THE MECHANISM OF THE ETARD REACTION

ILEANA NECSOIU, A. T. BALABAN, I. PASCARU, ELVIRA SLIAM, M. ELIAN and C. D. NENITZESCU

Chemical Institute of the R.P.R. Academy and Institute of Atomic Physics, Bucharest, Roumania

(Received 27 January 1963)

Abstract—Electron spin resonance measurements show that one of the two chromium atoms in Etard complexes is diamagnetic, hence sexivalent, whilst the other is paramagnetic, therefore the second chromium atom has a lower valency state and is probably quadrivalent. By decomposing the Etard complexes of diphenylmethane and of n-propylbenzene with sulphur dioxide containing solutions, the corresponding alcohols are obtained in appreciable amounts, along with the known ketones. Primary and secondary alcohols such as benzyl alcohol and benzhydrol are smoothly oxidized in aqueous suspension by one mole of chromyl chloride. Therefore, alcohols are probably the primary products in the hydrolysis of Etard complexes. It is admitted that the first step in oxidations by chromyl chloride consists in the transfer of a hydride ion from substrate to oxidant, converting one Cr(VI) atom to Cr(IV), which remains bound to a second Cr(VI) atom.

As ETARD observed in 1881, on treating various hydrocarbons RH with chromyl chloride in inert solvents such as carbon disulphide of carbon tetrachloride, brown amorphous precipitates are formed the purification of which is difficult because they are hygroscopic and scarcely soluble in most solvents. By decomposing these complexes with water, aldehydes or ketones are obtained, often in high yields, accompanied sometimes by smaller amounts of chlorinated derivatives of the initial hydrocarbons.

It is generally admitted that Etard complexes have the composition $RH \cdot 2Cr$ O₂Cl₂,¹⁻³ but there are cases such as $Ph_3CH \cdot CrO_2Cl_2^{1,2}$ when the hydrocarbon: chromyl chloride ratio is believed to be 1 : 1, and other cases when this ratio is intermediate between 2 and 3.⁴

Although the scope and limitations of the Etard reaction have been studied,¹ the structure of the complexes formed from chromyl chloride with hydrocarbons is less known. Structure (I) proposed by Etard⁵ contains two quadrivalent chromium atoms



¹ Review by W. H. Hartford and M. Darrin, Chem. Rev. 58, 1 (1958).

- * R. Slack and W. A. Waters, J. Chem. Soc. 599 (1949).
- ⁸ K. B. Wiberg, B. Marshall and G. Foster, Tetrahedron Letters, 345 (1962).
- ⁴ C. C. Hobbs and B. Houston, J. Amer. Chem. Soc. 76, 1254 (1954).
- ^a A. Etard, Ann. Chim. phys. [5], 22, 218 (1881).

and is the most widely used.^{1,3} Two other structures proposed later contain two sexivalent chromium atoms: formula II contains carbon-chromium bonds,⁶ and formula III contains hydrogen bonds between the hydrocarbon and chromyl chloride.¹

The structure of Etard complexes has been investigated in order to obtain information concerning the mechanism of chromic acid oxidations.

Electron spin resonance measurements

Wheeler measured the magnetic susceptibility of the chromyl chloride-toluene complex and found a value of 3.16 Bohr magnetons for one chromium atom.⁷ It follows that the Etard complex contains Cr(IV) and this was interpreted as support for formula I.

In the present work ESR measurements were effected on complexes of chromyl chloride with toluene, diphenylmethane and triphenylmethane.

As known,⁸ sexivalent chromium has no unpaired electrons and hence gives no ESR absorption, but in all other valency states (II–V) it has unpaired electrons and gives an ESR signal. On the basis of this difference it appeared possible to discriminate between Cr(VI) and chromium atoms of lower valence by determining the number of paramagnetic chromium atoms in known amounts *m* of complexes. The number *n* of chromium atoms in the sample is determined by the relationship:

$$n \times 10^{-19} = 60.23 \ m/M \tag{1}$$

Two inorganic ammino-complexes of trivalent chromium were employed as standards because the usual salts of Cr(III) contain water of crystallization which has an adverse effect on the characteristics of the resonant cavity. The number N of paramagnetic centres in Etard complexes was computed from the formula:

$$N = N_0 \frac{A}{A_0} \left(\frac{\Delta H}{\Delta H_0}\right)^2 \frac{H_{\rm m,0}}{H_{\rm m}}$$
(2)

where N_0 is the number of chromium atoms in the standard, A and A_0 are the amplitudes of resonance signals corresponding to sample and to standard, ΔH and ΔH_0 are line widths of the same curves between points of maximum slope (cf. Fig. 1). H_m and



FIG. 1.-Differential ESR signal of the Etard complex of triphenylmethane.

- ⁶ G. Rohde, Sammlung Chemischer und chemisch-technischer Vortäge, vol. 6, p. 241 F. Enke, Stuttgart (1901), cited after.¹
- 7 O. H. Wheeler, Canad. J. Chem. 36, 667 (1958); 38, 2137 (1960).
- ⁸ S. A. Altschüller and B. M. Kozyrev, *Elektronnyi paramagnitnyi rezonans*, p. 97. Fizmatghiz, Moscow (1961).

 $H_{m,0}$ are the amplitudes of the modulation field (peak-to-peak); both H_m and $H_{m,0}$ were equal to 10 oersteds.

As seen from Table 1, the ratio between the number of paramagnetic centres and the total number of chromium atoms in the sample is approximately 0.5 in the Etard complexes of di- and triphenylmethane, and is a little greater in the toluene complex. Thus in Etard complexes half of the chromium atoms appear to be paramagnetic, and half diamagnetic, hence sexivalent.

Sample No.	Complex	Amount m	Mol. weight M mg/mmole	No. of chro- mium atoms $n \times 10^{-19}$ after (1)	∆ <i>H</i> oersteds	۸ mm	No. of para- magnetic cen- tres $N \times 10^{-19}$ after (2)	Ratio N/n
۱	(PhCH ₃) _{1/2} ·CrO ₂ Cl ₂	17-1	201	5 1	562	54	3-5	•69
2	(Ph2CH2)1/3 CrO2Cl2	34 7	239	8.7	550	62	3.8	·44
3	(Ph ₃ CH) _{1/2} ·CrO ₂ Cl ₂	22 2	277	4 8	527	42	2.4	·50
4	[Cr(NH ₃) ₈](NO ₃) ₃ ·H ₂ O	26.0	358	4 35	500	84	4.35	1.00
5	[Cr(NH ₃) ₅ Cl]Cl ₂ (standard)	28.3	243	7.0	418	200	7.0 - N ₀	Taken 1.00

TABLE 1. PROPORTION OF PARAMAGNETIC CHROMIUM ATOMS IN ETARD COMPLEXES

It can be further observed that the half-breadth of the resonance curve decreases with increasing number of phenyl groups in Etard complexes; this effect may be caused by the reduction of dipole-dipole interactions owing to increasing volume.

The spectroscopic splitting factor g, determined with the aid of an internal standard of diphenylpicrylhydrazyl (DPPH), was found equal to 1.97 ± 0.01 in all three Etard complexes studied. The trivalent chromium complexes included in Table 1 under Nos. 4 and 5, as well as $Cr_2(SO_4)_3$ gave a g value of 1.97 ± 0.01 , in agreement with literature data.⁸ As yet no report has appeared about the g-factor of quadrivalent chromium compounds. The measurements with quadrivalent barium chromate $Ba_2CrO_4^{9}$ gave a value of 1.97 ± 0.01 . As there is no difference between the g-factors of tri- and quadrivalent chromium, therefore the valency state of paramagnetic chromium in Etard complexes cannot be inferred on the basis of ESR data.

In a forthcoming paper the ESR spectra of solutions of hydrocarbons, alcohols, ketones and carboxylic acids in chromyl chloride will be described and the hyperfine structure shown by the latter two classes of compounds will be analysed.

Reductive hydrolysis of Etard complexes

The chemical composition of Etard complexes is uncertain as these complexes cannot be recrystallized and obtained pure. The preparation of these complexes with dilute solutions of reagents in various ratios and handling them in a dry box, yielded complexes of toluene, diphenylmethane and triphenylmethane, elementary analyses of which agree with the usual¹⁻⁸ formula RH·2CrO₂Cl₂. It must be emphasized that the

^{*} R. Scholder and G. Sperke, Z. anorg. allg. Chem. 285, 49 (1956).

elementary composition of the chromyl chloride-triphenylmethane complex also corresponds, contrary to literature data, to the formula $Ph_3CH \cdot 2CrO_2Cl_2$. It is thus certain that the ratio chromyl chloride : hydrocarbon is invariably 1 : 2, and independent of the hydrocarbon structure.

This formula of the triphenylmethane-chromyl chloride complex is at variance with formula (I), which assumes the presence of two hydrogen atoms at the carbon atom undergoing oxidation by chromyl chloride. It was possible to prove chemically that in the $Ph_3CH\cdot 2CrO_2Cl_2$ complex one hydrogen atom has been oxidized by decomposing the complex with a concentrated aqueous solution of sodium azide. An over 90% yield of triphenylmethylazide together with small amounts of triphenylmethylcarbinol are thus obtained. This result agrees perfectly with that observed in the oxidation of triphenylmethane by chromic acid in a solution containing azide ions, where triphenylmethylazide was similarly formed.¹⁰ Therefore oxidations by chromic acid and by chromyl chloride present an analogy; a difference is that in the former case no intermediate complex may be isolated because chromic acid oxidations are effected in solvents like water or acetic acid which decompose the intermediates.

An explanation of the 1:2 ratio in the triphenylmethane-chromyl chloride complex is afforded by the supposition that in the Etard complex only one molecule of chromyl chloride which now contains a Cr(IV) atom is bound to the hydrocarbon residue, whilst the second molecule of chromyl chloride is bound to the first one, in a manner which remains to be established.

In order to prove whether this assumption fits the reactions of other Etard complexes, the diphenylmethane complex was decomposed by glacial acetic acid containing an excess of sodium azide. After extracting with ether, washing with water and evaporating the solvent, the reaction product was analysed by I.R. spectroscopy and found to consist of a complex mixture of : benzhydryl azide (identified by bands at 2105 and 1225 cm⁻¹, ¹¹ which appear also in triphenylmethylazide) formed in ca. 17% yield after the result of elementary analysis, admitting that no other nitrogen-containing product was present; benzophenone, identified by the band at 1668 cm⁻¹; benzhydrol, identified by bands due to associated OH stretching; and finally benzhydryl acetate, identified by ester bands and by hydrolysis to benzhydrol.

The formation of benzhydrol as a primary reaction product formed in prevailing yield in the hydrolysis of the diphenylmethane Etard complex was evidenced by decomposing this complex with a solution of sulphur dioxide in acetic acid. This reagent reduces Cr(VI) and Cr(IV) from the Etard complex to Cr(III), and thus preserves the primary product from further oxidation subsequent to hydrolysis. In the reaction product isolated after this treatment, benzhydrol was identified both by the I.R. spectrum and as N-phenylcarbamate; besides benzhydrol benzophenone is also formed.

The conclusion stemming from these experiments is that the primary product in the decomposition of the diphenylmethane Etard complex with water is benzhydrol, and that this product is further oxidized in aqueous solution to benzophenone by the second molecule of chromyl chloride, respectively chromic acid formed by its hydrolysis (and perhaps also by the Cr(IV) atom evidenced in the ESR measurements). Experimentally it was indeed proved that on treating an aqueous suspension of

¹⁰ I. Necsoiu and C. D. Nenitzescu, Chem. & Ind. 377 (1960).

¹¹ E. Lieber, C. N. R. Rao, T. S. Chao and C. W. W. Hoffman, Analyt. Chem. 29, 916 (1957).

benzyhdrol with one mole of chromyl chloride under conditions identical with those employed for hydrolyzing Etard complexes, benzophenone is obtained in quantitative yield. Similarly, the treatment of benzyl alcohol with water and one mole of chromyl chloride afforded benzaldehyde in ca. 90% yield.

The results of the chemical investigation show that in Etard complexes two molecules of chromyl chloride are taking part and only one hydrogen atom has been removed. This is in agreement with the ESR measurements which indicate that one chromium atom from the two molecules of chromyl chloride is diamagnetic hence sexivalent, and that only the other has a lower valency state, probably IV.

Recently Wiberg *et al.*³ studied the oxidation of n-propylbenzene with chromyl chloride. Besides the two ketones observed previously,¹² propiophenone and phenyl-acetone, these authors also identified 1-phenyl-1-chloropropane. On oxidizing 1-phenyl-2-dideuteropropane they obtained 1-phenyl-1-deuteroacetone evidencing the migration of one hydrogen from the β -position to the α -position of the propyl sidechain.

It appeared interesting to apply to the Etard complex of n-propylbenzene the reductive hydrolysis with a saturated aqueous solution of sulphur dioxide. The I.R. spectrum of the reaction product presents a broad maximum at ca. 3500 cm^{-1} due to associated hydroxy groups and CO stretching bands at 1683 and 1710 cm⁻¹. Gasliquid chromatography of the mixture reveals the presence of several components, identified by comparing retention times with those of authentic specimens: propenylbenzene, a ketone fraction with retention time close to propiophenone, an alcohol fraction with retention time close to 1-phenyl-1-propanol, and a compound which is very probably 1-phenyl-1-chloropropane. From this mixture α -naphthylisocyanate precipitates an α -naphtylcarbamate, identical with that prepared from authentic 1-phenyl-1-propanol. The ketones were precipitated as 2,4-dinitrophenylhydrazones. These observations lead to the representation from chart I for the reaction of n-propylbenzene with chromyl chloride, where the manner in which the chromium atoms are bound in the complex is not shown in detail.

CHART 1. REACTION OF *n*-*p***ROPYLBENZENE** WITH CHROMYL CHLORIDE



Discussion of the results

The analogy between the Etard reaction and the oxidations with chromic acid¹³ was pointed out earlier.² An Etard complex may be considered as a stabilized intermediate formed in an oxidation with a chromic(VI) derivative performed in a nonsolvating medium. It is conceivable that in chromic acid oxidations in aqueous or

¹⁸ W. V. Miller and G. Rohde, Ber. Dtsch. Chem. Ges., 23, 1070, 1356 (1890).

¹³ Cf. the complete review by W. A. Waters, Quart. Rev. 277 (1958).

acetic solution, a similar intermediate is involved but owing to immediate hydrolysis or acetolysis no isolation of the intermediate is possible in these cases. Some observations made in oxidations with chromic acid may therefore be used for interpreting the first step of the Etard reaction.

No electron transfer from a saturated hydrocarbon or an alcohol to a Cr(VI) derivative can take place unless it is accompanied by the transfer of a hydrogen nucleus. Hence this process involves the breaking of a C—H bond and, as the isotopic effect in the oxidations of D—CMe₂OH¹⁴,* and D—CEt₃¹⁵ proves, it occurs as the rate-determining step of the reaction.

An essential question is whether in the first step of the oxidation with chromic acid or other sexivalent chromium derivatives a hydride ion or a hydrogen atom is transferred from the substrate to the oxidant. The former¹⁵⁻¹⁷ as well as the latter¹⁸ possibility has been considered previously.

A hydride ion transfer is favoured by existing data. The relative oxidation rates of methyl, methylene, and methine groups by chromic acid were found to be¹⁹ approximately $1 : 10^2 : 10^3$. This ratio and especially that of the tertiary-bound hydrogen is closer to heterolytic reactions such as the solvolysis of alkyl bromides,²⁰ where the ratio is about $1 : 2-10 : 10^3-10^6$, than to homolytic reactions such as the halogenation of alkanes, where the reactivities in conditions of maximum selectivity (at 100°)²¹ are only 1 : 4 : 7. A conspicuous influence is exerted by the substituent on the oxidation rate by chromic acid of *p*-substituted 1-phenylethanols:²² the rate decreases in the order of decreasing electron-donating power of the substituent, MeO > Me₃C > Me > H > Cl > NO₂ as in solvolyses of substituted benzyl halides²³ and tosylates.²⁴

One may assume that an oxidant such as a Cr(VI) derivative behaves as a strongly electrophilic reagent, and that the oxidation consists in the elimination of a hydride ion by the substrate. Such a reaction would then be analogous to the abstractions of hydride ions by carbonium ions (A^{\oplus}) studied by Bartlett and his school:²⁵

Hydride abstraction: $R_3CH + A^{\odot} \rightarrow R_3C^{\odot} + HA$

First step in oxidation: $R_3CH + Cr(VI) \rightarrow R_3C^{\oplus} + HCr(IV)^{\odot}$

It must be emphasized that these schemes represent only the electron transfer in the first step of both processes and that they give no information about the more or

* The mechanism of Westheimer and coworkers involving an ester of chromic acid with secondary alcohols which is oxidized in a base-catalysed concerted process, is susceptible of a different interpretation, as pointed out by Rocek¹⁶ on the basis of kinetic data.

- ¹⁴ F. H. Westheimer and N. Nicolaides, J. Amer. Chem. Soc. 71, 25 (1949); A. Leo and F. H. Westheimer, *Ibid.* 74, 4383 (1952).
- 18 W. F. Sager and A. Bradley, J. Amer. Chem. Soc. 78, 1187, 4970 (1956).
- ¹⁴ J. Roček and J. Krupička, Coll. Czech. Chem. Com. 23, 2068 (1958); J. Roček, Ibid. 22, 1509, 1519 (1957).
- 17 D. P. Archer and W. J. Hickinbottom, J. Chem. Soc. 4197 (1954).
- ¹⁸ K. B. Wiberg and G. Foster, J. Amer. Chem. Soc. 83, 423 (1961); K. B. Wiberg and R. J. Evans, Tetrahedron 8, 313 (1960).
- ¹⁹ J. Roček, Nature, Lond. 184, 326 (1959); J. Roček, Chem. Listy. 51, 459 (1957); G. Foster and W. J. Hickinbottom, J. Chem. Soc. 680 (1960).
- ¹⁰ A. Streitwieser, Chem. Rev. 56, 615 (1956).
- ²¹ H. B. Hass, E. T. McBee and P. Weber, Ind. Eng. Chem. 28, 333 (1936).
- 22 H. Kwart and P. S. Francis, J. Amer. Chem. Soc. 77, 4907 (1955).
- 28 G. M. Bennett and B. Jones, J. Chem. Soc. 1815 (1935).
- ²⁴ J. K. Kochi and G. S. Hammond, J. Amer. Chem. Soc. 75, 3445 (1953).
- ²⁵ P. D. Bartlett, F. E. Condon and A. Schneider, J. Amer. Chem. Soc. 66, 1531 (1944); P. D. Bartlett and J. D. McCollum, *Ibid.* 78, 1441 (1956).

less free state of the carbonium ion formed in them. The appearance of free carbonium ions is determined by the nature of the initial hydrocarbon R_3CH , and by the solvating power of the solvent and does not depend on the nature of the electrophilic species unless the solvent is a poorly solvating medium as in the Etard reaction. In this case the electrophilic partner may become attached to the newly-formed organic cation in the form of an ion pair or of a covalent compound. In other words the situation arrived at by the abstraction of a hydride ion from a hydrocarbon R_3CH does not differ from that produced by the elimination of an anion X⁻ from R_3CX in solvolyses.

The appearance of carbonium ions with a degree of freedom corresponding to their structure (to the extent of the resonance or hyperconjugative stabilization) and to the dissociative power of the reaction medium is proved by trapping these ions as alkyl azides, if the oxidation is carried out in the presence of azide ions.¹⁰ The amount of organic azide formed evidently depends on the stability of the respective carbonium ions, in the prevailing conditions. It was thus found that the oxidation of Ph₃CH by chromic acid yields 97.5% azide, of Ph₂CHMe 51% azide, and of Et₃CH only ca. 10% azide along with large amounts of Et₃COH. Plausibly the Et₃C⁺ cation which is less stabilized and thus less selective than Ph₃C⁻ reacts more rapidly with solvent molecules than the latter.

The oxidation of a large number of branched alkanes by Hickinbottom *et al.*,²⁶ led to the conclusion that olefins appear as intermediates in these reactions. The most plausible hypothesis is that these olefins result from carbonium ions. The same conclusion is reached by studying the oxidation products of phenylalkanes.²⁷

A hydrogen atom of a C—H group in a saturated hydrocarbon, in a side-chain of an aromatic hydrocarbon, or in a primary or secondary alcohol, may undergo attack by nucleophilic (B), radical (R) or electrophilic reagents (E). The attack of a nucleophilic reagent on the proton of a C—H bond is exceptional and occurs only if the resulting carbanion is stabilized as in acetylene or cyclopentadiene. Such an attack involves a linear transition state (IV).



A linear transition state is also involved in the abstraction of a hydrogen atom from a C—H bond by a radical reagent. The theory of this transition state (V) is well known in the case of simple radical reactions.²⁸

In the case of an electrophilic reagent (E) which acts on the electrons of the C—H bond, a linear transition state is improbable and a triangular transition state (VI) with an electron pair divided between three centres is plausible. Such transition states were considered in the hydrolysis of alkyl-boranes,²⁹ and in hydride abstractions from hydrocarbons.³⁰ A reaction proceeding through this transition state will take place

¹⁰ G. Foster and W. J. Hickinbottom, J. Chem. Soc. 215 (1960).

²⁷ I. Necsoiu and C. D. Nenitzescu, Acad. R.P.R. Revue de Chimie, 6, 245 (1961).

²⁸ S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes* p. 87. McGraw-Hill, New York (1941).

²⁹ M. F. Hawthorne and E. S. Lewis, J. Amer. Chem. Soc. 80, 4296 (1958).

¹⁰ E. S. Lewis and M. C. R. Symons, Quart. Rev. 12, 230 (1958).

with retention of stereochemical configuration. This conclusion coincides with the experimental facts observed by Wiberg and Foster¹⁸ in the oxidation of (+)-3-methylheptane leading to (+)-3-methyl-3-heptanol, with retention of configuration in 70-85%.*

A cyclic transition state for the oxidative hydride abstraction from a saturated hydrocarbon was first proposed, as far as we are aware, by Roček *et al.*^{16,31} In the case of oxidations by chromyl chloride all facts so far known are well reflected by a cyclic transition state VII leading to Etard complexes represented by esters (VIIIa) or ion pairs (VIIIb-c) according to the solvent and to the nature of the R group.



Structure VIII for the Etard complexes is possible owing to the marked tendency of Cr(VI) oxyacids to exist in acid medium as pyroacids. In structure VIII one of the chromium atoms is quadrivalent and the other is sexivalent in agreement with magnetic and chemical data. Structure VIIIa assumes that the latter chromium atom bears a hydroxy group, but of course a tautomeric equilibrium is possible in the anions VIIIb-VIIIc. In complexes where the non-ionized form VIIIa predominates (when R⁺ is weakly stabilized by conjugation or hyperconjugation), the hydrolysis occurs by breaking of the Cr^{IV}-O bond,¹⁸ whilst in the solvolysis of ionized complexes VIIIb-c, the R⁺ cation reacts with solvent molecules as shown in reactions using the heavy oxygen isotope ¹⁸O.³²

EXPERIMENTAL

Electron spin resonance measurements

The ESR apparatus³³ had a quartz-stabilized working frequency of 9270 MHz. The field was varied linearly by means of a Miller integrator and the resonance signal recorded as the derivative of the absorption curve. Samples were weighed as solids in teflon vials of 5 mm external diameter and the resonance signals registered at room temperature. The g factor was determined relative to the known g-value of DPPH with samples containing an internal DPPH standard.

* The authors¹⁸ propose a mechanism involving a transition state of type (V) on the basis of which a retention of configuration can be conceived only with difficulty.

- ³¹ J. Roček, *Tetrahedron Letters* 4, 135 (1962). In this paper the author presents a new reaction mechanism based on the primary abstraction of a hydrogen atom, and proposes a transition state or a hybridized intermediate of an unusual type.
- ^{az} L. V. Sulima and I. P. Gragerov, J. Obshchei Khimii 29, 3825 (1959).
- ²³ I. Pascaru and A. Valeriu, Acad. R.P.R. Studii si cercetări de fizică 12, 165 (1961).

Complexes of phenylmethanes with chromyl chloride

After several experiments the following standard procedure was adopted: 0.06 mole hydrocarbon dissolved in 100 ml carbon tetrachloride or carbon disulphide was treated under powerful magnetic stirring in an atmosphere of dry argon with 0.04 mole $(3\cdot 3 \text{ ml})$ or 0.06 mole $(4\cdot 5 \text{ ml})$ chromyl chloride in 60 ml of the same solvent. The addition was effected during $1\cdot 5-2$ hr so that the temp did not exceed 35-45°. After 2 hr the precipitate was filtered off on a sintered glass filter and washed repeatedly with carbon tetrachloride, then dried by the passage of a stream of dryargon. All operations were conducted in a dry box. The yields were 96, 94 and 85% for triphenylmethane, diphenylmethane and toluene respectively.

Triphenvimethane Etard complex (the three samples analysed had initial ratios of Ph_CH : CrO_Cl_ as follows: 1 : 1, 1 : 2 and 3 : 2). Found: 1. C, 39:07; H, 2:98; Cl, 25:88

2. C, 40.60; H, 2.88; Cl, 25.09

3. C, 40.93; H, 2.81; Cl, 25.15; Cr, 18.18%.

Ph_CH.Cr_2O_4Cl4 requires: C, 41.18, H, 2.91; Cl, 25.59; Cr, 18.77%. (Ph_CH.CrO_2Cl4 would require: C, 57 16; H, 4 04; Cl, 17 76; Cr, 13 06%).

Diphenylmethane Etard complex. Found: C, 33-28; H, 2-93; Cl, 28-74; Cr, 21-90. Calc. for

C13H13C4Cr3O4: C, 32.73; H, 2.53; Cl, 29.66; Cr, 21.76. Toluene Etard complex. Found: C, 21.14; H, 2.37; Cl, 34.02; Cr, 25.24. Calc. for C7H9Cl4Cr3O4: C, 20.91; H, 2.01; Cl, 35.28; Cr, 25.89.

Decomposition of Etard complexes

The triphenylmethane-chromyl chloride complex on decomposition with water yielded 97% of triphenylcarbinol. On decomposition with a saturated aqueous solution of sodium azide it yielded 90% of triphenylmethyl azide; m.p. and mixed m.p. with authentic product 64°.

The diphenylmethane-chromyl chloride complex (6 g, 0.012 mole) was gradually added with good stirring to a solution of 8 g (0.12 mole) sodium azide in 150 ml glacial acetic acid. After shaking for 7 hr the mixture was diluted with water and extracted with ether. The residue obtained after washing, drying and evaporating the etheral solution, weighed 2.5 g and contained 17% diphenylmethyl azide, identified by bands at 2105 and 1255 cm⁻¹ (cf.¹¹). The I.R. spectrum also presented a band of associated $\dot{O}H$ groups at 3500 cm⁻¹ due to benzhydrol, two bands at 1240 cm⁻¹ (v C-O-) and 1740 cm⁻¹ (ν C–O) due to benzhydryl acetate and the 1668 cm⁻¹ band of benzophenone. Hydrogenation of the residue in ether in the presence of Pd-C 5% afforded diphenylmethylamine which was extracted from the ethereal solution with dil. hydrochloric acid; after evaporating the ether the product (2 g) was heated with alcoholic potassium hydroxide to hydrolyse the benzhydryl acetate; indeed, the ester bands were absent after this treatment, only an intense OH band was visible, along with the benzophenone CO band. By treating the residue with phenyl isocyanate, benzhydrol phenylcarbamate was obtained, m.p. 139° as indicated in the literature.34 (Found: C, 78 94; H, 5 89; N, 4.75. Calc. for $C_{211}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62%).

Benzhydrol was similarly identified in 36.4% yield in the mixture obtained by decomposing the Etard complex of diphenylmethane with a solution of sulphur dioxide in acetic acid.

Oxidation of benzhydrol and benzyl alcohol

Chromyl chloride (1.5 g, 10 mmole, 0.8 ml) was decomposed with 5 ml water, and then 1.8 g (10 mmole) benzhydrol added. Benzophenone was isolated in nearly quantitative yield (1.7 g) in a pure state, identified by mixed m.p., I.R. spectrum and its 2,4-dinitrophenylhydrazone. Benzyl alcohol was similarly oxidized in 90% yield to benzaldehyde identified as the 2,4-dinitrophenylhydrazone.

Decomposition of the n-propylbenzene-chromyl chloride complex with aqueous sulphur dioxide

By the above procedure the Etard complex was prepared from 12 g (100 mmole) n-propylbenzene and 10 g (5.2 ml, 65 mmole) chromyl chloride in 100 ml carbon tetrachloride. The complex (13 g) was decomposed with 150 ml water saturated with sulphur dioxide. The ethereal extract was washed with dil. alkali, then with water, dried and evaporated. Gas-liquid chromatography of the residue revealed that it consisted of 1% n-propylbenzene, 4% propenylbenzene, 16% chloropropylbenzene* (probably) and a major fraction (79%) of ketones and alcohols, of which 46% were ketones and 33% alcohols. The I.R. spectrum presented bands (in cm⁻¹) at 950 s, 973 w, 1003 m, 1015 m, 1078 m, 1181 m, 1222 vs, 1280 m, 1304 w, 1322 w, 1357 s, 1390 m, 1415 m, 1450 s, 1493 m, 1580 m, 1600 m, 1683 vs, 1710 s and a broad band at ca. 3500 m. Bands due to propiophenone are: 950, 1003, 1015, 1078, 1181, 1222, 1280, 1304, 1322, 1357, 1390, 1415, 1450, 1580, 1600 and 1683 cm⁻¹. The 1710 cm⁻¹ band is due to phenylacetone, and the 973, 1493 and 3500 cm⁻¹ bands are due to 1; phenyl-1-propanol; the last broad band appears at 3380 cm⁻¹ in pure 1-phenyl-1-propanol but at 3500 cm⁻¹ in a synthetic mixture ¹⁴ E. Bergmann and D. Wagenberg, Ber. Dtsch. Chem. Ges. 63, 2587 (1930).

of 1-phenyl-1-propanol with propiophenone. The reaction mixture on treatment with α -naphthyl isocyanate yielded an α -naphthylcarbamate with m.p. 96° which did not depress the m.p. of the authentic α -naphthylcarbamate of 1-phenyl-1-propanol (m.p. 101°)³⁴

I.R. absorption spectra were determined with a Jena U.R. 10 spectrophotometer. The gas chromatographic measurements were performed by Mrs. M. Fărcasiu.

Acknowledgements—We thank Professor Dr. R. Scholder, Technische Hochschule, Karlsruhe, for preparing and sending us a sample of Ba₂CrO₄. We also thank Professor P. Spacu from the Bucharest University for samples of inorganic complexes of chromium.

³⁵ A. Magnani and S. M. McElvain, J. Amer. Chem. Soc. 60, 813 (1938).