783. *Mechanism of Elimination Reactions. Part XVII.* The Comparative Unimportance of Steric Strain in Unimolecular Olefin Elimination.*

By E. D. HUGHES, C. K. INGOLD, and V. J. SHINER, JUN.

Rates of unimolecular solvolysis in aqueous ethyl alcohol, and the proportions of olefin formed, have been measured for some tertiary chlorides. A dominating electromeric effect appears to control the speed and direction of reaction in all simple cases, although in certain structures olefin formation may be assisted by special factors plausibly classified as hyperconjugative or synartetic. Steric strain appears to have no general importance in the range of unimolecular reactions studied.

IN previous papers (*Trans. Faraday Soc.*, 1941, **37**, 657; *J.*, 1948, 2038 *et seq.*) a theory of constitutional effects on olefin-forming elimination has been developed and illustrated. Polar and steric effects are recognised. The polar effects have both an electrostatic and a quantal factor, classified respectively as an inductive effect arising from electropolarity, an an electromeric effect dependent on unsaturation. The polar effects are often opposed, and which will dominate depends on structure, particularly on the strength of the electropolarity and the amount of the unsaturation; and it depends also on the mechanism of the elimination process, notably whether it is bimolecular or unimolecular. For alkyl compounds undergoing elimination by the unimolecular mechanism, the case we are going to discuss further, the dominating factor is the electromeric effect. The unsaturation here involved is that which permits hyperconjugation between alkyl groups and double bonds; and the classification of the factor as an electromeric effect means that the hyperconjugation is with the partly formed double bond in the transition state of the double-bond-forming process. When an alkyl group at either end of this partly developed double bond hyperconjugates with it, the transition state is stabilised, and the relevant olefin is formed more rapidly. These considerations lead to a pattern of constitutional effects on orientation, which include the Saytzeff rule; and to a corresponding pattern of effects on reaction rate.

From a kinetic standpoint, unimolecular elimination cannot in general be considered separately from unimolecular substitution; for the two processes occur together, and have a common rate-controlling step. The rate of this first step, that is, the overall unimolecular rate, can profitably be discussed in relation to structure. However, the separate rate of unimolecular elimination is not that of any single process, and thus is only indirectly connected with the constitutional factors which specifically influence olefin formation. On the other hand, the proportion in which the carbonium ion, formed in the rate-controlling step, breaks up to give olefins, is more directly dependent on the relevant structural factors, and constitutes the most suitable material available for discussion in this regard.

In the papers cited, the proportions in which individual olefins are formed in unimolecular solvolytic reactions of various secondary and tertiary alkyl halides and alkylsulphonium

---

* Part XVI, *J.*, 1948, 2093.

salts were discussed in relation to the theory of orientation by the electromeric effect. No other factor appeared to be of comparable importance, certainly not the steric factor, within the range of our experimental survey. Furthermore, it had been inferred theoretically that, relatively to substitution, steric factors are unimportant in elimination, because of the more exposed situation of hydrogen than of carbon; and that, relatively to bimolecular reactions of substitution or elimination, " steric effects are seldom important in unimolecular reactions," because of the smaller atomic congestion in the transition states of the latter. These arguments, whether from experiment or from theory, still seem to us satisfactory.

The phrase quoted is from Brown and Fletcher's summary (*J. Amer. Chem. Soc.*, 1950, **72**, 1223) of our conclusions, which they regard as " unfortunately " founded. They measured the proportions in which total olefins are formed in the unimolecular solvolysis of a number of tertiary alkyl chlorides, most of them having more complicated alkyl structures than those with which we opened work in this field. They concluded that the majority of their results are not consistent with the theory of dominating electromeric control, but that all difficulties are removed by the assumption of important steric strains.

We shall explain (*a*) that Brown and Fletcher apply the polar theory incorrectly, (*b*) that their experiments are imperfectly designed for comparison with theory, (*c*) that in a few of their most complicated alkyl structures, special effects of hyperconjugation or synartesis might be expected, which they do not consider, and (*d*) that, as was implicit in our treatment, exceptionally ramified structures would be required in order to bring steric factors into prominence. We shall also report a reinvestigation of some of their examples essentially in extension of our own earlier work on this subject. Our final conclusion will be that, apart from quite special complications as indicated under (*c*) above, the theory of dominating electromeric control gives a correct picture in this range of reactions.

Brown and Fletcher's figures for the percentage of total olefin formed in the solvolysis of chlorides $R^1R^2R^3C{\cdot}Cl$ in " 80% " aqueous ethyl alcohol at 25° are as follows (*neo*Pe = *neo*pentyl) :

$R^1R^2R^3$	Me_3	Me_2Et	$MeEt_2$	Et_3	Me_2Pr^n	Me_2Bu^n
Olefin	16	34	41	40	33	35
$R^1R^2R^3$	Me_2Pr^i	$MePr^i_2$	Et_2Pr^i	Me_2Bu^t	Et_2Bu^t	Me_2*neo*Pe
Olefin	62	78	80	61	90	65

These authors' first objection to the theory of dominating electromeric control relates to the series $R^1R^2R^3 = Me_3$, Me_2Et, $MeEt_2$, Et_3 : the initial rise in olefin proportion, as Me is replaced by Et, is not continued in the successive replacements, as they think it should be; and they see in the figures evidence of the incursion of a growing steric effect on olefin formation in the higher alkyl groups. This is, of course, erroneous. As was pointed out and illustrated extensively in our earlier papers, hyperconjugation acts from both ends of the developing double bond. When R^1 is changed from Me to Et, not only is the establishment of the double bond in R^1 accelerated (*e.g.*, by 6 times), but also its entrance into R^2, and into R^3, is retarded (*e.g.*, by a factor of $\frac{2}{3}$). Thus it is important to consider the separate branches of the tertiary groups, on the basis of representative analyses of the olefins formed : this Brown and Fletcher did not do. With estimates of double-bond development in the different branches, derived from our earlier analytical results, it is easy to see that, on the basis of the polar theory, we should expect the values for total olefin to behave in the way which Brown and Fletcher could not comprehend. In the following illustrative figures, the factors 6 and $\frac{2}{3}$, used throughout, reproduce not only Brown and Fletcher's olefin values, but also the known proportions of the isomeric amylenes :

		Me	5		Et	28		Et	19		Et	13
Each branch	C	Me	5	C	Me	3	C	Et	19	C	Et	13
		Me	5		Me	3		Me	2		Et	13
Total	15			34			40			39		

The other results of Brown and Fletcher, as listed above, can be understood on exactly the same lines, excepting the last three which are discussed below. It is curious that

Brown and Fletcher, who, as already noted, invoke steric strain in order to explain why certain of the olefin figures in the first line of the above list fail to increase with homology, use the same idea in explanation of why some of those in the second line are so high, without giving any generally applicable reason for the necessary change of outlook. We turn now to the three outstanding cases.

Since the group Me_2Bu^tC can develop a double bond only in the Me branches, a dominating electromeric effect would not have been expected to produce as high a proportion of olefin as is found. However, elimination with Wagner–Meerwein rearrangement might evidently occur here :

$$H{\cdot}CH_2{\cdot}CMe(Me){\cdot}\overset{+}{C}Me_2 \longrightarrow H^+ + CH_2{:}CMe{\cdot}CMe_2(Me)$$

and until this possibility is controlled the case is not suitable for comparison with the others, with respect to either polar or steric effects. Even if group migration does not actually occur, the presence of a system with that potentiality may have kinetic effects, as has been explained on several previous occasions. The group Et_2Bu^tC is in an entirely similar case. Comparing the two groups among themselves, we see a relation such as the electromeric effect might be expected to produce.

In discussing these cases, Brown and Fletcher have been led into an inapplicable criticism of the polar theory, having failed to distinguish kinetic effects on the initial heterolysis of an alkyl chloride from those on subsequent double-bond development by proton loss from the formed carbonium ion. Thus, on the basis of an argument about the stability of the olefin from $Bu^t{\cdot}CMe_2Cl$, they conclude that the polar theory requires the rate of unimolecular solvolysis of this chloride to be smaller than that applying to *tert.*-butyl chloride, $Me{\cdot}CMe_2Cl$. This does not follow at all, because the electromeric effect is claimed to be dominating only for the second reaction stage, in which a double bond is being produced, in these unimolecular eliminations. Actually the solvolysis rates are nearly the same, a fact which has already been used to show that even the higher chloride is insufficiently ramified to display appreciable steric strain (Brown, Davies, Dostrovsky, Evans, and Hughes, *Nature*, 1951, **167**, 987).

Before dealing with the last example, that of the group Me_2*neo*PeC, we may refer to Table 1, the main part of which records the present extension of our older data. Brown and Fletcher's figures for the proportion of total olefin agree tolerably well with those now recorded.

TABLE 1. *Solvolysis rates (k_1 in sec.$^{-1}$) and olefin proportions (mols. %) in unimolecular reactions of alkyl chlorides* $R^1R^2R^3CCl$ *in " 80% " aqueous alcohol at 25°.*

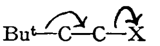
					Olefin (%)			
No.	R^1	R^2	R^3	$10^5 k_1$	R^1	R^2	R^3	Total
1	Me	Me	Me	0·92	5·3	5·3	5·3	16·0
2	Me	Me	Et *	1·50	3·0	3·0	27·3	33·3
3	Me	Et	Et	2·33	—	—	—	46·4
4	Me	Et	Et	2·77	14·7	14·7	14·7	44·1
5	Me	Me	*neo*Pe	19·0	31·3	31·3	5·5	68·1
Reaction with water (2 phases).†								
—	Me	Me	*neo*Pe	—	7·5	7·5	5	20

* *J.*, 1937, 283; 1948, 2065. † Brown and Berneis, *J. Amer. Chem. Soc.*, 1953, **75**, 10.

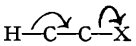
Brown and Fletcher did not analyse any of their olefin mixtures, but Brown and Berneis have recently returned to the study of dimethyl*neo*pentylcarbinyl chloride, and have examined the total proportion and composition of the olefin mixture produced when it is decomposed heterogeneously with water. Their results are entered at the foot of Table 1. Quantitatively, they are very different from ours for the homogeneous reaction in aqueous alcohol. But in either set of conditions the double bond enters more into either methyl branch than into the *neo*pentyl branch of the alkyl group, though we might have expected a small difference in the other direction, since the numbers of hydrogen atoms which, on proton loss from $(CH_3)_2\overset{+}{C}{\cdot}CH_2{\cdot}C(CH_3)_3$, would hyperconjugate with a double bond in the branches, Me, Me, and *neo*Pe, are 5, 5, and 6, respectively.

Brown and Berneis attribute this anomaly to a steric effect on the reactions of the carbonium ion, either a steric retardation of anion uptake with a consequent relative enhancement of proton loss, or a steric acceleration of proton loss by the direct squeezing-out of a proton, or both.* The first effect would heighten double-bond development in all three branches of the alkyl group, while the second would increase it specifically in the *neo*pentyl branch. But, as can be seen from Table 1 (compare cases nos. 1 and 5), the entry of the double bond into the *neo*pentyl branch is entirely normal: the anomaly consists wholly in facilitation of double-bond development in either methyl branch. This shows clearly that steric effects are not responsible.†

As Table 1 illustrates, the initial heterolysis of the chloride is appreciably accelerated by the presence of the *neo*pentyl branch of the alkyl group. We should like to account for this, as well as for the accelerated development of unsaturation in the methyl branches, on the same basis. A possible opportunity of doing so is suggested by the general chemistry of branched alkyl compounds containing quaternary γ-carbon, for instance as a β-situated *tert*-butyl substituent. Such compounds are prone to suffer degradative eliminations in which the *tert.*-butyl or similar β-substituent splits off (presumably as a carbonium ion) much as β-hydrogen would (as a proton) in ordinary elimination :

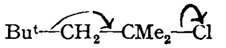


$Bu^t—C—C—X$

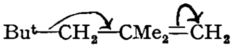


$H—C—C—X$

(Slowjanow, *Chem. Zent.*, 1907, II, **78**, 135; Whitmore and Stahly, *J. Amer. Chem. Soc.*, 1933, **55**, 4153; 1945, **67**, 2158; Brown, Davies, Dostrovsky, Evans, and Hughes, *loc. cit.*). This suggests that the *tert.*-butyl-to-carbon bond may be able to hyperconjugate like the hydrogen-to-carbon bond, and that, even in reactions in which no actual chain-splitting occurs, such hyperconjugation may affect reactivity. This assumption could account both for the accelerated heterolysis of our alkyl chloride and for the promoted development of unsaturation in its methyl branches :



$Bu^t—CH_2—CMe_2—Cl$



$Bu^t—CH_2—CMe_2—CH_2$

Naturally, we do not claim to have established this interpretation; but it does seem to fit the few facts we know, as the theory of steric strain does not.

We conclude that a case has not yet been made for the dominance of steric factors in unimolecular elimination from simple alkyl chlorides. Obviously, we do not deny that large steric effects might appear, if a sufficient density of ramification were built up in the reactants; but any such effects, if thus produced, would not detract from the fundamental dominance of polar factors in all simpler systems.

EXPERIMENTAL.

Materials.—The alkyl chlorides were prepared by methods which are sufficiently standard to need no description: generally, the related alcohols were made by Grignard methods, and converted by means of hydrochloric acid into the chlorides. Methyl *neo*pentyl ketone, the starting point for one of the Grignard reactions, was prepared as described by Mosher and Cox (*J. Amer. Chem. Soc.*, 1950, **72**, 3702).

Diethylmethylcarbinyl chloride (3-chloro-3-methylpentane) had b. p. 51·8—51·9°/85 mm., n_D^{25} 1·4185, triethylcarbinyl chloride (3-chloro-3-ethylpentane), b. p. 67·0—67·2°/58 mm., n_D^{25} 1·4308, and dimethyl*neo*pentylcarbinyl chloride (2-chloro-2 : 4 : 4-trimethylpentane), b. p. 45·0°/21 mm., n_D^{25} 1·4285. The last-named chloride was also prepared from di*iso*butylene and hydrochloric acid: this product had b. p. 43·2—43·3°/18 mm., n_D^{25} 1·4285.

The olefins, or olefin mixtures, formed from these chlorides had to be isolated in order to

---

* Brown does not usually distinguish between kinetic and thermodynamic steric effects, as we do here in describing Brown and Berneis's interpretation. These authors have stated that they "see no advantage" in signalising such distinctions (*J. Amer. Chem. Soc.*, 1953, **75**, 1). We are not of that opinion, because, among other reasons, molecules and transition states have different geometrical forms, and thus differ in steric behaviour.

† Brown and Berneis regard this reaction as belonging to that broad pattern of orientational effects in elimination which includes the Hofmann rule. They infer that such orientational effects may in general be determined, not by polar factors, but by steric strain. In our view, this striking thesis needs better support than has yet been offered.

permit the checking of the method used in their analytical determinations. 3-Ethylpent-2-ene had b. p. 95·5—95·7°, n_D^{25} 1·4121, and the mixed hexenes had b. p. 64·9—70·4°, n_D^{25} 1·3941—1·4015, whilst a fractionation of the di*iso*butylenes gave : 24 g., b. p. 101·1—101·2°, n_D^{25} 1·4064; 20 g., b. p. 101·2—103·4°, n_D^{25} 1·4065—1·4108; and 6 g., b. p. 103·4—104·7°, n_D^{25} 1·4135.

Kinetic Runs.—These were conducted at 25° in " 80% " ethyl alcohol, a mixture of 4 vols. of ethyl alcohol with 1 vol. of water. The initial concentrations of alkyl chloride were of the order of 0·05M. In some runs the solution was made alkaline initially to such an extent that it became nearly neutral ultimately, whilst in other runs the solution was initially neutral and became acid. Total solvolysis was determined by titration with acid or alkali as necessary, whilst olefin development was measured in a simultaneously withdrawn sample by reaction with bromine.

Both the aliquot method and the sealed-tube method were used. In the former, samples of 5 c.c. were run, one of each pair into ethyl alcohol at 0°, for subsequent acid-alkali titration with methyl-red as indicator, and the other into a stoppered tube at −80°, for the determination of olefin. In the latter method, batches of 32 sealed tubes, each containing 5 c.c. of reaction mixture under nitrogen, were placed simultaneously in the thermostat and were withdrawn two at a time, one to be broken under ethyl alcohol at 0°, and the other chilled to −80°. The first pair of readings were taken to correspond to " zero " time, whilst a pair taken after more than 10 half-lives gave the composition at " infinite " time.

Olefin Determinations.—We found the work of Brown and Fletcher difficult to reproduce closely, because the excesses of bromine used are not given, though they are stated to be important. Thus in blank experiments with di*iso*butylenes and bromine, the latter in an excess of 35 c.c. of 0·02N-thiosulphate, we obtained, by their described procedure, results about 10% too low.

We therefore reverted to the extraction method described by Hughes, Ingold, Masterman, and MacNulty (*J.*, 1940, 899), but with the modification that, although freshly distilled chloroform is retained as the solvent for bromination, the bromine solution was first made up and standardised in carbon tetrachloride, in which it is more stable than in chloroform. It is a feature of the general method that, for each olefin to be determined, control analyses are made with weighed olefin samples in order to find the corrections, if any, which are required to cover losses from evaporation, incomplete extraction, etc. Determinations with olefins not previously treated by this method gave the following correction factors : olefins from diethylmethylcarbinyl chloride (excess of bromine used, 15—35 c.c. of 0·02N-thiosulphate), 1·03; olefin from triethylcarbinyl chloride (excess of bromine, 9—20 c.c. of the thiosulphate), 1·00; olefins from dimethyl*neo*pentylcarbinyl chloride (excess of bromine, 9—11 c.c. of the thiosulphate), 1·03.

Olefin Recovery.—An experiment with dimethyl*neo*pentylcarbinyl chloride will be described, in which both olefin and alcohol were recovered in fair yield, the latter containing an undetermined amount of the corresponding ethyl ether. The chloride (10 g.) was kept for 4 days at 25° with a small excess of alkali in " 80% " ethyl alcohol (250 c.c.). After dilution with water (500 c.c.), the mixture was extracted once with *iso*pentane (50 c.c.), and the extract was washed with water (3 × 50 c.c.), dried (K_2CO_3), and fractionated. The olefin (4 c.c.) had b. p. 101—102°, n_D^{25} 1·4075, and the alcohol (2·5 c.c.) b. p. 71°/47 mm., n_D^{25} 1·4189.

Olefin Isomer Ratios.—The refractive-index method used by Dhar, Hughes, and Ingold (*J.*, 1948, 2065) gave results of somewhat unsatisfactory consistency ($\pm 6\%$) in application to di*iso*butylenes, and we therefore supplemented it with an infra-red method, which gave an improved consistency ($\pm 1\%$).

We separated the isomers by distillation. Their physical constants are as follows, the first figure of each pair being that given by Straiff, Zimmerman, Soule, Butt, Sedlak, Willingham, and Rossini (*J. Res. Nat. Bur. Stand.*, 1948, **41**, 223), while the second is that obtained in this work : 2 : 4 : 4-trimethylpent-1-ene, b. p. 101·2°, 101·2°/760 mm., n_D^{25} 1·4062, 1·4064; 2 : 4 : 4-trimethylpent-2-ene, b. p. 104·7°, 104·7°/760 mm., n_D^{25} 1·4137, 1·4133. Our distillation curve showed that the first isomer was pure, whilst the second, originally present in much smaller amount, was not quite pure. Therefore we have used our own refractive index for the former olefin, but the figure of Rossini *et al.* for the latter, when computing compositions of mixtures from their refractive indices.

The infra-red method employed a band of 2 : 4 : 4-trimethylpent-1-ene at 765 cm.$^{-1}$, a frequency at which, as far as we could ascertain, 2 : 4 : 4-trimethylpent-2-ene has no absorption. The plot of composition against optical density at this frequency was linear to within 1% in the composition range 80—100% of 2 : 4 : 4-trimethylpent-1-ene.

Illustrative Results.—A summary of our kinetic results has already been given in Table 1.

By way of example, some more detailed data are given here for the solvolysis of dimethyl*neo*pentylcarbinyl chloride. Table 2 records a run in acid solution by the aliquot method, Table 3 summarises the results for total solvolysis rate and total olefin production for this chloride and Table 4 the results for the composition of olefin.

TABLE 2. *Solvolysis of dimethyl*neo*pentylcarbinyl chloride in* 80% *aqueous ethyl alcohol at* 25°. (*Run No.* 4.)

[Alkali titres in c.c. of 0·0363N-sodium hydroxide per 5-c.c. sample. Thiosulphate titre in c.c. of 0·01975N-thiosulphate for the reaction product of a 5-c.c. sample with 10 c.c. of 0·0808N-bromine.]

Time (hr.)	NaOH (c.c.)	k_1 (hr.$^{-1}$)	$Na_2S_2O_3$ (c.c.)	Olefin fraction
0·000	0·27	—	40·23	—
0·200	1·39	0·690	38·10	0·680
0·450	2·10	0·698	35·90	0·622
0·700	2·86	0·684	33·95	0·679
0·950	3·54	0·690	32·35	0·676
1·450	4·56	0·688	29·88	0·676
1·950	5·31	0·694	28·20	0·670
∞	7·07	—	25·02	—

[From graph, k_1 = 0·686 hr.$^{-1}$. Olefin fraction (selected average) 0·676.]

TABLE 3. *Solvolysis of dimethyl*neo*pentylcarbinyl chloride in* 80% *aqueous ethyl alcohol at* 25° (*Summary*).

Run	1	2	3	4	5	6 *
Conditions	Acid	Acid	Alkaline	Acid	Alkaline	Alkaline
k_1 (hr.$^{-1}$)	0·684	0·688	0·669	0·686	0·629	0·689
Olefin fraction	—	0·694	0·684	0·676	0·686	0·680

[Selected means : k_1 = 0·686 hr.$^{-1}$. Olefin fraction = 0·681.]

* By the tube method; runs 1—5 by the aliquot method.

TABLE 4. *Analysis of mixtures of* 2 : 4 : 4-*trimethylpent*-1-*ene and* 2 : 4 : 4-*trimethylpent*-2-*ene.*

	2 : 4 : 4-Trimethylpent-1-ene (%)		
	By distlln.	By refraction	By infra-red
Equilibrium mixture	83	83	85
Solvolysis run 11	—	88	93
„ 12	—	97 mean 90	91 mean 92
„ 13	—	85	93

(A 50 : 50 mixture of the isomeric hydrocarbons was subjected to solvolysis conditions. The recovered material, examined by the refraction and infra-red methods, showed no change of composition greater than the error of measurement.)

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.

[*Received, July* 10*th*, 1953.]