidation by chromyl chloride of methylcyclohexane also leads to a larger number of products than previously known, namely: 1-methyl-1-cyclohexanol, hexahydrobenzaldehyde, 1-methylcyclopentylaldehyde, 2-methylcyclohexanone and 1-methyl-1-chlorocyclohexan-2-one. The last three compounds were produced also in the reaction of 1-methylcyclohexene with chromyl chloride. The mechanism of these reactions is discussed.

THE oxidation of n-propylbenzene with chromyl chloride was first investigated by Étard<sup>2</sup> who reported hydrocinnamaldehyde. A few years later, von Miller and Rhode<sup>3</sup> and then Dollfus<sup>4</sup> showed that the principal products formed in the hydrolysis of the n-propylbenzene complex with chromyl chloride are: methyl benzyl ketone, benzaldehyde and an unidentified chloroketone together with small amounts of propiophenone. Wiberg *et al.*<sup>5</sup> identified in the reaction product of n-propylbenzene with chromyl chloride (the ratio hydrocarbon: oxidant being 1:1) three components: 1-chloro-1-phenylpropane (yield 30%), methyl benzyl ketone (18%), and propiophenone (3·3%). The last compound could be found only in the hydrolysis products of the complex, while 1-chloro-1-phenyl-propane and methyl benzyl ketone were isolated both from the filtrate (24% and 6% respectively) and from hydrolysis of the complex (6·5% and 10·5% respectively).

On oxidation of n-propyl- $\beta d_2$ -benzene, Wiberg *et al.*<sup>5</sup> obtained methyl benzyl ketone containing 60% of the initial deuterium migrated in the  $\alpha$  position. The same authors by oxidizing 1-phenylpropene with chromyl chloride isolated as sole reaction product methyl benzyl ketone.

In a previous paper, Necsoiu *et al.*<sup>6</sup> obtained on oxidation of n-propylbenzene with chromyl chloride results differing from the above authors. In particular, by decomposing the Étard complexes with aqueous sulphur dioxide solution, they isolated

<sup>4</sup> W. Dollfus, Ber. Disch. Chem. Ges. 26, 1970 (1893).

<sup>&</sup>lt;sup>1</sup> Paper II, Tetrahedron 22, 3037 (1966).

<sup>&</sup>lt;sup>2</sup> A. Étard, Ann. Chim. Phys. (5) 22, 218 (1881).

<sup>&</sup>lt;sup>8</sup> W. von Miller and G. Rhode, Ber. Dtsch. Chem. Ges. 23, 1070 (1890).

<sup>&</sup>lt;sup>5</sup> K. B. Wiberg, B. Marshall and G. Foster, Tetrahedron Letters 345 (1962).

<sup>&</sup>lt;sup>6</sup> I. Necșoiu, A. T. Balaban, I. Pascaru, E. Sliam, M. Elian and C. D. Nenitzescu, *Tetrahedron* 19, 1133 (1963).

besides the two mentioned ketones, a phenylpropanol. The present investigation has been undertaken in order to clarify these discrepancies.

All experiments were performed using carbon tetrachloride as solvent, the molar ratio hydrocarbon:chromyl chloride being 1:1, which means 100% excess of hydrocarbon if the composition of the Étard complex is regarded as being RH·2CrO<sub>2</sub>Cl<sub>2</sub>. The chromyl chloride was completely used in the reaction.

When the presence of any traces of water was carefully excluded the filtrate contained neither ketones nor any other oxygenated compound. However, the filtrate and the washings contained all the 1-chloro-1-phenylpropane. Ketones are formed only on hydrolysis of the Étard complex, so that their presence in the filtrate may be considered as originating from partial hydrolysis during the preparation or filtration operations. The presence of 1-chloro-1-phenylpropane among the hydrolysis products of the Étard complex<sup>5</sup> proves that the precipitate was not sufficiently washed after filtration.

The 1-chloro-1-phenylpropane results from a secondary reaction and is formed in amounts varying from traces to a yield of 30%, based on the chromyl chloride introduced in the reaction. The conditions which promote this side reaction of the Étard reaction are not understood, nor are they reproducible. With certain samples of chromyl chloride, the chlorination could be reduced to less than 1%.

On hydrolysis of the Étard complex of n-propylbenzene, a mixture of six compounds was obtained. When an aqueous solution of  $SO_2$  was used for the decomposition a seventh reaction product appeared, namely 1-phenylpropan-1-ol (Table 1). The composition of the reaction mixture was established by gas chromatography, the retention times of each compound being compared with authentic samples. Six of the reaction products were subsequently isolated in a pure state by preparative VPC and identified by comparing their IR spectra with authentic samples or by preparation of derivatives.

Table 1 indicates that the yields in the Étard oxidation products correspond to about 80% based on the chromyl chloride introduced in the reaction (considering that 1 mole of hydrocarbon binds 2 moles of chromyl chloride, the rest of the chromyl chloride being consumed mostly in the formation of 1-chloro-1-phenylpropane). An increase in the temperature during the Étard complex formation influences appreciably the ratio of methyl benzyl ketone: propiophenone; its value is  $2\cdot 2$  at 0° and about 1 at 30°. The elevation of the decomposition temperature of the Étard complex between the same limits increases slightly the amount of benzaldehyde, decreases the methyl benzyl ketone proportion and does not influence the yields in propiophenone, chloroketones and 1-phenyl-1-propene.

Whatever the mechanism of the oxidation of n-propylbenzene, it is to be expected that the attack of the oxidant should take place in the  $\alpha$  position of the side chain. Therefore it is surprising at first sight that methyl benzyl ketone is the main reaction product. The possibility of its being the result of a molecular rearrangement, which in some way accompanies the oxidation reaction, should be taken into consideration.

It is known that 1,2-epoxyphenylpropane rearranges into methyl benzyl ketone.<sup>7</sup> McKenzie *et al.*<sup>8</sup> established that this rearrangement occurs quantitatively, in a

<sup>&</sup>lt;sup>7</sup> Th. Zinke and K. Zahn, Ber. Disch. Chem. Ges. 43, 849 (1910). J. Levy and F. Gombinska, C.R. hebd. Séances Acad. Sci. 188, 711 (1929); Bull. Soc. Chim. Fr. (4) 49, 1765 (1931).

<sup>\*</sup> A. McKenzie, E. M. Luis and A. G. Mitchel, Ber. Dtsch. Chem. Ges. 65, 798 (1932).

Starting material	n-Propylbenzene					1-Phenyl- 1-propene		1,2- Epoxy- 1-phenyl propane	Allyl- ben- zene
mole %	1	2	3	4	5	6	7	8	9
C <sub>4</sub> H <sub>4</sub> —CH=CH—CH <sub>4</sub>	4.6	9.3	4.6	4.9	2.2	0	0	0	0
C <sub>4</sub> H <sub>4</sub> —CH=O	1.8	8∙4	22.5	24.3	30.5	9.1	28.7	13-5	45·2
C.HCHCO-CH.	56·0	39.9	<b>49</b> ∙0	<b>47</b> ∙8	41.6	43·1	36-3	35.5	<1
C <sub>t</sub> H <sub>s</sub> COCH <sub>s</sub> CH <sub>s</sub>	30-5	37.7	21.4	20.0	20·9	<1	3.4	17.6	11.3
C <sub>4</sub> H <sub>5</sub> —CO—CH=CH <sub>3</sub>	0	0	0	0	0	14.4	26.2	15-1	0
C,H,-CHCl-CO-CH	<1	3.0	2.5	2.9	4.6	31.8	4.5	18.4)	42·5
C <sub>t</sub> H <sub>s</sub> COCHCCH <sub>s</sub>	<1	1.7	<1	<1	<1	1.6	0.7	<1	
C <sub>t</sub> H <sub>s</sub> -CHOH-CH <sub>t</sub> -CH <sub>t</sub>	6.6	<1	<1	<1	<1	0	0	0	0
Yields <sup>10</sup>	68·8	<del>79</del> ·4	79·5	70·5	7 <b>5</b> ∙2	63·3	<b>69</b> ∙6	71-0	37.1

 TABLE 1. PRODUCTS OF THE ÉTARD REACTION OF N-PROPYLBENZENE,

 1-PHENYLPROPENE AND 1,2-EPOXY-1-PHENYLPROPANE

1. Complex prepared at  $0^{\circ}$  and decomposed at  $0^{\circ}$  with saturated aqueous solution of SO<sub>3</sub>. In this experiment 31.3% of 1-chloro-1-phenylpropane was isolated.

2. Complex prepared at 30°, decomposed with water at 0°.

3, 4, 5. Complexes prepared at 0° and decomposed with water at 0°, 50° and 100°, respectively.

6. Complex prepared at 0°, decomposed with aqueous SO<sub>2</sub> saturated at 0°. (Found: C, 36.88; H, 3.44; Cl, 26.51; Cr, 16.27. Calc. for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>CrCl<sub>2</sub>: C, 39.58; H, 3.69; Cl, 25.97; Cr, 19.05%.)
7. Complex prepared at 0°, decomposed with water at 0°.

8. Chromyl chloride introduced at 0°; the reaction mixture decomposed with water at 0° without isolation of the complex.

9. Complex prepared at 0° and decomposed with water at 0°. (Found: C, 31.08; H, 3.11; Cl, 32.22; Cr, 19.27. Calc. for  $C_9H_{10}O_2CrCl_3$ : C, 39.58; H, 3.69; Cl, 25.97; Cr, 19.05%.)

10. All yields are based on the chromyl chloride introduced in the reaction.

few seconds by the action of zinc chloride. 1,2-Epoxyphenylpropane is converted by 2N  $H_2SO_4$  at 20° into 1-phenyl-1,2-propyleneglycol and this glycol affords under the action of conc  $H_2SO_4$  methyl benzyl ketone.<sup>8</sup> Therefore, we submitted 1,2-epoxyphenylpropane and 1-phenyl-1-propene, from which the epoxide could arise, to the action of chromyl chloride under conditions similar to those used for n-propylbenzene. The results of these experiments are presented in Fig. 1. As it can be seen, not only the main reaction products, but also those arising in small amounts, are identical for all three compounds submitted to the oxidation by chromyl chloride.

The appearance of the epoxide as an intermediate also explains in a simple way the still non-clarified deuterium migration, observed during the formation of methyl benzyl ketone by the oxidation of labelled n-propylbenzene:<sup>5</sup>

$$O$$

$$C_{4}H_{4}-CH_{4}CD_{5}CH_{4} \rightarrow C_{4}H_{4}-CH-CDCH_{4} \rightarrow C_{4}H_{4}-CHDCOCH_{4}$$

The ring openings of epoxides in acid catalysis and the isomerizations of the epoxides to carbonyl derivatives, are controlled by a general principle: the ring opening of the epoxide takes place through the intermediate formation of the most stable carbonium ion (tert  $> \sec > prim$ ).<sup>9</sup>

S. Winstein and R. B. Henderson, Heterocyclic Compounds Vol. 1; p. 1. Wiley, New York (1950).



FIG. 1 Vapour phase chromatogram of the reaction products resulting from the chromyl chloride oxidation of n-propylbenzene, 1-phenyl-1,2-epoxypropane and 1-phenyl-1propene. In each case the maximum corresponding to the unreacted starting material (an excess of which was used) have been omitted.

According to House<sup>10</sup> the isomerization reactions of the epoxides, e.g. 1,2-epoxy-1phenylpropane (I), with an acid catalyst such as  $MgBr_2$ , can be represented by a mechanism of the following type:



<sup>10</sup> H. O. House, J. Amer. Chem. Soc. 77, 5083 (1955).

The transition state or intermediate III has been formulated above, for simplicity, as an open carbonium ion but a resonance II  $\leftrightarrow$  III is more likely with an incompletely developed charge on the benzylic carbon.

Hickinbottom *et al.*<sup>11</sup> obtained in several cases epoxides on oxidation of olefins with chromic anhydride in acetic anhydride solution (but not in acetic acid or water solutions). The same authors argue that the epoxides themselves are not intermediates in chromic acid oxidations but that the oxidation products are derived from some addition complex of the olefins with the oxidizing agent.

Cristol and Eilar<sup>12</sup> isolated complexes of olefins with chromyl chloride in the ratio 1:1, later confirmed by Stairs.<sup>13</sup> These complexes afforded on hydrolysis chlorohydrins, more precisely the complexes resulted from 1-olefins gave the chlorohydrins which correspond to an *anti*-Markownikoff addition of hypochlorous acid.<sup>12</sup>

Taking into account the electrophilic character of chromyl chloride, Cristol and Eilar considered three transition states, V, VI and VII, which might play a part in the formation of the Étard complex VIII of an 1-terminal olefin:



The transition state VII may be excluded from the outset in the case of n-propylbenzene because the formation of the two isomeric ketones cannot be explained simply in this way. Moreover VII should give solely a *cis*-chlorohydrin in the case of cyclohexene.<sup>14</sup> The transition state V explains satisfactorily the isomerizations which accompany sometimes the chromyl chloride oxidations. However if only V would contribute to this reaction, cyclohexene should afford only the *trans*-chlorohydrin, while actually *cis*-chlorohydrin is also formed in proportion of 3:2. If VI alone would represent the transition state of the main reaction, the ratio between the two isomeric chlorohydrins should be 1:1. In view of the above observations, it can be admitted that the transition state of the complex formation from an olefin with chromyl chloride, is best represented by V, with a considerable contribution of VI (at least in the case of cyclohexene). The analogy between V and II on one side and VI and III on the other side becomes evident and this explains in the case of the n-propylbenzene, the formation of the  $\beta$ -ketone, identical with that from the epoxide in Lewis acid catalysis.

However, subsequent to the Étard reaction, oxidations are possible and even probable. This explains the constitution of the reaction products obtained from n-propylbenzene, 1,2-epoxy-1-phenylpropane, 1-phenylpropene and, surprisingly,

<sup>&</sup>lt;sup>11</sup> M. A. Davis and W. J. Hickinbottom, J. Chem. Soc. 2205 (1958) and earlier Refs. cited therein.

<sup>&</sup>lt;sup>13</sup> S. J. Cristol and K. R. Eilar, J. Amer. Chem. Soc. 72, 4353 (1950).

<sup>&</sup>lt;sup>18</sup> R. A. Stairs, Canad. J. Chem. 38, 2028 (1960).

<sup>&</sup>lt;sup>14</sup> R. A. Stairs, D. G. M. Diaper and A. L. Gatzke, Canad. J. Chem. 41, 1059 (1963).

from allylbenzene as well (Table 1). The two chloroketones noted by f and g (Fig. 1) result most likely from the corresponding chlorohydrins, by a secondary oxidation during the hydrolysis of the Étard complex. The unsaturated ketone d results from the chlorohydrin corresponding to ketone g by elimination of hydrogen chloride and subsequent oxidation in a way which has been discussed by Stairs *et al.*<sup>14</sup> for alkenes. The fact that the unsaturated ketone could not be found among the chromyl chloride oxidation products of n-propylbenzene is probably due in this case to the low yield of chlorinated products.

The two saturated ketones namely methyl benzyl ketone and propiophenone (c and e in Fig. 1) are obviously the result of a rearrangement through intramolecular hydride transfer. This occurs probably in the nonpolar anhydrous reaction medium during the formation of the complexes XI and XIII which afford by hydrolysis the ketones c and e:



The driving force for the formation of compounds X and XII results on one hand from release of strain energy associated with the opening of the epoxide ring and on the other from the stabilizing influence of the oxygen atom on the adjacent cationic center of XI and XIII which, as known, is considerable<sup>15</sup> exceeding that of a phenyl group. The two complexes XI and XIII are therefore of comparable stability, with a slight advantage in favour of XIII on account of benzylic conjugation.

On the other hand it can be supposed that between the two structures X and XII, which represent the two open forms of the epoxide derivative IX, the former (X) should be much more stable than XII, according to the general rule of the opening of asymmetrically substituted epoxide rings. Therefore it is not surprising that among the reaction products methyl benzyl ketone predominates over propiophenone.

The above proposed mechanism stipulates an internal hydride migration for the formation of both isomeric ketones resulting from the Étard oxidation of n-propylbenzene. The hydride transfer  $\beta \rightarrow \alpha$  during the formation of methyl benzyl ketone was proved earlier.<sup>5</sup> It would be interesting to verify whether a hydride transfer  $\alpha \rightarrow \beta$  takes place during the Étard oxidation of n-propyl-1-d<sub>2</sub>-benzene, i.e. whether the propiophenone resulting from this hydrocarbon contains deuterium linked to  $C\beta$ .

Treatment of 1,2-epoxy-1-phenylpropane with chromyl chloride leads, as it was shown before, to products identical with those obtained from the corresponding olefin. Probably, owing to its strong electrophilic character, the chromyl chloride,

<sup>&</sup>lt;sup>16</sup> C. K. Ingold, Structure and Mechanism in Organic Chemistry p. 334. Cornell Univ. Press, Ithaca, New York (1953).

in a solvent lacking donor properties such as carbon tetrachloride, behaves as a Lewis acid, for example  $MgBr_2$  or  $BF_3$ ; its oxidizing action begins only later, during the hydrolysis.

The Étard complex of n-propylbenzene unlike that of 1-phenylpropene has a composition corresponding to 1 mole of hydrocarbon to 2 moles of  $CrO_2Cl_2$ . As previously shown,<sup>1</sup> it is most likely that this compound corresponds to formula XIV, since in the case of formula XV, the sole reaction product should have been propiophenone:



There are two ways in which a compound of the type XIV could react in order to give the observed reaction products. One is the elimination of one proton from  $C\beta$  and of the  $Cr_sO_4Cl_4H$  group from  $C\alpha$ . Thus 1-phenylpropene should result, and subsequently it could react with chromyl chloride as described. Another possibility is the intramolecular hydride transfer to the Cr(VI) group of complex XIV. The transition state or intermediate IX could result in this way. The first hypothesis is more likely taking into account that small amounts of 1-phenylpropene have been found among the reaction products (Table 1 and Fig. 1).

The 1-phenyl-1-propanol identified in the reaction mixture results from the initial Étard complex by the mechanism described in the previous communication. As regards the benzaldehyde, identified among the reaction products, it results probably from a more advanced oxidation by chromic acid of one of the reaction products in aqueous solution during the final hydrolysis.

## Étard reaction of methylcyclohexane

Tillotson and Houston<sup>16</sup> prepared in 1951 an Étard complex of methylcyclohexane corresponding to the molar ratio 1:2. By its decomposition with water, these authors have obtained in 25% yield an aldehyde assigned the structure of hexahydrobenzaldehyde. Wiberg *et al.*<sup>6</sup> on repeating this reaction isolated only 2-methylcyclohexanone and 2-chloro-2-methylcyclohexanone. In view of these contradictory results a new investigation of the Étard oxidation of methylcyclohexane was necessary.

Unpublished earlier experiments performed in our laboratory had shown that on hydrolysis of the Étard complex of methylcyclohexane, an aldehyde is formed in appreciable amount, which however is not the hexahydrobenzaldehyde since it gives on oxidation an acid different from cyclohexanecarboxylic acid.

In the present paper the reaction products were firstly identified by gas chromatography, then separated by preparative VPC and their IR spectra were compared with authentic samples. In this way the following compounds were identified (Fig. 2): 1-methylcyclopentylaldehyde (15.6%), 1-methylcyclohexanol (1.5%), hexahydrobenzaldehyde (2.4%), 2-methylcyclohexanone (36.7%) and 2-chloro-2-methylcyclohexanone (43.8%). The total yield is 53% based on the chromyl chloride introduced in the reaction.

<sup>16</sup> A. Tillotson and B. Houston, J. Amer. Chem. Soc. 73, 221 (1951).



FIG. 2 Gas chromatogram of the Étard reaction products of methylcyclohexane.

The Étard complex of 1-methylcyclohexene was also prepared. By decomposing it with water and using the same method as for n-propylbenzene the following products were identified: 1-methylcyclopentylaldehyde (38.5%), 2-methylcyclohexanone (52.5%) and 2-chloro-2-methylcyclohexanone (9.3%). The overall yield is 68% based on the chromyl chloride introduced in the reaction.

Tiffeneau and Tchoubar<sup>17</sup> observed that 1,2-epoxy-1-methylcyclohexane is converted by magnesium bromide in ethereal solution at 0° into *trans*-2-bromocyclohexanol while at higher temperatures 1-methylcyclopentylaldehyde is formed. Naqvi *et al.*<sup>18</sup> could not isolate the bromohydrin but obtained at 0° only 1-methylcyclopentylaldehyde. At 60° these workers isolated a mixture of 2-methylcyclohexanone (36%) and methyl cyclopentyl ketone (10%). There are signs which indicate however the formation of a bromohydrin. The fact that at lower temperatures only the five-membered aldehyde is formed, while at higher temperatures the main reaction product is a six-membered ketone indicates that in the first case the reaction occurs under kinetic control while in the second case an equilibrium takes place leading to the more stable isomer. Actually it is known that 1-methylcyclopentylaldehyde is converted under the action of a Lewis acid (AlCl<sub>3</sub>) in almost quantitative yield into 2-methylcyclohexanone.<sup>19</sup>

The formation of common products in these two reactions indicates common, or at least similar, intermediates. The Étard reaction of methylcyclohexane can be explained best by the appearance of intermediates similar to those admitted by Cristol<sup>12</sup> and Stairs<sup>14</sup> (V  $\leftrightarrow$  VI). However it does not seem probable that during the Étard reaction of methylcyclohexane an equilibrium of the type discussed above for the epoxide rearrangement should take place. It is more likely that the Étard reactions, just like other oxidations with Cr(VI) derivatives, should occur under kinetic control. The interpretation of Chart I seems quite plausible.

From an examination of Dreiding models it can be seen that 1,2-epoxy-1-methylcyclohexane may exist in two non-equivalent conformations, corresponding to the

<sup>&</sup>lt;sup>17</sup> M. Tiffeneau and B. Tchoubar, C.R. hebd. Séances Acad. Sci. 207, 218 (1938).

<sup>&</sup>lt;sup>18</sup> S. M. Naqvi, J. P. Horwitz and R. Filler, J. Amer. Chem. Soc. 79, 6283 (1957).

<sup>&</sup>lt;sup>19</sup> C. D. Nenitzescu and D. Curcăneanu, Ber. Disch. Chem. Ges. 71, 2063 (1938).



two half-chair conformations of cyclohexene, recently designated as the R- and L-forms.<sup>20</sup>

Such conformations can be adopted also by the transition state of the Étard reaction of 1-methylcyclohexene (XVI and XIX in Chart I). If it is admitted that in both conformers (XVI and XIX) the epoxide opens so that the positive charge be localized on the tertiary carbon as in XVII and XX and if on the other hand it is admitted that in the rearrangement the *trans* rule is observed, it can be seen that one of the conformers (XVI) will afford an aldehyde with a cyclopentane ring and the other one (XIX) a ketone with an unrearranged six-membered ring.

The ratio between XXI and XVIII in the reaction product mixture of methylcyclohexane and chromyl chloride is about  $2\cdot3$  while for 1-methylcyclohexene this ratio is about  $1\cdot35$ . These figures indicate that the conformers XVI and XIX are of comparable stability in the absence of more precise indications about the path by which the main reaction product, chloroketone XXIII, is formed.

Chloroketone XXIII is certainly formed by secondary oxidation during the hydrolysis of some chlorohydrins. From XVII a XXII-cis complex can arise and from XX a XXII-trans one, each of them giving on hydrolysis the corresponding chlorohydrins. Both on oxidation afford the chloroketone XXIII. The measurement of the ratio between the two isomeric cis-trans chlorohydrins could furnish an indication as to the relative proportions between the conformations XVI and XIX in equilibrium.

Among the minor products of the Étard reaction of methylcyclohexane are 1-methylcyclohexanol (XXV) and hexahydrobenzaldehyde (XXVIII). According to the above described mechanism it seems very likely that they result from the initial

<sup>20</sup> M. P. Hartshorn and D. N. Kirk, Tetrahedron 21, 1547 (1965).



Étard complex of methylcyclohexane (XXIV). The course of these secondary reactions is shown, together with that of the main reactions, in Chart II. It is admitted, as in the case of the Étard complex of n-propylbenzene, that the main reaction is a  $\beta$ -elimination which provides an olefin, in the present case 1-methylcyclohexene, which subsequently reacts according to Chart I. The small amounts of hexahydrobenzalde-hyde (XXVIII) result in this case from the methylenecyclohexane (XXVI).

#### EXPERIMENTAL

Starting materials. n-Propylbenzene was prepared by the Clemmensen reduction<sup>31</sup> of propiophenone (73% yield), b.p.<sub>760</sub> 159.4°. Purity 99.6% (gas-chromatography).

trans-1-Phenylpropene was prepared by the dehydration of 1-phenyl-1-propanol<sup>22</sup> with KHSO<sub>4</sub> by the Gauthier method<sup>23</sup> (80% yield); b.p.<sub>10</sub> 64-65°, 99 6% purity (gas-chromatography).

threo-( $D_1L$ )-1,2-Epoxy-1-phenylpropane was obtained by the epoxidation of trans-1-phenyl-1propene by the method of Ogata<sup>24</sup> (with H<sub>2</sub>O<sub>2</sub> and acetonitrile, in methanol in the presence of Na<sub>3</sub>HPO<sub>4</sub>), b.p.<sub>1.5</sub> 83-84°, purity about 98% (the IR spectrum<sup>26</sup> indicates the presence of about 2% of ketonic material).

Allylbenzene was prepared<sup>24</sup> from PhMgBr and allyl bromide in 78% yield, b.p.<sub>7e0</sub> 156–158°. Purity 99.5% (gas-chromatography).

Methylcyclohexane purchased from Eastman-Kodak Co was of 99.9% purity (gas-chromatography).

1-Methylcyclohexene was prepared from 1-methylcyclohexanol,<sup>\*7</sup> by dehydration with POCl<sub>s</sub> in pyridine, the only known method by which a content of less than 1% of methylenecyclohexane can be provided,<sup>\*8</sup> yield 88%, b.p.<sub>760</sub> 109-111°, purity 99% (gas-chromatography).

Chromyl chloride prepared after Sisler<sup>39</sup> was used immediately after distillation.

General method of obtaining the complexes.<sup>•</sup> In a 750 ml 4-necked round-bottomed flask provided with a mechanical stirrer, a reflux condenser (protected by means of a CaCl, tube), a thermometer, a

\* The methylcyclohexane complex was prepared according to Tillotson and Houston.<sup>16</sup>

- <sup>21</sup> E. Clemmensen, Ber. Dtsch. Chem. Ges. 46, 1837 (1913).
- <sup>22</sup> K. Hess and H. Rheinboldt, Ber. Dtsch. Chem. Ges. 54, 2043 (1921).
- <sup>23</sup> D. Gauthier and P. Gauthier, Bull. Soc. Chim. Fr. 53, 323 (1933).
- <sup>24</sup> Y. Ogata and Y. Sawaki, Tetrahedron 20, 2065 (1964).
- <sup>25</sup> J. Sicher and M. Svoboda, Coll. Czech. Comm. 20, 1402 (1955).
- <sup>38</sup> E. B. Hershberg, Helv. Chim. Acta 17, 351 (1934).
- <sup>37</sup> W. A. Mosher, J. Amer. Chem. Soc. 62, 522 (1940).
- <sup>38</sup> R. R. Sauers, J. Amer. Chem. Soc. 81, 4873 (1959).
- <sup>29</sup> H. E. Sisler, Inorganic Synthesis, vol. II; p. 205. McGraw-Hill, New York (1946).

dropping funnel and an inlet tube for inert gas (argon), placed in an ice-water bath, 0.1 moles of reactant (n-propylbenzene, 1-phenylpropene, 1,2-epoxy-1-phenylpropane, allylbenzene, methylcyclohexene etc.) were introduced as a 10% soln in dry CCl<sub>4</sub>. Then 0.1 moles chromyl chloride (as 20% soln in dry CCl<sub>4</sub>) were added dropwise with stirring, in an inert gas atmosphere, over a period of about 2 hr. The chromyl chloride was added as such a rate that the temp remained between 0° and 2°.

Stirring and cooling were maintained for 1 hr, during which time the chromyl chloride was completely consumed and finally the reaction mixture was allowed to reach room temp for a few hr.

The complex was filtered off with suction in a closed system and throughly washed with dry  $CCl_4$  (100 ml of  $CCl_4$  for 20 g of complex).

The complexes were decomposed by pouring them under efficient stirring into water (temp between 0° and 100°), in aqueous solns saturated with SO<sub>2</sub> (at 0°) and in aqueous solns saturated with NaHSO<sub>2</sub> (at 0°), using about 100 ml of decomposing soln for 10 g of complex.<sup> $\bullet$ </sup>

The resulting aqueous solns were extracted<sup>†</sup> with several portions of 150 ml ether for 10 g of complex. The combined ethereal layers were washed with 5% NaHCO<sub>3</sub>aq, then with water, dried on Na<sub>3</sub>SO<sub>4</sub> and evaporated *in vacuo* (water-pump) using a 20 cm Vigreux column.

The composition (qualitative and quantitative) of the residues (weighed and kept under dry argon) was determined by gas-chromatography.

For the reaction products of n-propylbenzene and related substances an Apiezon L column was used (25% on Chromosorb-W, 2 m at 150° and 86 ml/min of H<sub>2</sub>). The results were verified on a Tween-80 (1.30 m) column and on dodecyl phtalate (1 m).

For the reaction products of methylcyclohexane and 1-methylcyclohexene a dodecylphtalate column was used (25% on celite-C22, at 150°, 1 m and 120 ml/min of  $H_2$ ).

The results of the experiments are given in Table 1 so that in the following only the identification of the main products of the reaction will be described.

Benzaldehyde. Chromatographic maximum (a) (Fig. 1). Gas chromatographic retention time identical to that of an authentic sample. Isolated by preparative gas-chromatography.

2,4-Dinitrophenylhydrazone, m.p. 235° (lit.<sup>40</sup> m.p. 236-238°) from EtOH, mixed m.p. 237° (with an authentic sample, m.p. 238°).

Methyl benzyl ketone. Chromatographic maximum (c) (Fig. 1). Gas-chromatographic retention time identical to that of an authentic sample.<sup>\$1</sup> Isolated by preparative gas-chromatography.

2,4-Dinitrophenylhydrazone, m.p. 148° (lit.<sup>38</sup> m.p. 150-152°) from EtOH, mixed m.p. 149° (authentic 2,4-dinitrophenylhydrazone, m.p. 150°).

IR Spectrum (in CCl<sub>4</sub> and CS<sub>4</sub>): 3093 ms; 3080 shm; 3072 ms; 3035 s; 3010 m; 2965 m; 2925 m; 1718 vvs; 1610 ms; 1540 s; 1463 s; 1430 s; 1363 vs; 1325 ms; 1294 ms; 1230 vs; 1196 m; 1160 vs; 1080 ms; 1035 ms; 750 vs; 700 vs; 634 mw; 620 mw;  $542 \text{ s cm}^{-1}$ . Identical to the spectrum of an authentic sample.

*Propiophenone.* Chromatographic maximum (e) (Fig. 1). Gas-chromatographic retention time identical to an authentic sample.<sup>34</sup> Isolated by preparative gas-chromatography and converted into 2,4-dinitrophenylhydrazone, m.p. 187° (lit.<sup>34</sup> m.p. 187–189°) from EtOH, mixed m.p. 188° (authentic 2,4-dinitrophenylhydrazone, m.p. 190°).

IR spectrum (in CCl<sub>4</sub> and CS<sub>2</sub>): 3095 ms; 3070 ms; 3045 m; 3034 m; 2987 s; 2945 sm; 2910 m; 1695 vvs; 1608 sm; 1593 m; 1470 sm; 1460 s; 1425 m; 1386 ms; 1380 s; 1223 vs; 1184 ms;

\* The complex of the 1,2-epoxy-1-phenylpropane was decomposed without previous filtration, in the presence of  $CCl_4$ , at 0°, using water, the ratio between water and complex being that indicated above.

 $\dagger$  In the case of the decompositions with sat. solns of SO<sub>2</sub> or NaHSO<sub>3</sub>, after extraction with ether, the reaction mixture was made alkaline with Na<sub>2</sub>CO<sub>2</sub> and steam-distilled. The distillate was again extracted with ether and the ether layer added to the main portion.

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<sup>35</sup> S. H. Tucker, M. Whalley and J. Forrest, J. Chem. Soc. 3194 (1949).

<sup>44</sup> M. Tuot and M. Guyard, Bull. Soc. Chim. Fr, 1086 (1947).

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1016 m; 955 s; 757 vs; 690 vs; 647 wm; 567 m cm<sup>-1</sup>. Identical to the spectrum of an authentic sample.

Phenyl vinyl ketone. Chromatographic maximum (d) (Fig. 1). Isolated by preparative VPC from the decomposition mixture of the Étard complexes of 1-phenylpropene and 1,2-epoxiphenylpropane.

IR spectrum<sup>35</sup> (in CS<sub>2</sub> and CCl<sub>4</sub>): 3304 w; 3080 m; 3070 ms; 3065 shm; 3010 w; 1678 vvs; 1662 m; 1617 m; 1605 wm; 1585 wm; 1468 ms; 1324 m; 1291 m; 1190 mw; 1160 s; 1020 w; 1006 w; 900 s; 785 ms; 700 s; 575 s; 450 mw; 410 mcm<sup>-1</sup>.

1-Phenyl-1-chloro-2-propanone. Chromatographic maximum (f) (Fig. 1). Isolated by preparative gas-chromatography (and in larger amounts from the decomposition mixture of the complexes of 1-phenylpropene and 1,2-epoxy-1-phenylpropane). (Found: C, 65.76; H, 5.74; Cl, 18.41. C<sub>9</sub>H<sub>9</sub>ClO requires: C, 64.11; H, 5.38; Cl, 21.03%.)

IR spectrum (in CS<sub>2</sub> and CCl<sub>4</sub>) almost unchanged<sup>18</sup> compared to that of methyl benzyl ketone: 3095 m; 3072 sm; 3038 s; 3014 m; 2985 m; 2935 mw; 2870 wm; 1720 vvs; 1690 shm; 1610 mw; 1503 s; 1463 s; 1430 s; 1363 vs; 1293 wm; 1265 ms; 1230 vs; 1198 vs; 1158 s; 1080 m; 1036 m; 830 s; 778 sm; 746 vs; 738 vs; 698 vvs; 630 ms; 573 s; 545 vs; 475 wm cm<sup>-1</sup>.

1-Phenyl-2-chloro-1-propanone. Chromatographic maximum (g). Isolated by preparative gaschromatography. (It was formed in small amounts in the decomposition mixture of the complexes of 1-phenylpropene and 1,2-epoxy-1-phenylpropane and only in traces in the decomposition of the complexes of *n*-propylbenzene).

IR spectrum (in CCl<sub>4</sub>) almost unchanged<sup>26</sup> compared to that of propiophenone: 3095 s; 3070 s; 3040 s; 2929 s; 2940 ms; 1697 vvs; 1608 ms; 1593 ms; 1460 s; 1425 s; 1385 ms; 1351 s; 1325 s; 1295 vs; 1259 vs; 1249 s; 1204 s; 1184 s; 1162 mw; 1130 mw; 1080 m; 1067 m; 1033 m; 1006 s; 958 vs; 910 mw cm<sup>-1</sup>.

1-Phenylpropan-1-ol appeared in the reaction mixture of the complexes of n-propylbenzene, decomposed with aqueous saturated solns with SO<sub>2</sub> at 0°. Gas-chromatographic retention-time identical to that of an authentic sample.<sup>22</sup>

1-Chloro-1-phenylpropane appeared in various amounts only in the filtrate of the n-propylbenzene Étard complexes. Gas-chromatographic retention time identical to an authentic sample.\*'

1-Methylcyclopentylaldehyde (XVIII). Isolated by preparative gas-chromatography (Fig. 2).

IR spectrum (in CS<sub>1</sub> and CCl<sub>2</sub>): 2968 vvs; 2940 shvs; 2878 vs; 2805 s; 2700 s; 1737 vvs; 1462 s; 1430 m; 1400 mw; 1370 vs; 1225 vs; 1095 mw; 1060 w; 990 vw; 900 mw; 882 mw; 790 mw; 765 w; 660 wm; 530 s cm<sup>-1</sup>. This spectrum shows the presence of an aliphatic aldehyde, different from cyclohexylaldehyde, probably 1-methylcyclopentylaldehyde.

To verify this hypothesis, the crude residue left after the decomposition of the methylcyclohexane complex was oxidized with  $Ag_aO.^{36}$  The filtered oxidation mixture was extracted with ether. The gas-chromatogram of the concentrated extract indicates the disappearance of the peaks corresponding to this aldehyde and to hexahydrobenzaldehyde.

On the other hand the working up of the extracted aqueous filtrate (acidfication, repeated extractions with ether, drying of the ethereal solutions and evaporation of ether) yielded a carboxylic acid, b.p.<sub>10</sub> 119–121°. The IR spectrum of this acid is superposable on that of authentic 1-methylcyclopentanecarboxylic acid.<sup>30</sup> (excepting a few weak bands belonging to cyclohexanecarboxylic acid): 2972 vvs; 2880 s; 2680 (m, flat); 1760 shmw; 1718 vvs; 1476 ms; 1462 s; 1418 ms; 1388 mw; 1293 s; 1210 ms; 1170 shmw; 1130 mw; 950 m cm<sup>-1</sup> (in CCl<sub>4</sub>).

This aldehyde appeared also among the decomposition products of the methylcyclohexane and 1-methylcyclohexene complexes, in the former case in proportion of 15.6 mole% and in the latter 38.5 mole%.

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2-Methylcyclohexanone (XXI). Gas-chromatographic retention time identical to that of an authentic sample.<sup>40</sup> This compound was formed in proportion of 36.7 mole% among the decomposition products of the methylcyclohexane complex and in 52.5 mole% among those of the 1-methylcyclohexene complex.

2-Methyl-2-chlorocyclohexanone (XXIII). The gas-chromatographic retention time is identical to that of an authentic sample.<sup>41</sup> It was isolated by preparative gas-chromatography (Fig. 2) and the IR spectrum (in CS<sub>3</sub> and CCl<sub>4</sub>) is superposable on that of authentic substance: 2985 ms; 2950 vs; 2903 m; 2872 ms; 2844 m; 1734 vvs; 1458 s; 1439 s; 1387 ms; 1355 mw; 1346 mw; 1320 m; 1290 m; 1261 mw; 1230 m; 1184 mw; 1146 m; 1128 s; 1120 shms; 1090 s; 1068 mw; 1026 m; 993 m; 942 mw; 908 mw; 871 m; 847 mw; 822 m; 727 mw; 678 mw; 600 s; 522 m; 488 ms; 425 m cm<sup>-1</sup>.

The largest amount of this chloroketone was found (in the proportion of 43.8 mole%) among the decomposition products of the methylcyclohexane complex; among the decomposition products of the 1-methylcyclohexane complex it appeared in the proportion of only 9.5 mole%.

1-Methylcyclohexanol (XXV). The gas-chromatographic retention time is identical to that of an authentic sample.<sup>37</sup> This compound appeared only among the decomposition products of the methylcyclohexane complex in proportion of 1.45 mole%.

*Hexahydrobenzaldehyde* (XXVIII). The gas-chromatographic retention time is identical to that of an authentic sample.<sup>48</sup> The sample isolated by preparative gas-chromatography left in the atmosphere for 24 hr, gave a IR spectrum identical to that of an authentic cyclohexanecarboxylic acid<sup>48</sup> (owing probably to the rapid autoxidation of hexahydrobenzaldehyde): 2945 vvs; 2863 s; 2676 (flat); 1765 shwm; 1720 vvs; 1462 m; 1430 ms; 1340 shm; 1322 m; 1305 m; 1270 s; 1222 m; 1190 w; 1155 w; 1145 w; 1120 vs; 1042 vs; 950 m (flat); 900 wm cm<sup>-1</sup> (in CCl<sub>4</sub>).

The hexahydrobenzaldehyde among the decomposition products of the methylcyclohexane complex was in proportion of 2.38 mole%.

The gas-chromatographic analyses were carried out with a Willy-Giede apparatus, type GCHF-18/2. The IR spectra were registered with a Jena-UR 10 spectrophotometer.

<sup>40</sup> Commercial product.

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