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CHROMYL CHLORIDE OXIDATIONS—II

OXIDATION OF STYRENES[1]

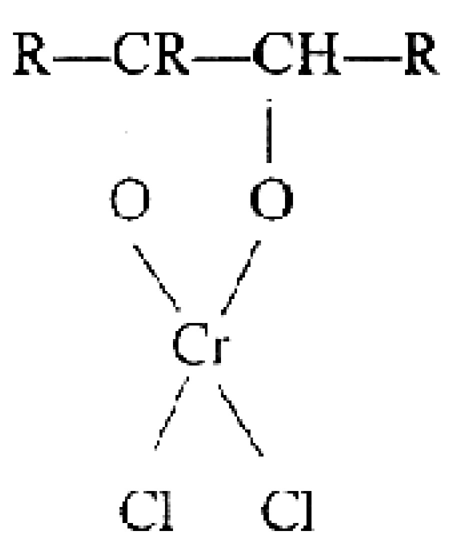
F. FREEMAN, R. H. DUBOIS[2] and N. J. YAMACHIKA[3]

Abstract—Chromyl chloride oxidation of 1-phenylpropene, 2-phenylpropene, and 1,1-diphenylethene gives 1-phenyl-2-propanone, 2-phenylpropanal, and 1,1-diphenylethanal, respectively, as the *sole* products of rearrangement. The yield of carbonyl product appears to be greatest when one side of the double bond is 1,1-disubstituted. The suggested mechanism involves an electrophilic attack of chromyl chloride at the carbon of the C—C double bond to give a resonance stabilized carbonium ion-like intermediate which rearranges to the observed products.

RECENTLY several conflicting reports have appeared concerning the mechanisms, intermediates, and products of the chromyl chloride oxidation of aryl alkanes (Étard reaction) and styrenes.[4–8] Although Wiberg *et al.*[4–5] have postulated that the Étard reaction proceeds via styrene intermediates, no comprehensive studies have been reported on the oxidation of styrenes and substituted styrenes.[6–11] Nenitzescu *et al.*[8] reported that the chromyl chloride oxidation of *trans*-1-phenylpropene (I) gave *seven* products, including 1-phenyl-2-propanone (II) and 1-phenyl-1-propanone (III). In contrast, it has been reported[4, 12] that II is the only product isolated. During our studies of the chromyl chloride oxidation of styrenes, it was found that under certain reaction conditions I gives II as the only ketonic product.[11] A side reaction, double bond cleavage, gives benzaldehyde.

$$\underset{\text{I}}{trans\text{—}C_6H_5CH{=}CHCH_3} + CrO_2Cl_2 \xrightarrow[CH_2Cl_2]{0\text{–}5^\circ} \underset{\text{II}}{C_6H_5CH_2COCH_3} + C_6H_5CHO \qquad (1)$$

It has also been reported[1] that oxidation of 1,1-disubstituted alkenes gives excellent yields of aldehydes. However, Stairs *et al.*[13] obtained a mixture of products, including chlorohydrins, from the oxidation of cyclohexene, cyclopentene, and 1-hexene. Similar results were obtained from alkenes by Cristol and Eilar.[14] In order to account for the variety of products from aryl alkanes and unsaturates, various intermediates



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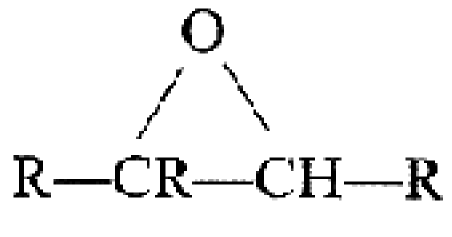
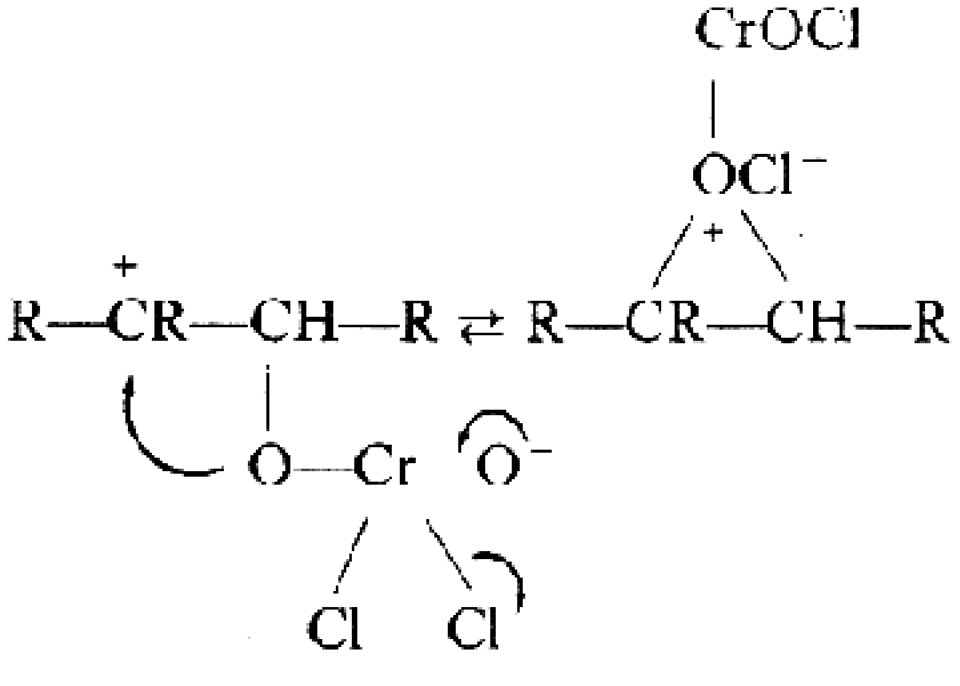


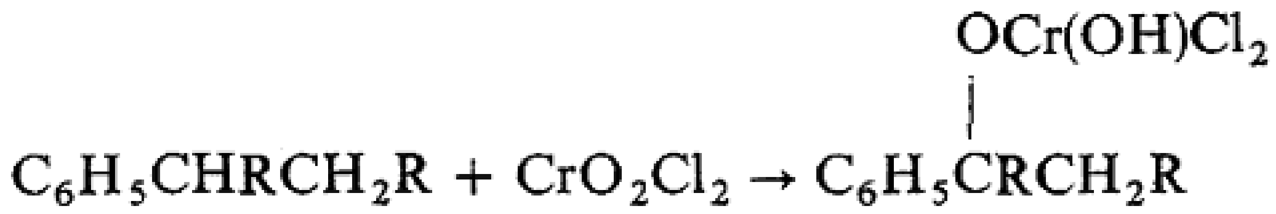
V



VI VII

(IV–VII) have been postulated.[1,5,8] The present investigation was undertaken to clarify some of the inconsistencies in order to gain a better insight into the mechanisms of chromyl chloride oxidations. 2-Phenylpropene (VIII), 1,1-diphenylethene (IX), and I were selected for study.

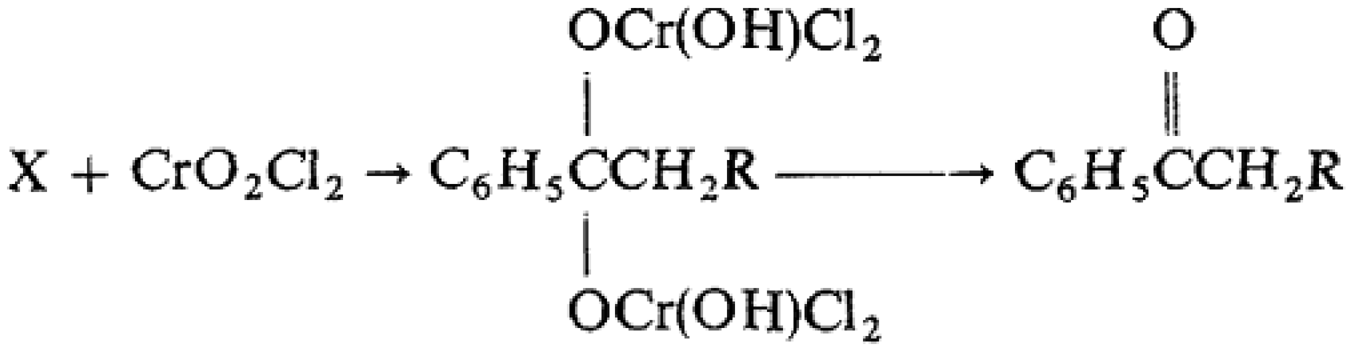
The chromyl chloride oxidation of *n*-propylbenzene,[4–8] toluene,[15–16] and diphenylmethane[17] suggest that the Étard reaction proceeds via a free radical mechanism to give the intermediate X. α-Elimination gives the styrene intermediate (XII) which reacts with another molecule of chromyl chloride to give the observed products.[4]



$$\mathrm{C_6H_5CHRCH_2R + CrO_2Cl_2 \rightarrow C_6H_5\overset{\overset{OCr(OH)Cl_2}{|}}{C}RCH_2R} \qquad (2)$$

R = H, alkyl or aryl

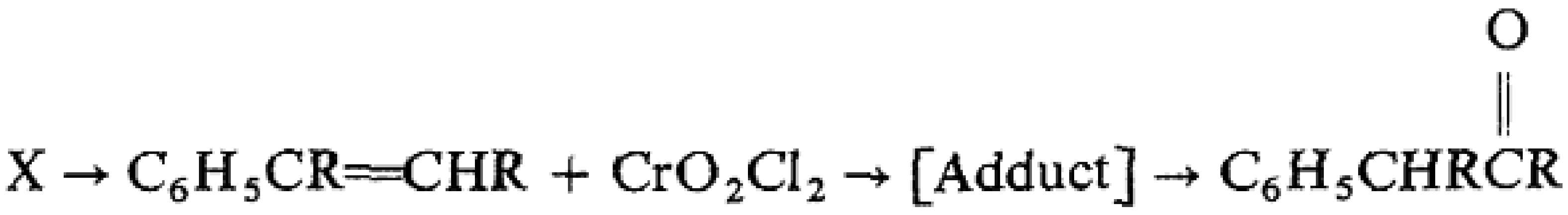
X



$$\mathrm{X + CrO_2Cl_2 \rightarrow C_6H_5\underset{\underset{OCr(OH)Cl_2}{|}}{\overset{\overset{OCr(OH)Cl_2}{|}}{C}}CH_2R \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}CH_2R} \qquad (3)$$

XI

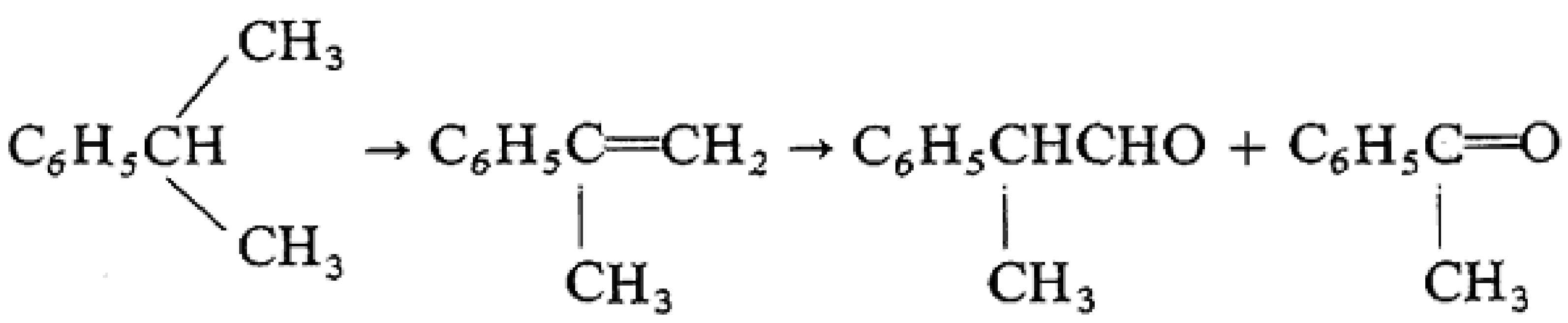
Étard Complex



$$\mathrm{X \rightarrow C_6H_5CR{=}CHR + CrO_2Cl_2 \rightarrow [Adduct] \rightarrow C_6H_5CHR\overset{\overset{O}{\|}}{C}R} \qquad (4)$$

XII

Additional support for this mechanism is obtained from the observation that VIII and isopropylbenzene give 2-phenylpropanal (XIII) as the major oxidation product.[6,11] These data demonstrate that styrenes are indeed intermediates in the Étard reaction.[7a] Further, intramolecular hydride transfers[1,11] and alkyl migration[1] indicate that a carbonium ion or a partial positive charge may be formed at some point in the reaction with alkenes and styrenes.



$$\mathrm{C_6H_5CH(CH_3)_2 \rightarrow C_6H_5\underset{\underset{CH_3}{|}}{C}{=}CH_2 \rightarrow C_6H_5\underset{\underset{CH_3}{|}}{C}HCHO + C_6H_5\underset{\underset{CH_3}{|}}{C}{=}O} \qquad (5)$$

VIII XIII (trace)

$$\mathrm{(C_6H_5)_2C{=}CH_2 \rightarrow (C_6H_5)_2CHCHO + (C_6H_5)_2C{=}O} \qquad (6)$$

IX XIV

Table 1 shows the oxidation products from several styrenes under a variety of conditions. It is seen that the equilibrium lies farther to the right with 1,1-disubstituted

TABLE 1. CHROMYL CHLORIDE OXIDATION OF SUBSTITUTED STYRENES AT 0–5°

Styrene	Addition time, min[a]	Reaction time, min	% Conversion[b]	Products, Yield (%)			
				Rearrangement		Cleavage	
I[c]	25	0	56·1	II	39·1	C_6H_5CHO	24·1
				III	0·0		
I[d]	25	60	52·1	II	42·4	C_6H_5CHO	16·3
				III	1·9		
VIII[e]	45	15	100	XIII	60	$C_6H_5COCH_3$	trace
IX[f]	25	60	100	XIV	62·7	$(C_6H_5)_2CO$	3·4

[a] Includes 5 min of stirring with zinc dust after addition of CrO_2Cl_2.

[b] Includes an incalculable amount of polymerization.

[c] 17·5% *trans*-I isomerized to *cis*-I.

[d] 12·7% *trans*-I isomerized to *cis*-I.

[e] Co-addition.

[f] Two unidentified peaks (<1·5% each of total peak area) with shorter retention times than IX were observed.

alkenes. This appears to result in less C=C double bond cleavage, which presumably occurs during hydrolysis.[8,*] Isomerization of I could occur during oxidation[†] or in the acidic hydrolysis step.[20]

A plausible mechanistic scheme to explain the formation of the observed carbonyl products involves an electrophilic attack of chromyl chloride at the carbon of the C=C double bond to give IVa. Although the less stable carbonium ion IVb contributes very little to the contributing resonance structures, it provides a reasonable path to III. Since hydride migrates to the *complete* exclusion of methyl in VIII and phenyl in IX, it appears that the stabilized tertiary benzylic carbonium structure IVa makes a considerable contribution along the reaction pathway.[‡] Also, IV can rearrange to the epoxide V which can be isomerized to the carbonyl product under the acidic reaction conditions.[1,8,22,23]

Alternatively, due to steric factors, chromyl chloride can add to the carbon of the double bond which is farthest removed from the chain branching in the chain attached to the other carbon of the double bond.[1] This would yield the most stable carbonium (intermediate VI) in a stepwise addition.[‡]

The significant difference between these results[1,11] and previous reports[4,8] are probably due to the vastly different experimental procedures. In our experiments the chromyl chloride–styrene adduct is decomposed *in situ* under reductive hydrolytic conditions while other workers[4,8] isolated the adduct and hydrolyzed under reducing and non-reducing conditions. Subsequent reactions, e.g. oxidation, chlorination, double bond cleavage, etc. probably occur during isolation of the adduct and during non-reductive hydrolysis.[*,§,18]

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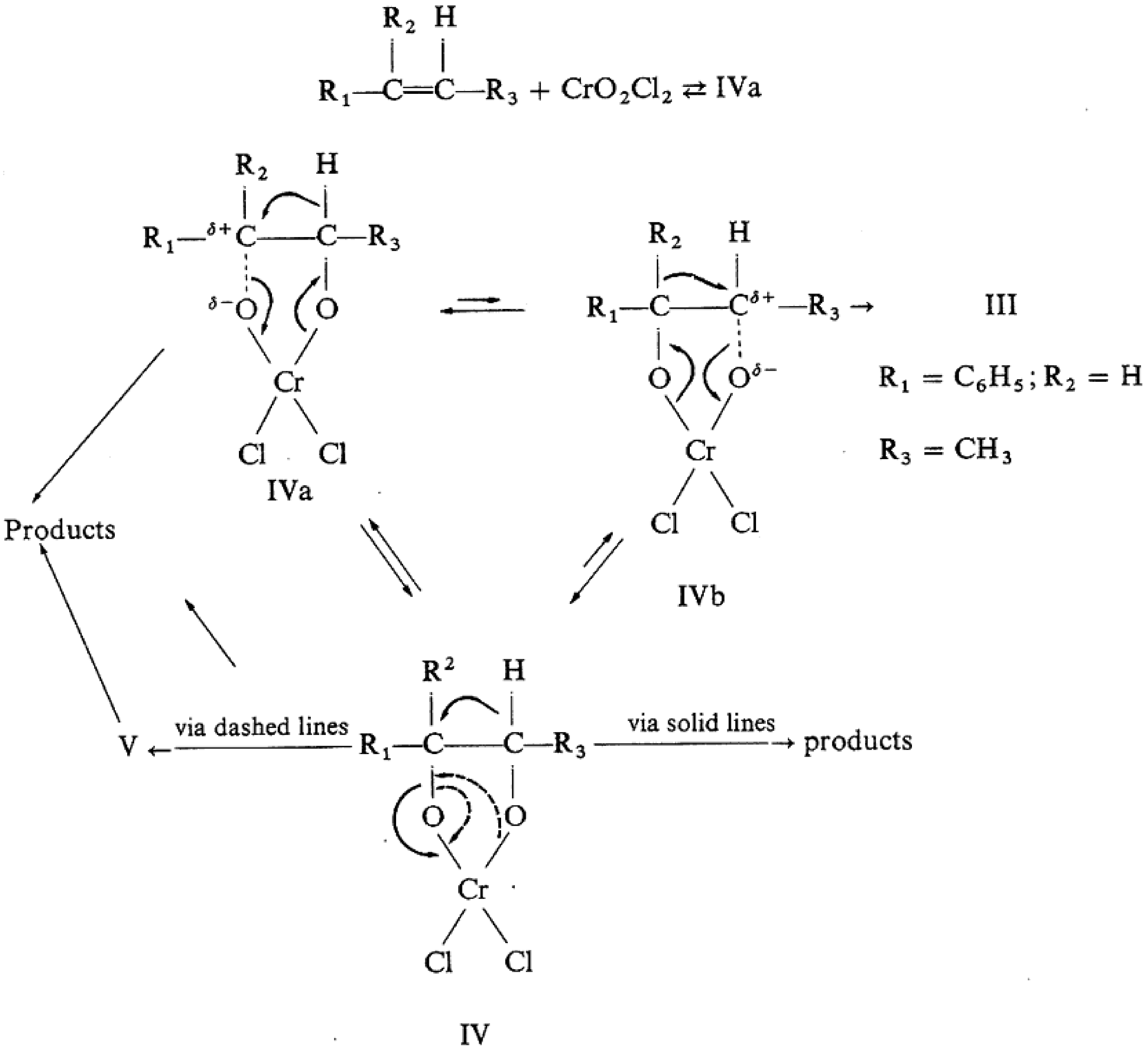
[*] It is known that chromic acid cleaves C=C double bonds.[18]

[†] Chromyl chloride is a Lewis acid.[19]

[‡] Kinetic studies of appropriately substituted styrenes will resolve this point.

[§] Electrophilic attack of chromyl chloride at the centre of unsaturation is considered the initial oxidation reaction.

SCHEME I



Two additional examples are described for a simple one-step synthesis of carbonyl compounds from readily available alkenes (VIII and IX).[1] For example, XIII is generally prepared from glycidic acids, glycols or epoxides.[24, 25]

EXPERIMENTAL

M.ps were taken on a Thomas–Hoover apparatus and are uncorrected. VPC analyses were preformed on a Wilkens Aerograph A-90-S gas chromatographic instrument.

Starting materials. cis- and *trans*-1-phenylpropene, 2-phenylpropene and 1,1-diphenylethene,[26a] chromyl chloride,[26b] and CH_2Cl_2[26c] were obtained commercially. The solvent and reactants were distilled immediately before use.

Oxidation of 1,1-*diphenylethene* (IX). To a 500 ml 3-necked round-bottomed flask provided with a dropping funnel (with $CaCl_2$ drying tube), a thermometer and a mechanical stirrer, 5·4 g (0·03 mole) of IX and 100 ml of CH_2Cl_2 were added. Temp was maintained between 0 and 5° during the dropwise addition (20 min) of 5·0 g (0·032 mole) chromyl chloride in 50 ml CH_2Cl_2. The reaction mixture was stirred between 0 and 5° for 1 hr and 10·9 g (0·15 mole) 90% Zn dust was added.* After stirring 5 min, 15 g ice and 15 g water were added and the resulting mixture was stirred for 15 min. The mixture was steam distilled through an Eastman condenser connected with a 32·5 cm Liebig condenser packed with stainless steel gauze. After two liters of distillate were collected, the Liebig condenser was washed with 100 ml CH_2Cl_2. Steam distillation was continued until the distillate gave a negative test with 2,4-dinitrophenylhydrazine soln. Each liter of distillate was washed twice with 50 ml portions CH_2Cl_2. The combined organic solns were distilled

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* Baker and Addamson 90–95% technical zinc dust. *Caution*: Although we have not experienced any difficulties, it is possible that the finely divided metal may ignite spontaneously with air when damp.

through a 56 cm vacuum jacketed Vigreux volumn to remove most of the CH_2Cl_2 while maintaining the liquid in the flask below 50°C.Distillation with a semi-micro Vigreaux Bantamware column removed the remaining CH_2Cl_2.

The reaction products were analyzed on a 5 ft × $\frac{1}{4}$ in silicone SF 96 column (10% on Chromasorb W, at 180° with He flow of 100 ml/min). Co-injections with authentic samples and derivatization were used to verify the products.

1,1-*Diphenylethanal.* 2,4-Dinitrophenylhydrazone, m.p. 150–151·5° (lit.[27] m.p. 150–151°) from aq. EtOH, mixed m.p. 150–151·5° with an authentic sample.

Oxidation of trans-1-phenylpropene (I). The same procedure described above was used except the reaction products were analyzed on a 10 ft × $\frac{1}{4}$ in 10% Apiezon L on 25% DMCS on 60·80 Chromosorb W column (50 ml H_2/min) with an internal standard at 150°. The results were verified on a 5 ft × $\frac{1}{4}$ in 10% Carbowax 20 M on Chromosorb W column.

For the shorter reaction time (Table 1), Zn dust was added immediately after addition of chromyl chloride, the reaction mixture was stirred 5 min and then worked up as described above.

Oxidation of 2-phenyl-1-propene (VIII). In a 3 l. 3-necked flask fitted with a mechanical stirrer, thermometer, and dropping funnel apparatus (with $CaCl_2$ drying tubes) was placed 800 ml CH_2Cl_2. The dropping funnel apparatus consisted of a Claisen adapter fitter with two 250 ml dropping funnels. The dropping funnel directly over the flask had an extension through the Claisen head that extended to about 2·5 cm from the CH_2Cl_2. The dropping funnel with the extension was charged with 158 g (1·02 mole) chromyl chloride and 200 ml CH_2Cl_2, and the other funnel was charged with 118·2 g (1 mole) and 200 ml CH_2Cl_2. The flask was immersed in an ice–salt bath and the stirred CH_2Cl_2 cooled to 0–5°. The solns in the dropping funnels were added dropwise to the stirred CH_2Cl_2 simultaneously (keeping the chromyl chloride slightly ahead of VIII) while maintaining the temp between 0 and 5° (about 40 min). The resulting reaction mixture was worked up as described above, and the residue was distilled at 68–74° (5 mm) [lit.[25] b.p. 90–93° (10 mm)] to give 80 g (60%) of XIII. The 2,4-dinitrophenylhydrazone, from aq. EtOH, had m.p. 136–137° (lit.[23] m.p. 136–137°); mixed m.p. 136–137° with an authentic sample.

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