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ÉTARD REACTION—II[1]

STRUCTURE OF THE CHROMYL CHLORIDE COMPLEXES OF PHENYLMETHANES

I. NECŞOIU, V. PRZEMETCHI, A. GHENCIULESCU, C. N. RENTEA and C. D. NENITZESCU
Institute of Organic Chemistry of the Academy of S. R. Rumania, Bucharest

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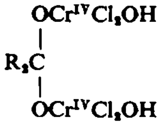
Abstract—Hydrolysis of the Étard complexes of diphenylmethane and toluene by water and other hydroxylic solvents, with or without added sulphur dioxide, gave besides benzophenone and benzaldehyde substantial amounts of benzhydrol and benzyl alcohol. Hence it is concluded that during the formation of Étard complexes, at least partially, one hydrogen atom of the side chain is substituted by the oxidant. Hydride exchange reactions are described between the Étard complex of triphenylmethane on one hand and ethyl ether and cycloheptatriene on the other hand. In the former case besides triphenylmethane, a complex of the ether with one mole of chromyl chloride was obtained while in the latter case a tropylium salt could be isolated. The oxidation of the C—H sigma bond by chromyl chloride and chromic acid is considered as an electrophilic substitution at the saturated carbon atom.

THE brown amorphous precipitates which are formed from chromyl chloride and alkanes or aromatic hydrocarbons with a saturated side chain correspond to the formula $RH \cdot 2CrO_2Cl_2$.[2] On hydrolysis these compounds gave as main reaction products aldehydes or ketones. In 1881 Étard assigned the structure I to these compounds. Later several other structures were proposed[2] among which no one can be considered as rigorously proved. The determination of the structure of Étard complexes meets with considerable difficulties since owing to their complete insolubility in unreactive solvents, the usual purification methods are not applicable.[3] Nor can the methods of optical and NMR spectroscopy be applied. The structure of Étard complexes are of interest in view of the relation between oxidations by chromyl chloride and chromic acid.[4]



$$R_2C\begin{cases}OCr^{IV}Cl_2OH\\OCr^{IV}Cl_2OH\end{cases}$$

I

$$\underset{\text{IIa}}{R_2CH{-}OCrCl_2OCrCl_2O_2H} \rightleftharpoons \underset{\text{IIb}}{R_2CH^{\oplus}[OCrCl_2OCrCl_2O_2H]^{\ominus}}$$

Since an excess of triphenylmethane gives with chromyl chloride one single

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[1] Part I: I. Necsoiu, A. T. Balaban, I. Pascaru, E. Sliam, M. Elian and C. D. Nenitzescu, *Tetrahedron* **19**, 1133 (1963).

[2] Cf. the excellent review by W. H. Hartford and M. Darin, *Chem. Rev.* **58**, 1 (1958).

[3] Elementary analyses often show considerable differences from the formula $RH{-}2CrO_2Cl_2$; C. C. Hobbs and B. Houston, *J. Amer. Chem. Soc.* **76**, 1254 (1954).

[4] W. A. Waters, *Quart. Rev.* **12**, 277 (1958).

complex $(C_6H_5)_3CH{\cdot}2CrO_2Cl_2$, which on hydrolysis affords a quantitative yield of triphenylmethanol, structure I is excluded at least in this case. In a previous paper[1] the structure II was proposed in which two chromyl groups replaced one single hydrogen of the initial hydrocarbon and were linked through an oxygen atom. In formula II one of the chromium atoms was tetravalent and the other hexavalent.

It was admitted that the Étard complexes have in the solid state an ester structure of the type IIa and that they can dissociate to form the ion pair IIb. This latter structure explains many of the Étard complex reactions. The ionization is evidently favoured on one hand by the stability of the resulting carbonium ion and on the other hand by the solvation power towards anions of the solvent. Water for instance produces ionization but of course a rapid reaction with the arising ions takes place.

The above conception on the ionic structure of Étard complexes is based on a series of experimental facts. According to Sulima an Gragerov[5] who used ^{18}O enriched water the hydrolysis occurs through alkyl-oxygen cleavage. This can be explained by a solvolytic mechanism of type SN1. If the hydrolysis is carried out in acetic acid containing sodium azide, organic azides are obtained. The Étard complex of triphenylmethane affords triphenylmethylazide in 90% yield besides small amounts of triphenylmethanol, while from the Étard complex of diphenylmethane, diphenylmethylazide is formed in 17% yield besides benzhydrol, benzhydryl acetate and benzophenone. In a previous paper[6] similar azides have been obtained in the presence of azide ions on oxidation with chromic acid of aromatic and branched saturated hydrocarbons. Hence the conclusion was drawn that the oxidation mechanism by chromic acid and chromyl chloride of saturated hydrocarbons show a marked analogy.

A compound of structure IIa or IIb would be expected to give on hydrolysis an alcohol. Usually this cannot be isolated because it is further oxidized by excess of oxidant (Cr(IV) and Cr(VI)) liberated on hydrolysis. It was shown[1] that if hydrolysis of Étard complexes by water is carried out, benzhydrol and benzyl alcohols are readily oxidized by chromyl chloride to the corresponding carbonyl compounds. However the benzhydrol could be isolated as its acetate in appreciable amounts, by decomposing the Étard complex of diphenylmethane with acetic acid containing sulphur dioxide. Under these conditions, the excess of oxidant reacts more rapidly with sulphur dioxide than with the secondary alcohol present in the reaction mixture.

It has been assumed[7] that benzhydrol could result from a reduction of benzophenone or of the Étard complex of diphenylmethane by sulphur dioxide. This possibility was discarded by hydrolysing the Étard complex of diphenylmethane with water without addition of any reducing agent, but in the presence of a solvent immiscible with water namely carbon tetrachloride. The oxidation of benzhydrol slows down appreciably in the carbon tetrachloride phase. In this way benzhydrol–benzophenone ratios as high as 20:70 could be obtained. Evidence was also furnished that this benzhydrol was not formed by way of benzhydryl chloride, a byproduct of the reaction. Thus it is proved beyond doubt that, at least in the proportion indicated above, benzhydrol is a primary reaction product in the hydrolysis of the Étard complex of diphenylmethane.

By decomposing the Étard complex of toluene with water only a small amount of

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[5] L. V. Sulima and I. P. Gragerov, *J. Obshch Khim* **29**, 3825 (1959).

[6] I. Necsoiu and C. D. Nenitzescu, *Chem. & Ind.* 377 (1960).

[7] K. B. Wilberg and R. Eisenthal, *Tetrahedron* **20**, 1151 (1964).

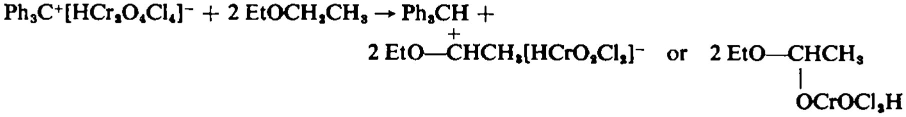
benzyl alcohol is formed. However when alcohols containing SO_2 are used for the decomposition, besides the benzaldehyde, benzyl alcohol is obtained in amounts which largely exceed the error of the analytical method used (VPC). The largest amounts of benzyl alcohol were obtained by decomposing the Étard complex of toluene with t-butanol containing SO_2 (17% benzyl alcohol). Decomposition of the Étard complex of toluene with formic or acetic acid and SO_2 gave besides benzaldehyde and benzyl alcohol the respective esters of the alcohol (Experimental).

During the oxidation of alkyl benzenes with chromyl chloride,[2] a side reaction takes place leading to products with chlorinated side chains. For instance, toluene yields benzyl chloride, diphenylmethane yields benzhydryl chloride, etc. The mechanism of the chlorination by chromyl chloride has not been studied. The ratio between the products formed by oxidation and chlorination may vary considerably. The proportion of chlorinated products is not influenced by the initial concentration of reactants and remains approximately the same with or without traces of water, and in the presence or absence of oxygen. The chlorinated product appears mostly in the solvent while the precipitate, if thoroughly washed with solvent (CCl_4 or CS_2) gives on hydrolysis practially only the oxidation product. Hence it can be admitted that the chlorination and oxidation reactions (formation of Étard complex) occur simultaneously and independently. In experiments in which larger yields of chlorinated product were obtained, the chromyl chloride complex showed the largest differences as compared to the ideal formula $RH \cdot 2CrO_2Cl_2$. The complexes obtained under these conditions contain larger amounts of chromium and therefore lower amounts of carbon than calculated from the above formula. The precipitaties are probably mixtures in varying proportions of $RH \cdot 2CrO_2Cl_2$ and a still unknown inorganic chromium oxychloride.

Hydride transfer with Étard complexes

Sulima and Gragerov,[5] showed without experimental details that Étard complexes of triphenylmethane and of *o*-nitrotoluene regenerate the initial organic substrate on treatment with dry ether. No indications were made as to the fate of the ether and chromyl chloride.

In our hands, the reaction of the Étard complex of triphenylmethane with ether yielded 91% triphenylmethane. At the same time a complex of ethyl ether with chromyl chloride could be isolated, in 1:1 proportion. It is well known that ethers are good hydride ion donors towards carbonium ions.[8,9] For this reason the reaction may be formulated as involving carbonium ions:



$$Ph_3C^+[HCr_2O_4Cl_4]^- + 2\,EtOCH_2CH_3 \rightarrow Ph_3CH + 2\,EtO\text{—}\overset{+}{C}HCH_3[HCrO_2Cl_2]^- \quad \text{or} \quad 2\,EtO\text{—}\underset{\substack{|\\ OCrOCl_2H}}{C}HCH_3$$

IIIa IIIb

This chromyl chloride complex of ethyl ether gave on hydrolysis acetaldehyde and ethyl acetate. The formation of acetaldehyde confirms the structure III. The ethyl

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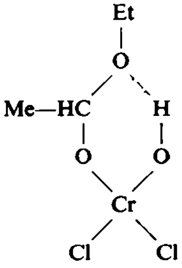
[8] F. J. Norris, *Organic Syntheses* Coll. I, p. 548. Wiley, New York (1956).

[9] H. Meerwein, *Angew. Chem.* **67**, 374 (1955); H. Meerwein, H. Allendörfer, P. Beckmann, Fr. Kunert, H. Morschel, F. Pawellek and K. Wunderlich, *Ibid.* **70**, 211 (1958).

acetate results either from a higher oxidized product or from a derivative simultaneously chlorinated and oxidized at the same carbon atom.

It is known that one of the best hydride donors is cycloheptatriene.[10] On treatment with this hydrocarbon, in carbon tetrachloride solution, the chromyl chloride complex of triphenylmethane regenerates an almost quantitative yield of the initial hydrocarbon. The resulting tropylium ion was also isolated as its perchlorate.

Chromyl chloride complexes in a 1:1 ratio are known in the case of olefins[11,12] metallyl chloride,[11] benzyl chloride[2] and benzhydryl chloride.[13] The nonintervention of the second chromyl chloride molecule is probably due to the stabilization of the primary complex (1:1) through an intramolecular hydrogen bond, as in IV for the ethyl ether:



IV

In the following paper[14] it is shown that the reaction between alkylbenzenes and chromyl chloride also takes place in its primary step through an 1:1 type adduct.

DISCUSSION

Evidence had been advanced by Wheeler[15] that the reaction of toluene with chromyl chloride in carbon tetrachloride proceeds in two steps: the formation of a soluble species followed by the precipitation of the brown insoluble product. Stairs and Burns[16] and Stairs[17] showed that the Étard reaction is first order in hydrocarbon and first order in chromyl chloride. Therefore only one molecule of chromyl chloride seems to be involved in the rate determining step, the subsequent binding of the second chromyl chloride molecule being fast. A kinetic isotope effect was observed in the forming of the Étard adduct of deuterated toluene in CS_2, which indicates the breaking of a carbon–hydrogen bond of the methyl group in the rate determining step.[18]

All these observations are in accordance with the facts presented now and earlier.[1] They show that the Étard complexes correspond in an essential proportion, if not totally, to a structure in which one hydrogen atom of the initial hydrocarbon is substituted by the oxidant. The Étard adducts may possibly be represented by IIa or IIb. Although in these formulae the coordination number of one of the chromium

[10] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Amer. Chem. Soc.* **79,** 4557 (1957).

[11] S. J. Cristol and K. R. Eilar, *J. Amer. Chem. Soc.* **72,** 4353 (1950).

[12] R. A. Stairs, D. G. M. Diaper and A. L. Gatzke, *Canad. J. Chem.* **41,** 1059 (1963).

[13] Unpublished observation of this laboratory.

[14] Paper III. *Tetrahedron* in press.

[15] O. H. Wheeler, *Canad. J. Chem.* **38,** 2137 (1960).

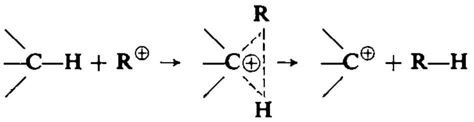
[16] R. A. Stairs and J. W. Burns, *Canad. J. Chem.* **39,** 960 (1961).

[17] R. A. Stairs, *Canad. J. Chem.* **42,** 550 (1964).

[18] O. H. Wheeler, *Canad. J. Chem.* **42,** 706 (1964).

atoms is 5. Secondly a chloroester of the type IIa should be soluble in non-polar solvents considering the relatively small molecule. The insolubility of the Étard complexes in all the solvents with which they do not react and their amorphous state would suggest a polymer or a highly associated structure which could exist only in the solid state. One possibility would be that several molecules of the primary adduct R—OCrCl$_2$OH could add to the excess molecules of chromyl chloride, through hydrogen bonds or in some way not yet specified. These associations would be formed only in the solid state, in which the ratio 1 RH:2CrO$_2$Cl$_2$ is approximately maintained. Elucidation of the structure of Étard complexes needs further research, but we think that facts known so far can best be explained by the hypothesis that during the formation of these compounds the first step is the substitution of a single hydrogen atom with a group resulting from the oxidant. The primary complexes thus formed may in some cases undergo subsequent transformations, namely more advanced oxidations or eliminations leading to olefins when the molecular structure allows it.

In the previous paper,[1] a mechanism was proposed for the chromyl chloride attack on saturated hydrocarbons (and similarly for the chromic acid oxidation), namely an electrophilic attack of the oxidant at the carbon atom of a C—H group (SE mechanism). Such a reaction is uncommon with hydrocarbons. So far electrophilic substitutions at the saturated carbon atom have been studied especially in the case of organometallic compounds, the leaving group being a metal cation. Recently an appreciable number of electrophilic substitutions at a saturated carbon have been investigated by Cram *et al.*[19] In all these reactions the leaving group is a proton. The hydride transfer from a saturated hydrocarbon to a carbonium ion implies also the attack of an electrophile at a saturated carbon and therefore belongs to the SE type mechanism. A mechanism involving a frontal attack of the carbonium ion and a cyclic transition state in which the electron pair of the C—H bond which is being broken is shared between three atoms has been proposed:[20]



The electrophilic substitutions of the hydrogen linked to a saturated carbon atom are so seldom encountered probably because only few electrophiles are strong enough to attack the sigma electrons of a C—H bond. Reactants capable of such an attack are, besides the carbonium ions, chromium compounds such as CrO$_2$Cl$_2$ or HCrO$_4^-$ and probably also other oxides or ions of transition metals in their higher valency states. The outstanding electrophilicity of these reactants is due to their great tendency to accommodate electrons donated by the substrate, in the vacant *d* orbitals of the transition metal. On the other hand, oxidants such as the ions HCrO$_4^-$, MnO$_4^-$, unlike the carbonium ions, do not react with donor molecules in solvents such as water, acetic acid etc.

The participation of *d* orbitals to the metal-oxygen bonds in CrO$_2$Cl$_2$, HCrO$_4^-$

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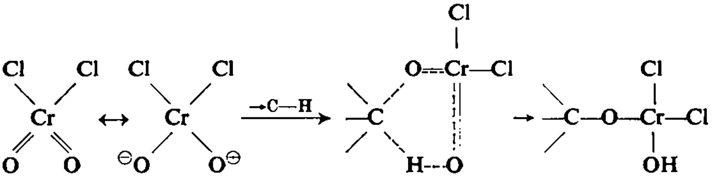
[19] D. J. Cram, *Chem. Eng. News* **41**, No. 33, 92 (1963); D. J. Cram and L. Gosser, *J. Amer. Chem. Soc.* **85**, 3890 (1963) and other papers by the same workers cited therein.

[20] E. S. Lewis and U. C. R. Symons, *Quart. Rev.* **12**, 230 (1958).

[21] K. B. Wiberg and G. Foster, *J. Amer. Chem. Soc.* **83**, 423 (1961).

etc., opens the possibility for one of the oxygen atoms to behave as an electrophile and for the other as a nucleophile during the transition from oxidation state Cr(VI) to Cr(IV). This can be formally expressed by resonance structures of the type V. The driving force of the reaction is the formation of two new bonds, C—O and H—O in VII. It seems very plausible that formation of these new bonds should proceed simultaneously with the breaking of the C—H bond, through a cyclic transition state VI. In this case the mechanism would be SE_2. Formally the transfer of a hydride ion, from the organic compound to the oxidant takes place.



V VI VII

It may be expected on the basis of anology[19,20] that such a process would occur with retention of configuration. It is of interest to note that oxidation of (+)-3-methylheptane with chromic acid in acetic acid to the tertiary alcohol proceeds with 70–85% retention of configuration.[21]

Recently our interpretation[1] of the Étard reaction has been strongly criticized by Wiberg and Eisenthal.[7] These authors disagree both with the proposed structure for the chromyl chloride complexes and the discussed reaction mechanism. Wiberg and Eisenthal's support of the old structure I for the chromyl chloride complex of toluene, is based on the fact that the hydrolysis of this compound even under reducing conditions "leads largely to benzaldehyde". As shown above, in this reaction benzyl alcohol is also formed. The formation of benzhydrol isolated as its acetate by the decomposition of the Étard complex of diphenylmethane with acetic acid containing sulphur dioxide is simply obviated by the phrase "presumably a reduction has occurred", despite the fact that sulphurous acid does not reduce the carbonyl compounds.

The mechanism of the oxidation reactions of saturated hydrocarbons with chromic acid should be homolytic according to Wiberg and Eisenthal.[7] The activated complex, represented by formula VIII, is supposed to arise through the abstraction of one hydrogen atom from the hydrocarbon by the oxidant. In this way the chromium atom passes into the oxidation state Cr(V) and the hydrocarbon into a free radical. These species are supposed to coexist within a solvent cage. Their recombination leads to the ester of a chromium (IV) derivative, represented by IX:

$$\underset{}{R_3CH + H_2CrO_4} \rightarrow \underset{\text{VIII}}{[R_3C{\cdot}H_3CrO_4]} \rightarrow \underset{\text{IX}}{R_3C\text{—}O\text{—}Cr(IV)}$$

This conception implies the transfer of a second electron from the radical to the oxidant during the formation of the carbon–oxygen bond (VIII → IX). It is even admitted that when a highly stabilized carbonium ion may be formed, the reaction within the solvent cage is:

$$\underset{\text{VIII}}{R_3C \cdot H_3CrO_4} \rightarrow \underset{\text{X}}{[R_3C^+H_3CrO_4^-]}$$

This exception is supposed to account for the results of the oxidations of hydrocarbons in the presence of azide ions[6] and for the molecular rearrangements associated sometimes with the chromic acid oxidations of hydrocarbons.[22] It can be easily seen that IX and X, which can be still written in their dehydrated form, respectively $R_3C—OCrO_2H$ and $R_3C^+HCrO_3^-$, represent the two equilibrium forms, the covalent and the ionized one, of the same compound (similarly to the equilibrium $IIa \rightleftarrows IIb$). As regards the transition state VIII there are serious objections.

One of the principal drawbacks of the radical mechanism through the transition state VIII is its inability to account for the preponderant retention of the steric configuration by the oxidation of (+)-3-methylheptane.[21] It is known that the majority of the reactions of optically active compounds occuring through free radicals lead to optically inactive products. Among a few exceptions are the thermal decompositions of the optically active acyl peroxides RCO_2O_2CR leading to esters of the type RCO_2R in which both R groups preserve their initial configuration. This was tentatively explained either by a mechanism implying a cyclic transition state or by formation of the radicals $RCO_2\cdot$ and $R\cdot$ in a solvent cage, which recombine before having the opportunity to assume a planar configuration and a random orientation in solution.[23] For instance a cage effect was successfully invoked in order to explain the thermal decomposition of molecules like azo-bis-isobutyronitrile in inert solvents.[24] It is unlikely that in the oxidation in solution of a saturated hydrocarbon with a solvated $HCrO_4^-$ ion, the free radical and the Cr(V) derivative should persist in a solvent cage under conditions in which the racemization of the free radical would not occur. Products of dimerization or disproportionation which characterize the formation of free radicals have never been observed during the chromic acid oxidations. Obviously the retention of configuration in the oxidation of (+)-3-methylheptane is best explained by a concerted bimolecular mechanism similar to the above one proposed for the transition state by the formation of the Étard complexes.

Wiberg and Eisenthal also show[7] that the reactivity of toluene, diphenylmethane and triphenylmethane towards chromyl chloride (1:100:1000) and towards chromic acid oxidation in 91% acetic acid (1:6·3:8·1) resembles more the reactivity of the same hydrocarbons towards a hydrogen atom abstraction by bromine atoms (1:7:5·5) than towards the solvolysis of benzyl, benzhydryl and triphenylmethyl halides ($1:10^5:10^7$). These relative rates are presented as arguments against the heterolytic cleavage of a CH bond and in favour of a radical mechanism. Actually these data merely suggest that the charge density at the carbon atom, in going from the initial state to the transition state during the oxidation is small. A similar small separation of charges is to be expected also in the case of a mechanism implying a transition state VI. Relative rates of SE_2 reactions concerning the electrophilic substitutions at mercury bearing carbon atoms are available. In the neutral acetolysis of di-s-butylmercury and di-n-butylmercury, as well as in the triiodide ion cleavage of the corresponding RHgI compounds, the relative rate factors are small (10 and 7).[25]

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[22] F. Mares and J. Rocek, *Coll. Czech. Chem. Comm.* **26**, 2355 (1961).

[23] cf. for Refs, E. L. Eliel, *Stereochemistry of Carbon Compounds* p. 383. McGraw-Hill, New York, London (1962).

[24] cf. C. Walling, *Free Radicals in Solution* p. 76. Wiley, New York (1957).

[25] S. Winstein and T. G. Traylor, *J. Amer. Chem. Soc.* **77**, 3747 (1955).

Furthermore, the rate sequence s-Bu > n-Bu is that predicted for the SE_2 mechanism[26] and corresponds to that observed in chromic acid oxidations (sec. > prim.).

The arguments put foward by Wiberg and Eisenthal[7] are therefore not conclusive and we consider that both the experimental facts presented by the authors cited[21] and our findings are better explained by the mechanism given in our previous paper[1] and more extensively developed in the present work.

EXPERIMENTAL

Étard complex of triphenylmethane

The triphenylmethane complex with chromyl chloride was prepared by the standard procedure[1] and used after filtration in a dry box, in argon, and washing with dry CCl_4.

a. *Hydride ion exchange with ethyl ether.* To 40 ml abs ethyl ether 1·5 g triphenylmethane complex (containing 0·66 g, i.e. 2·7 mmole triphenylmethane) were added. The mixture was kept in an inert gas at room temp for 6 hr. The brown reaction mixture deposited a black-brown tarry substance which after decanting the ethereal layer and several washings with ether, crystallized in bright black-brown plates. (Found: I. C, 18·77; H, 4·09; Cl, 25·74; Cr, 25·42. II. C, 19·52; H, 3·95; Cl, 31·80; Cr, 24·10. $C_4H_{10}O{\cdot}CrO_2Cl_2$ requires: C, 20·90; H, 4·40; Cl, 25·42; Cr, 22·71%.)

The decanted ethereal layer was washed with a cold sat. $NaHCO_3$aq. The aqueous layer was again extracted with about 100 ml ether in several portions, and after drying and evaporation of the combined ethereal layers, 0·6 g of crystals were left, m.p. 83°, yield 91%; from EtOH, m.p. 92° and mixed m.p. with triphenylmethane 93°.

An ethyl ether complex directly prepared in an argon atm, with efficient stirring and cooling, by introducing dropwise 15·5 g CrO_2Cl_2 (8 ml or 0·1 mole) dissolved in 75 ml CCl_4, into a solution of 14·8 g (23 ml or 0·2 mole) ethyl ether in 50 ml CCl_4, was decomposed with ice-water after filtration and washing with CCl_4. After steam-distilling the decomposition mixture, the CCl_4-layer in the distillate, after drying showed AcOEt bands in the IR spectrum. In the aqueous layer acetaldehyde was identified by its dinitrophenylhydrazone, m.p. 148°, mixed m.p. with an authentic sample 153°.

b. *Hydride ion exchange with cycloheptatriene.* In 20 ml dry CCl_4 were suspended 2·7 g of the Étard complex of triphenylmethane (containing 1·2 g, i.e. 4·92 mmoles triphenylmethane). After introduction of argon gas, 0·45 g (4·29 mmoles) cycloheptatriene[27] were added and the mixture was refluxed for 3 hr. After cooling it was filtered, and the brown precipitate washed twice with 10 ml dry CCl_4. The filtrate left to evaporate furnished a slightly yellow crystalline residue of 1·2 g (yield about 100%), m.p. 91·5° (from EtOH) and mixed m.p. with an authentic sample of triphenylmethane 92°. The light-brown powdery complex on the filter was decomposed at 0° in 50 ml 10% perchloric acid solution containing 2 g oxalic acid (as a reducing agent). The white crystals isolated in a small amount, washed with alcohol and ether and dried show the following IR spectrum (KBr): 3070 vw; 3020 mw; 1484 ms; 1280 vw; 1100 vs (ClO_4^-); 674 w; 638 ms; 626 vs (ClO_4^-). These bands correspond to those of the tropylium cation[28] and of the perchlorate anion.[29]

The IR spectrum of the crude precipitate before the washing did not show any absorption in the region 1500–1800 cm^{-1}, indicating the absence of tropone and confirming that tropylium perchlorate is the decomposition product of the new complex of cycloheptatriene, formed through a hydride exchange with the Étard complex of triphenylmethane.

Étard complex of diphenylmethane

In about 90 ml CCl_4, 7 g diphenylmethane complex with chromyl chloride[1] were suspended and the mixture decomposed by stirring it with 100 ml water at 0°. After separation of the CCl_4 layer, the aqueous layer was extracted once with 30 ml CCl_4. The combined extracts were washed with cold water, then with 5% $NaHCO_3$aq, then again with water, dried on $MgSO_4$ and evaporated *in vacuo*. The quantitative determination of the decomposition products in the residue was effected by IR spectroscopy using the 607 cm^{-1} band for diphenylmethane, the 582 cm^{-1} band for benzhydryl

[26] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 244 (1935).

[27] D. G. Lindsay and C. B. Reese, *Tetrahedron* **21**, 1673 (1965).

[28] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **76**, 3203 (1954).

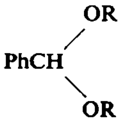
[29] S. D. Ross, *Spectrochim. Acta* **18**, 225 (1962).

TABLE 1. WATER DECOMPOSITION PRODUCTS OF THE ÉTARD COMPLEX OF DIPHENYLMETHANE

Decomposition product (% mole)				Yield[a] %
Ph_2CH_2	Ph_2CHCl	Ph_2CHOH	$Ph_2C{=}O$	
1·1	4·5	20	74·5	81
2·2	6·3	20·5	70·5	51·5
1·5	5·3	21·9	71·7	77

[a] Yields based on the hydrocarbon contained in the complex.

TABLE 2. DECOMPOSITION PRODUCTS OF THE ÉTARD COMPLEX OF TOLUENE BY USING DIFFERENT SOLVENTS

Decomposition medium	Decomposition product (% mole)					Yield[a] %
	PhCHO	$PhCH_2OH$	$PhCH_2OCOR$	 $PhCH\genfrac{}{}{0pt}{}{\diagup OR}{\diagdown OR}$	$PhCH_2Cl$	
$CH_3COOH + SO_2$	89·1	6·3	4·4	—	—	61·5
HCOOH	96	2·6	1·4	—	—	70
$HCOOH + SO_2$	82	—	12·8	—	4·85	54
$tBuOH + SO_2$	75	17·2	—	—	7·8	68·6
MeOH	69·34	5·11	—	25·5	—	50
$MeOH + SO_2$	83	13	—	2·4	1·66	70
$H_2O + FeSO_4$	94	4	—	—	3	57
H_2O/CCl_4	97	1	—	—	2	60

[a] Yields based on the hydrocarbon contained in the complex.

[b] Decomposition conditions are similar to those for diphenylmethane.

chloride, the 597 cm^{-1} band for benzhydrol and the 638 cm^{-1} band for benzophenone. The precision of the method is at least 1·5%. Qualitative and quantitative control of the composition of the mixture formed on decomposition was also carried out by gas-chromatography, the benzhydrol being determined as its methyl ether. A good agreement between the two methods was found. In Table 1 the results are given for 3 experiments carried out in the above manner.

Étard complex of toluene

The complex of toluene with chromyl chloride[1] was decomposed with the solvents indicated in Table 2. After working up the decomposition mixtures, the reaction products were identified and determined by gas-chromatography (Apiezon L column of 1 m/6 mm, 25% on Sterchamol, at 120°, 120 ml of H_2/min). The retention times of the oxidation products were compared with authentic samples.