425. *Mechanism of Elimination Reactions. Part XV. Olefin Elimination from* sec.-iso*Amyl Iodide and from the* sec.-iso*Amyl-dimethyl-sulphonium Ion.*

By E. D. Hughes, C. K. Ingold, and A. M. M. Mandour.

It is shown that methyl*iso*propylcarbinyl (*sec.-iso*amyl) iodide is decomposed by ethyl-alcoholic potassium hydroxide, in conditions determining the bimolecular mechanism of elimination, to give olefins in which the double bond becomes established mainly along the *iso*propyl branch, rather than along the methyl branch, of the secondary alkyl group; and also that the dimethyl-*sec.-iso*amylsulphonium ion is decomposed in aqueous solution in conditions favourable to the unimolecular mechanism to give an olefin mixture displaying the same kind of orientational effect in a quantitatively more extreme form. The former result confirms the conclusion, of which other evidence exists (Part X), that a non-terminal orientation of the double bonds is preferred in bimolecular eliminations of secondary alkyl halides, just as it has been shown to be in those of tertiary alkyl halides (Part XI). The latter result proves what has not been established elsewhere, namely, that a qualitatively similar orientation of the double bond is a property of unimolecular eliminations involving secondary alkyl groups, just as it is independently shown to be for corresponding reactions of tertiary alkyl groups (Parts XI and XIV).

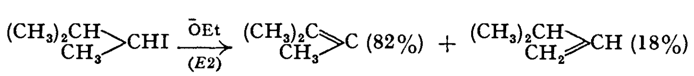
The experiments here reported were carried out in 1930, but were not published at the time because they did not appear to assist with the problem to the solution of which they were directed. As a matter of fact they could not so assist, because Organic Chemistry was not then sufficiently advanced: the bimolecular and unimolecular mechanisms of substitution and elimination had not been discovered, and hyperconjugation was as yet unrecognised. Today, however, it is possible to attach significance to these early experimental results, which in effect extend certain later measurements reported in the preceding papers.

The problem which was thus prematurely attempted was that of the antithesis between Hofmann's rule of the preferential elimination of ethylene from quaternary ammonium salts and Saytzeff's rule for olefin elimination from secondary and tertiary alkyl halides—the situation being that Hofmann's rule agrees with, but Saytzeff's rule is contrary to, the theory of the inductive effect. We need neither go into the problem here, nor describe our incomplete working hypothesis of 1930 concerning a phenomenon the full explanation of which only became clear to us several years later; for in the next paper we shall state the problem and the explanation, since it will be our main purpose there to present the evidence on which our interpretation rests.

The experiments now to be described were on the lines of some which Lucas, Young, and their collaborators were carrying out at about the same period or a little earlier, and of others which we and our colleagues have since performed, on the compositions of the mixtures of isomeric olefins which are produced by the alkaline decompositions of branched-chain alkyl halides, or branched alkyl-dimethylsulphonium salts (cf. Parts X, XI, XIII, and XIV). In the present experiments an alkyl halide, and an alkyl-dimethylsulphonium ion having the same branched alkyl groups, were examined.

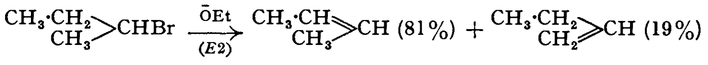
The study was concerned with the group *iso*propylmethylcarbinyl (*sec.-iso*amyl) $(CH_3)_2CH{\cdot}\dot{C}H(CH_3)$, and was directed to determining to what extent an olefinic double bond is accepted into the *iso*propyl branch, and to what extent into the methyl branch, when the group is eliminated as olefin by the alkaline decomposition of its iodide, or by decomposition of the related dimethylsulphonium hydroxide. The group was chosen as a secondary alkyl group in which the two branches present different numbers of β-hydrogen atoms, and thus permit the formation of olefins having different numbers of alkyl residues attached to the unsaturated carbon atoms. This particular alkyl group was selected with a view to avoiding the complication which made Lucas and Young's work, and also some of ours, difficult, namely, that of having to deal with a type of olefin one of the position-isomerides of which has two stereoisomeric modifications—with the result that a mixture of three closely similar olefins requires to be analysed. The methyl*iso*propylcarbinyl group is the simplest secondary alkyl group which can give two, but no more than two, olefins. They are trimethylethylene and *iso*propylethylene; and the binary mixtures of these isomerides can be accurately analysed, without the use of large quantities, by measurement of a suitable physical property, *e.g.*, the refractive index.

The decomposition of *sec.-iso*amylcarbinyl iodide was effected with the aid of concentrated ethyl-alcoholic potassium hydroxide. Although we had no appreciation of the importance of the point at the time, it is now quite clear, from the kinetics work described in Part X, that the bimolecular mechanism, *E*2, must have been in exclusive control. The results are shown in the following scheme:



$$\begin{matrix}(CH_3)_2CH\\ CH_3\end{matrix}\!\!>CHI \xrightarrow[(E2)]{\bar{O}Et} \begin{matrix}(CH_3)_2C\\ CH_3\end{matrix}\!\!\geqslant C\ (82\%) + \begin{matrix}(CH_3)_2CH\\ CH_2\end{matrix}\!\!\geqslant CH\ (18\%)$$

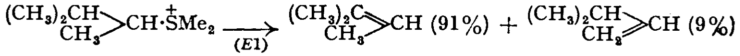
These analytical data are probably good to 1%. Comparison may be made with the figures obtained under similar conditions by Lucas and his collaborators, and again by Woolf (cf. Part X), for the lower-homologous *sec.*-butyl bromide:



$$\begin{matrix}CH_3{\cdot}CH_2\\ CH_3\end{matrix}\!\!>CHBr \xrightarrow[(E2)]{\bar{O}Et} \begin{matrix}CH_3{\cdot}CH\\ CH_3\end{matrix}\!\!\geqslant CH\ (81\%) + \begin{matrix}CH_3{\cdot}CH_2\\ CH_2\end{matrix}\!\!\geqslant CH\ (19\%)$$

We should have expected the two sets of data to fall as they actually do, but perhaps a little further apart. However, the figures last given depend, as has been mentioned, on a difficult analysis, and may be in error by 3%.

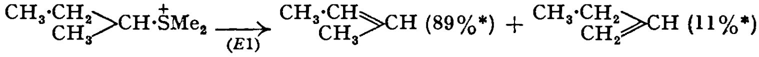
The decomposition of the dimethyl-*sec.-iso*amylsulphonium ion was carried out in a dilute aqueous solution, which was alkaline, but contained no alkali in excess over the sulphonium ion. It is obvious from our present knowledge of the kinetics of the aqueous decompositions of secondary alkyl-sulphonium ions (cf. Gleave, Hughes, and Ingold, *J.*, 1935, 236) that the unimolecular elimination mechanism, *E*1, must have been in practically exclusive control. The results themselves confirm this. For instance, the total yield of olefin was 7%; and that is what it should be if the decomposition were unimolecular (cf. Part X, Table III *); whereas a yield of the order of 60% would have been produced if the reaction had been bimolecular (cf. Part XIII, Table I). The proportions of the isomerides, which are as follows, confirm the same conclusion :



$$\begin{matrix}(CH_3)_2CH\\CH_3\end{matrix}\!\!>CH\cdot\overset{+}{S}Me_2 \xrightarrow[(E1)]{} \begin{matrix}(CH_3)_2C\\CH_3\end{matrix}\!\!>CH\ (91\%) + \begin{matrix}(CH_3)_2CH\\CH_2\end{matrix}\!\!>CH\ (9\%)$$

In a bimolecular decomposition the above proportions would be approximately reversed, so that what is here the minor isomeride would become the major one. This will be evident from the results of Parts XIII and XIV.

We do not possess any directly determined figures for the proportions in which the isomeric olefins are formed in the unimolecular decompositions of the lower-homologous, *sec.*-butylsulphonium ion, or for the proportions in which they are formed in the unimolecular reaction of *sec.*-butyl bromide—a datum that would be equivalent, since both decompositions proceed through the same carbonium ion (cf. Part VI). The difficulty has been that the small yield (8%) of total olefins formed in the unimolecular reactions of these secondary alkyl compounds did not in our hands produce samples large enough for the satisfactory analysis of a ternary mixture of olefins (cf. Part X). This difficulty did not arise in the *sec.-iso*amyl example, which was so chosen that the formed olefin mixtures would be binary, and a comparatively small sample sufficient for analysis. However, we can estimate the proportions in which the olefins should be formed in the unimolecular decomposition of a *sec.*-butyl halide or sulphonium ion, on the basis of certain measured proportions for tertiary alkyl compounds. In the bimolecular reaction of *tert.*-amyl bromide with ethoxide ions, the amylene with a terminal double bond is produced to the extent of 29% of the total amylenes. In the unimolecular reaction of *tert.*-amyl bromide, or in that of the dimethyl-*tert.*-amylsulphonium ion, the proportion of this amylene is reduced to 16 ± 2% (Parts XI and XIV). In the bimolecular reaction of *sec.*-butyl bromide with ethoxide ion, the butylene with a terminal double bond is formed to the extent of 19% of the total butylenes (Part X). Hence we should expect that, in the unimolecular reaction either of *sec.*-butyl bromide, or of the dimethyl-*sec.*-butylsulphonium ion, the proportion of the terminally unsaturated butylene would be reduced in roughly the same ratio, *i.e.*, to 11 ± 1%. Thus we can predict as follows :



$$\begin{matrix}CH_3\cdot CH_2\\CH_3\end{matrix}\!\!>CH\cdot\overset{+}{S}Me_2 \xrightarrow[(E1)]{} \begin{matrix}CH_3\cdot CH\\CH_3\end{matrix}\!\!>CH\ (89\%^*) + \begin{matrix}CH_3\cdot CH_2\\CH_2\end{matrix}\!\!>CH\ (11\%^*)$$

(* Roughly estimated from data on other compounds.)

The corresponding figures for the reaction of the dimethyl-*sec.-iso*amylsulphonium ion should be similar, but a little more spread apart, just as in fact the determined figures are (see above).

The composition of the olefins formed in the unimolecular reaction of the *sec.-iso*amylsulphonium ion shows that unimolecular elimination from secondary alkyl-sulphonium salts corresponds to Saytzeff's rule. This, though it follows indirectly from the rate data reported in Part X, has not elsewhere been directly proved. The analytical data recorded in Part XIV show directly that unimolecular elimination from tertiary alkyl-sulphonium ions corresponds to Saytzeff's rule. Thus the present work establishes that there is no difference between the unimolecular reactions of secondary and tertiary alkyl groups in this respect.

In view of the results and conclusions of Part VI, the olefin compositions for the unimolecular decomposition of the *sec.-iso*amylsulphonium ion should apply equally to the unimolecular reactions of the *sec.-iso*amyl halides, and, in particular, to that of the iodide. On comparing this olefin composition with the above recorded composition of the olefins obtained in the bimolecular decomposition of *sec.-iso*amyl iodide, one observes that, whilst both bi- and uni-molecular elimination from this secondary alkyl halide follow the Saytzeff rule, the unimolecular reaction exhibits more strongly the particular type of orientation which the rule specifies. Quite similar conclusions follow from the analytical data, recorded in Part XI, concerning the olefins formed in the bi- and uni-molecular decompositions of *tert.*-amyl bromide. In this matter also, the present work establishes that secondary and tertiary alkyl groups act alike.

---

* It is true that this Table refers to alkyl bromides; but then the yield in which olefins are formed in the unimolecular decompositions of alkyl halides and alkyl-sulphonium ions with the same alkyl group under the same conditions should be almost the same, since the reactions proceed through the same carbonium ion; and in fact, the yields have been found to be nearly the same in the investigated examples (cf. Part VI, Table I).

The work described in Parts X, XI, XIII, and XIV has yielded data on the proportions in which isomeric olefins are formed in certain bimolecular eliminations involving secondary and tertiary alkyl halides and sulphonium ions; and also on unimolecular elimination from certain tertiary alkyl compounds. The work now recorded completes a series, inasmuch as it provides a direct determination, the only one so far made, of the proportions in which isomeric olefins are produced in unimolecular elimination from a secondary alkyl compound.

EXPERIMENTAL.

Materials.—Trimethylethylene was obtained by distilling a commercial sample, through a column, to constant b. p. (36°). *iso*Propylethylene was prepared from carefully purified *iso*amyl alcohol, by conversion into the iodide, and treatment of the latter with hot, saturated, ethyl-alcoholic potassium hydroxide. The resulting hydrocarbon was purified by being kept in contact, with frequent shaking for 2 hours at 0°, with twice its volume of concentrated aqueous sulphuric acid (2 vols. of sulphuric acid + 1 vol. of water). After being dried with sodium, it had b. p. 21·5°. *sec.*-*iso*Amyl iodide was prepared from this hydrocarbon by keeping it overnight at 20° with a saturated solution of hydrogen iodide in glacial acetic acid. The oil was separated and distilled (b. p. 135—139°); and the distillate was shaken for 2 hours at 20° with a large excess of water, and then for 2 hours with a further quantity of water. The iodide was finally washed with dilute aqueous sodium hydroxide, dried, and distilled (b. p. 138—139°). The *sec.*-*iso*amyl iodide was allowed to combine with dimethyl sulphide in solution in methyl cyanide at 30° for 10 days. The separated salt (yield 60—70%) consisted essentially (analysis) of dimethyl-*sec.*-*iso*amylsulphonium iodide contaminated with some trimethylsulphonium iodide. This contaminant we did not remove, since it seemed a difficult thing to do, and it could not interfere with the formation or isolation of the amylenes, as described below.

Olefin Elimination from sec.-iso*Amyl Iodide.*—The iodide was dropped on to boiling, saturated, ethyl-alcoholic potassium hydroxide. The hydrocarbons, after passing through a reflux condenser at 40°, water at 40°, and drying tubes of potassium carbonate at 40°, were condensed at −80°. The last traces of the hydrocarbon were carried over in nitrogen, after addition of some water to the boiling alkaline solution. After being finally dried with sodium, the amylene mixture, which was distilled completely without a column, had b. p. 23—35°.

*Olefin Elimination from Dimethyl-*sec.-iso*amylsulphonium Hydroxide.*—An aqueous solution of the dimethyl-*sec.*-*iso*amylsulphonium iodide was treated with a small excess of silver oxide. The filtered solution was distilled, using an all-glass apparatus, into a cooled receiver, where it was treated with a quantity of aqueous mercuric chloride more than sufficient to absorb the sulphides. From this receiver the amylenes were drawn by pumping, in a slow stream of air, through two further traps containing mercuric chloride solution, through calcium chloride and phosphoric anhydride, and into a receiver cooled in liquid air. The product was quite free from sulphides. After being kept for some time in contact with sodium, it was distilled completely without a column. The yield was 6·6%, calculated on pure dimethyl-*sec.*-*iso*amylsulphonium iodide.

Analysis of the Olefin Mixtures.—The refractive indices required for the analysis of the amylenes derived from *sec.*-*iso*amyl iodide were measured at 12·5° with the aid of a modified Pulfrich refractometer (60° prism), by Bellingham and Stanley, belonging to the University of Leeds. The refractive indices (λ Hg 5461 A.) were as follows: trimethylethylene, 1·33966; *iso*propylethylene, 1·32027; mixture, 1·33615. The composition of the mixture is thus: trimethylethylene, 81·9%; *iso*propylethylene, 18·1%. By the courtesy of Sir Jack Drummond, the measurements of refractive index needed for the analysis of the amylene mixture derived from dimethyl-*sec.*-*iso*amylsulphonium hydroxide were made at 4° in a cold-room in the Department of Biochemistry of University College, London. In this case an ordinary Pulfrich instrument was used, and observed angles were used directly for the interpolation required to give the composition of the mixture. The angles (λ Hg 5461 A.) were as follows: trimethylethylene, 0° 0′ 36″; *iso*propylethylene, 3° 13′ 18″; mixture, 0° 17′ 12″. The resulting composition is as follows: trimethylethylene, 91·4%; *iso*propylethylene, 8·6%.

THE UNIVERSITY, LEEDS.
UNIVERSITY COLLEGE, LONDON, W.C.1.

[*Received, January 15th,* 1948.]