

Figure 1. Tetraethylammonium methoxide elimination.

detailed in Table II. The reaction was followed only by bromine titration under the assumption that competition by substitution would not invalidate the relative rates. A reaction mixture from which the base was omitted gave negligible reaction when exposed to the conditions which caused substantial conversion in the presence of base. It is possible that some S<sub>N</sub>2 reaction occurs in the presence of base, but this could not be detected by titration of the base under the pseudounimolecular conditions used here. The reactions were followed until 30–40% of the theoretical amylene was produced.

**Rate of Elimination by Triethylsulfonium Bromide.** Both the aqueous and methanolic reactions were followed by titration of unused base and measurement of the volume of ethylene gas evolved. The analytical procedures are described above, and the kinetic data appear in Table II. Reactions were followed to 30–40% completion.

**Rate of Elimination by Tetraethylammonium Bromide.** The treatment of this reaction was the same as for triethylsulfonium bromide in methanolic sodium methoxide, except that before titrating unconsumed base it was necessary to add 4–5 ml. of water to a 1-ml. portion of reaction mixture and boil for 1 min. to expel triethylamine.

**Typical Determination of Rate Constant.** For the elimination by tetraethylammonium ion the appropriate rate equation is

$$dC/dt = -kC^2$$

in which  $C$  is the concentration of substrate and also of base (initial value = 1  $M$ ). The data in Table III were collected for a pressure of 1360 atm. and a temperature of 104.8°.

Table III

Time, hr.	Vol. of C <sub>2</sub> H <sub>4</sub> , <sup>a</sup> ml.	Concn. of base, $M$	$k_{\text{ethylene}}$	$k_{\text{base}}^b$
5.00	6.90	0.810	0.050	0.047
7.00	8.35	0.758	0.048	0.046

<sup>a</sup> The calculated volume of ethylene at completion is 34.6 ml.

<sup>b</sup> Units are l./mole hr.

**Typical Determination of Volume of Activation.** From the data of Table II, values of  $\ln(k_p/k_0)$  were computed and plotted against pressure as shown in Figure 1. A graphical determination of the slope gives  $\Delta V^*/RT$ .

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## Mechanisms of Elimination Reactions. VI. The Effect of the Leaving Group on Orientation in E2 Reactions<sup>1,2</sup>

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When 2-halopentanes are treated with ethoxide ion in refluxing ethanol, the proportion of 1-pentene in the olefinic product increases in the order  $I < Br < Cl < F$ . When 2-halo-2-methylbutanes are treated with ethoxide ion in refluxing ethanol, the proportion of 2-methyl-1-butene in the olefinic product increases in the order  $Br < Cl < F$ . In both series, the fluoride shows clearly Hofmann-rule behavior (>70% 1-olefin). 2-Methyl-2-

butyl chloride and bromide give less 2-methyl-1-butene when thiophenoxide is the base than when ethoxide is the base. The bearing of these results on current theories of steric and electronic effects in elimination reactions is discussed.

The tendency of some elimination reactions to give mainly the more substituted olefin (Saytzeff rule) and others to give mainly the less substituted olefin (Hofmann rule) has been explained by Ingold in terms of

(1) This work was supported by the National Science Foundation.  
(2) Preliminary account: W. H. Saunders, Jr., S. R. Fahrenholtz, and J. P. Lowe, *Tetrahedron Letters*, No. 18, 1 (1960).

**Table I.** Olefin Proportions from 2-Pentyl Halides<sup>a</sup>

Expt. no.	X in RX	Concn. of RX, M	Concn. of EtO <sup>-</sup> , M	Yield, %		
				Olefin <sup>b</sup>	1-Pentene <sup>c</sup>	<i>trans</i> -/ <i>cis</i> -2-Pentene <sup>d</sup>
1	F	1.0	1.2	<i>e</i>	81.7 ± 1.2 <sup>f,g</sup>	2.6 <sup>f,g</sup>
2	F	0.5	2.4	<i>e</i>	83.3 ± 0.4 <sup>f,g</sup>	2.6 <sup>f,g</sup>
3	Cl	1.0	1.0	6-24 <sup>h</sup>	36.2 ± 0.4	3.7
4	Cl	1.0	1.2	23-29 <sup>h</sup>	34.0 ± 0.6 <sup>f</sup>	3.2 <sup>f</sup>
5	Cl	1.0	1.9	33 <sup>h</sup>	37.7 ± 0.3	3.6
6	Br	1.0	1.0	77-82	24.6 ± 0.4	3.6
7	Br	1.0	2.0	...	25.1 <sup>i</sup>	4.0
8	I	1.0	1.1	63	19.8 ± 0.4	4.0
9	I	1.0	2.2	80	19.3 <sup>i</sup>	4.2

<sup>a</sup> Run with sodium or potassium ethoxide in absolute ethanol at reflux for 6-16 hr. <sup>b</sup> Isolated yields. Range of yields from two or more experiments is given where available. <sup>c</sup> Figure is average, with average deviation, of two or more entirely separate reactions. Unless otherwise noted, analysis was on a 25-ft. didecyl phthalate column. <sup>d</sup> Unless otherwise noted, analysis was on a 15-ft. column of silver nitrate in ethylene glycol. <sup>e</sup> No olefin yield reported, as the yield of substitution product, if any, was not determined. Assuming that only elimination occurred, conversions of around 50% were obtained. <sup>f</sup> Analysis on a 20-ft adiponitrile column. <sup>g</sup> Run at 120° in a sealed tube for 70-80 hr. <sup>h</sup> Unreacted chloride recovered. <sup>i</sup> Single result.

**Table II.** Olefin Proportions from 2-Methyl-2-butyl Halides<sup>a</sup>

Expt. No.	X in RX	Concn. of RX, M	Concn. of EtO <sup>-</sup> , M	Yield, %	
				Olefin <sup>b</sup>	2-Methyl-1-butene <sup>c</sup>
1	F	1.0	1.2	7-15 <sup>d,e</sup>	69.5 ± 0.1
2	F	0.5	2.4	15-52 <sup>d</sup>	70.8 ± 4.0
3	Cl	1.5	1.7	71	43.1 ± 0.6 <sup>f</sup>
4	Cl	1.5	1.7	30	38.8 ± 0.8 <sup>f</sup>
5	Cl	1.5	3.0	46-70	44.7 ± 0.6
6	Cl	1.5	3.0	95-100	45.0 ± 0.1 <sup>g</sup>
7	Cl	0.75	1.7	80-88	37.0 ± 0.2
8	Cl	0.75	3.4	54-80	35.6 ± 0.3
9	Br	1.0	1.1	...	34.8 ± 0.4 <sup>h</sup>
10	Br	1.5	1.7	56-70	33.5 ± 1.0 <sup>h</sup>
11	Br	1.5	1.7	80-88	37.4 ± 0.6 <sup>h</sup>
12	Br	1.5	3.4	92-97	37.9 ± 0.6
13	Cl	1.5	1.7 <sup>i</sup>	68	31.6 ± 2.1
14	Br	1.5	1.7 <sup>i</sup>	67-84	25.7 ± 0.3

<sup>a</sup> Run with sodium or potassium ethoxide in absolute ethanol at reflux for ca. 10 hr. <sup>b</sup> See footnote b, Table I. <sup>c</sup> See footnote c, Table I. <sup>d</sup> Run for 13-104 hr. in a sealed tube at 120°. Yields are based on gas chromatographic analysis for olefin and unreacted alkyl fluoride. <sup>e</sup> The 15% is lower than expected (ca. 50%) for these conditions, so some loss of product may have occurred. The isomer proportion is essentially the same as in the other experiments, indicating no *selective* loss. <sup>f</sup> These two figures obtained by two different workers at least three years apart. <sup>g</sup> 1-5% of tetrahydrofuran added with no apparent effect. <sup>h</sup> These three figures obtained by three different workers over a span of 5-6 years. <sup>i</sup> Base was sodium thiophenoxide.

electronic effects.<sup>3</sup> These explanations have been challenged by Brown,<sup>4</sup> who suggests various ways in which steric effects may also influence rates and product distributions. A particularly controversial aspect of his ideas has been the contention that increasing the steric requirements of the leaving group in E2 reactions increases the proportion of less substituted olefin.<sup>4-6</sup>

(3) (a) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. Mandour, G. A. Maw, and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948); (b) W. Hanhart and C. K. Ingold, *ibid.*, 997 (1927); (c) C. K. Ingold, *Proc. Chem. Soc.*, 265 (1962).

(4) H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, 78, 2203 (1956), and preceding papers.

**Table III.** Summary of Olefin Proportions<sup>a</sup>

Alkyl halide, RX	1-Olefin, %
C <sub>3</sub> H <sub>7</sub> (CH <sub>3</sub> )CHF	82
C <sub>3</sub> H <sub>7</sub> (CH <sub>3</sub> )CHCl	35
C <sub>3</sub> H <sub>7</sub> (CH <sub>3</sub> )CHBr	25
C <sub>3</sub> H <sub>7</sub> (CH <sub>3</sub> )CHI	20
C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> CF	71
C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> CCl	45
C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> CBr	38
C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> CCl	32 <sup>b</sup>
C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> CBr	26 <sup>b</sup>

<sup>a</sup> Figures are reasonable averages from Tables I and II. Data at highest base concentrations only used for *t*-amyl halides. <sup>b</sup> Base was thiophenoxide.

There is indeed such a parallelism, but in most of his examples the same trend is predicted by an explanation based on the ease of heterolysis of the C-X bond and the inductive effect of X. Only when X is halogen did it appear to be possible to make a clear-cut distinction between steric and electronic explanations. As will be seen below, more recent evidence introduces some ambiguities even here.

Brown<sup>4,5</sup> reported several cases of no significant effect on the 1-/2-olefin ratio of changing the halogen. He explained the lack of trend by pointing out that the covalent radius increases with the size of the halogen, and thus that the larger halogens are farther from the site of interference. Our studies were undertaken to check this earlier work and to see whether the observed pattern held under a wider range of examples.

We examined the products from E2 reactions of the 2-pentyl and 2-methyl-2-butyl halides with ethoxide ion in ethanol. Our data are recorded in Tables I and II. Experiments using thiophenoxide as well as ethoxide are also recorded in Table II. The results of all these experiments are summarized in Table III for clarity. All analyses were by gas chromatography.

Because some of our figures differed significantly from those of Brown,<sup>4,5</sup> certain experiments were done by two or three different workers to test the reproducibility of our procedures. The relevant experiments are: 3 and 4, Table I; 3 and 4, and 10 and 11, Table II. These reveal a 2-4% variation from one experimenter to another. This range is outside the probable combined errors of the individual results, but is not sufficient to upset the qualitative picture. The *trans*-/*cis*-2-pentene ratios show somewhat more variation than the 1-pentene yields. The proportion of 1-pentene appears unaffected by changes in concentration of either halide or base (Table I), but the same is not true of the proportion of 2-methyl-1-butene (Table II) for reasons to be discussed below.

Various control experiments were done to check the validity of our results. Starting materials were examined by means of gas chromatography and/or infrared spectra. Special care was taken in looking for 3-pentyl halide in the 2-pentyl halide, and none of the results quoted used reactants containing significant amounts of this contaminant. In addition, we showed that none of the olefins underwent isomerization under the reaction conditions. Finally, a synthetic mixture

(5) H. C. Brown and O. H. Wheeler, *ibid.*, 78, 2199 (1956).

(6) C. H. Schramm, *Science*, 112, 367 (1950).

of the 2-methylbutenes was recovered with no change in composition from simulated reaction mixtures under the conditions used for the chloride and bromide, and also under the more stringent conditions used for the fluoride.

Another set of control experiments was undertaken to see if we were dealing with pure E2 reactions, uncomplicated by concomitant solvolyses. Rough kinetic measurements on 2-pentyl chloride, bromide, and iodide, as well as the constancy of olefin proportions with changing base concentrations, show that there is no problem in the 2-pentyl series. The 2-methyl-2-butyl fluoride does not solvolyze appreciably under reaction conditions as long as a weak base (sodium acetate) is present to inhibit acid-catalyzed decomposition. The 2-methyl-2-butyl chlorides and bromides, however, solvolyze rapidly enough that the solvolysis cannot be entirely suppressed even at the highest base concentrations attainable. This conclusion from rough rate constants is supported by the trends toward more 1-olefin at higher base and halide concentrations (Table II). These trends are not entirely regular, perhaps because the reaction mixtures were inhomogeneous at the higher concentrations and the effective base concentration therefore uncertain. Nonetheless, it seems reasonable to assume that the experiments giving higher proportions of 1-olefin from both chloride and bromide are those in which solvolysis was most successfully repressed, for the solvolysis gives less than 20% of 1-olefin.<sup>7</sup> The error due to solvolysis is undoubtedly lessened by the relatively low elimination-substitution ratio in the solvolysis (*ca.* 70% substitution),<sup>7,8</sup> compared to the much higher yields of elimination product in the second-order reaction. We did not consider kinetic checks on the reactions with thiophenoxide necessary, since *t*-butyl chloride reacts with thiophenoxide ten times faster than with ethoxide.<sup>9</sup>

The results in Tables I-III show that the proportion of 1-olefin increases in the order  $I < Br < Cl < F$ . This is the order one would expect if the amount of double-bond character in the transition state is the controlling factor. Ease of heterolytic cleavage of the carbon-halogen bond runs  $I > Br > Cl > F$ , so that carbanion character should increase, and double-bond character decrease, along the series. The inductive order of the halogens ( $F > Cl > Br > I$ ) would also favor increasing carbanion character, though this is probably of minor importance. The decrease in the *trans*/*cis*-2-pentene ratio from iodide to fluoride provides independent evidence for decreasing double-bond character. Interestingly, these ratios exceed the gas-phase equilibrium ratio (2.3:1)<sup>10</sup> of *trans*/*cis*-2-pentene at 75°.

We originally interpreted<sup>2</sup> our results as excluding definitively the steric requirements of the leaving group as a factor affecting olefin proportion, for the trends clearly run counter to the expected order of size of halogen atoms. A recent study of the equatorial-axial equilibrium in halocyclohexanes, however, reveals a trend of apparent steric requirements (as judged by de-

creasing axial isomer at equilibrium) that runs  $F < I < Br < Cl$ .<sup>11,12</sup> This unexpected result renders less persuasive our evidence from the chloride, bromide, and iodide. Our most striking change in olefin proportion, from the fluoride to the chloride, remains in disagreement with the steric explanation. One cannot confidently conclude much from the magnitudes of the effects observed by Berlin and Jensen, for their work was done at very low temperatures (-82 to -93°) and in carbon disulfide, and these equilibria are known to be solvent dependent.<sup>13</sup> The conformational requirements of halogens seem in general to be small, for *cis*-4-methylcyclohexyl bromide prefers by nearly 5:1 the conformation with bromide axial and methyl equatorial.<sup>13</sup> The likelihood that the still smaller differences on changing from one halogen to another would have significant chemical effects does not seem great. Taken at face value, the energy differences reported by Berlin and Jensen are far too small to account for the variations in olefin proportion that we observe from chloride to bromide to iodide.

The thiophenoxide-promoted eliminations (Table II) show the same order of effect of halogen as the ethoxide-promoted eliminations. Also, they show a considerably higher proportion of 2-methyl-2-butene.<sup>14</sup> As thiophenoxide should be bulkier than ethoxide, the steric requirements of the base do not seem an important influence here. A transition state close to that for E1 reaction is indicated, for the proportion of 2-methyl-2-butene from the bromide (74.3%) approaches the figure for the E1 reaction (82%).<sup>7</sup> Thiophenoxide-promoted eliminations have been suggested<sup>15</sup> to be merged substitution-elimination<sup>16</sup> processes, but there is no compelling evidence for this viewpoint.

A few discrepancies exist between our results and Brown's.<sup>4,5</sup> The 30% 2-methyl-1-butene he reports from 2-bromo-2-methylbutane is only 4% below our lowest result and is probably reasonably accurate, for the base concentration used (1.0 M) would allow more E1 reaction than any of our conditions. Brown's 1-pentene proportions from 2-pentyl bromide and iodide (31 and 30%, respectively) are somewhat farther from ours, though only the iodide is beyond any reasonable allowance for combined errors. Analysis of this three-component product mixture by the methods available to Brown (infrared spectra and refractive indices) should be quite difficult and rather sensitive to impurities. In fact, the necessity of fractionating the samples so as to remove all solvent could have affected the product ratio. That his procedure did not detect the fairly small difference between the bromide and iodide that we found is not at all surprising.

The pattern of our results is entirely consistent with an explanation in which the carbanion character of the transition state, and hence the rate-depressing effect of  $\beta$ -alkyl substitution, increases in the order  $I < Br < Cl < F$ . This increase in carbanion character is expected

(11) A. J. Berlin and F. R. Jensen, *Chem. Ind.* (London), 998 (1960).

(12) The relevance of this work to elimination reactions was first discussed by R. L. Klimisch, Ph.D. Thesis, Purdue University. We are indebted to Professor H. C. Brown for presenting to us the substance of this discussion.

(13) E. L. Eliel, *ibid.*, 568 (1959).

(14) Professor S. Winstein (private communication) has made the same observation on the chloride.

(15) E. L. Eliel and R. S. Ro, *Tetrahedron*, 2, 353 (1958).

(16) S. Winstein, D. Darwish, and N. J. Holness, *J. Am. Chem. Soc.*, 78, 2915 (1956).

(7) M. L. Dhar, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2065 (1948).

(8) E. D. Hughes and B. J. McNulty, *ibid.*, 1283 (1937).

(9) P. B. D. de la Mare and C. A. Vernon, *ibid.*, 41 (1956).

(10) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, 36, 559 (1946).

from the increase in difficulty of breaking the C-X bond along the same series. The results on the fluorides are inconsistent with a steric effect of the leaving group, and the steric effects of the other three halogens, though in the proper order, are probably too small to cause the observed variations in olefin proportions. The applicability of our conclusions to leaving groups with large steric requirements, such as dialkylsulfonium and trimethylammonium, is perhaps debatable. It seems unnecessary to invoke a steric effect, however, under circumstances where the behavior of the groups can be explained by a transition state possessing high carbanion character.

Some special discussion of the results on the alkyl fluorides seems called for, as they provide the only data that are inescapably at odds with the steric effect of the leaving group. Reaction conditions were necessarily more strenuous (120° in a sealed tube vs. refluxing ethanol) than for the other halides because of the much lower reactivity of the fluorides. Any change in the observed trend in isomer ratios seems highly unlikely, for the ratio of 1- to 2-olefin should, if anything, be closer to statistical at 120 than at 78°.

Though we did not establish the kinetic order of our reactions of fluoride with base, this has been done under comparable conditions on *t*-pentyl fluoride and a "sec-amyl fluoride" which was probably a mixture of 2- and 3-pentyl fluorides.<sup>17</sup> The rate constants reported by Chapman and Levy<sup>17</sup> predict half-lives under our conditions of the order of 100 hr., in agreement with the approximately 50:50 mixture of olefin and unreacted fluoride that we detected by gas chromatography in reaction mixtures run for this period of time. The low reactivity of alkyl fluorides in base-promoted eliminations is further shown by the work of DePuy and Bishop<sup>18</sup> on the 2-arylethyl fluorides. The high Hammett  $\rho$ -value of +3.1 (compare +2.6 for chlorides and +2.1 for bromides and iodides) at 30° confirms the high sensitivity to inductive effects of substituents that we have observed.

Both of our alkyl fluorides were obtained in poor yield (10% or less), along with considerable olefin which was removed by treatment with bromine (see Experimental). The fluorides were distilled from this mixture under reduced pressure, and the absence of olefin or other volatile contaminants was shown by gas chromatography. No further distillation was performed in order to avoid any possible autocatalytic decomposition of the fluorides.<sup>19</sup>

Though we cannot conceive of any substances other than the expected fluorides that might show the behavior these products did in the subsequent eliminations, the poor yields in preparation and the absence of conventional criteria of purity such as boiling ranges made further evidence on the structures desirable. Consequently, we obtained proton and fluorine magnetic resonance spectra.<sup>20</sup>

The spectra are complex because of splitting by both protons and fluorine. The proton spectrum (neat) of *t*-pentyl fluoride shows a triplet at  $\tau$  9.05 (4-CH<sub>3</sub>) which

(17) N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1673 (1952).

(18) C. H. DePuy and C. A. Bishop, *J. Am. Chem. Soc.*, **82**, 2535 (1960).

(19) N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1677 (1952).

(20) We are indebted to Professor R. W. Taft, Jr., for obtaining the F<sup>19</sup> magnetic resonance spectra, and to Professor L. D. Colebrook of this department for aid in interpreting both sets of spectra.

partially overlaps multiplets due to the 3-CH<sub>2</sub> and 1-CH<sub>3</sub> groups. The center of the 1-CH<sub>3</sub> multiplet is at  $\tau$  8.73 and the coupling constant between the fluorine and the 1-CH<sub>3</sub>,  $J_{H-F}$ , is 21 c.p.s. The fluorine resonance spectrum (25% in CCl<sub>4</sub>) appears to be a septet with  $J_{H-F} \cong 9.5$  c.p.s. and a fluorine shift equivalent to +26.8 p.p.m. from an internal tetrachlorotetrafluorocyclobutane (measured relative to external hexafluorobenzene and converted) standard.<sup>21</sup> Splitting into a septet is predicted for interaction with the 1-CH<sub>3</sub> groups alone, but is experimentally indistinguishable from that predicted for interaction with the 1-CH<sub>3</sub> and the 3-CH<sub>2</sub> groups as well, with  $J_{H-F}$  about the same for both (nine lines, but with the outermost pair very weak).

The proton spectrum of 2-pentyl fluoride shows multiplets centered around  $\tau$  8.77 and 5.53, the latter for the 2-CH proton and the former encompassing all other protons. The coupling constant,  $J_{H-F}$ , is about 49 for the interaction between F and 2-CH and about 23 c.p.s. for the interaction between F and 1-CH<sub>3</sub> and/or 3-CH<sub>2</sub>. Coupling between 1-CH<sub>3</sub> and 2-CH protons occurs with  $J_{H-H} = 6.2$  c.p.s. Chemical shifts are  $\tau$  5.53 for 2-CH, 8.77 for 1-CH<sub>3</sub>, and 9.05 for 5-CH<sub>3</sub>. The fluorine resonance spectrum appears to be a sextet. It can be interpreted as two overlapping quartets with  $J_{H-F}$  46 for interaction with the 2-CH, and 23 c.p.s. for interaction with 1-CH<sub>3</sub> and/or 3-CH<sub>2</sub> (see comments on *t*-pentyl fluoride spectrum). The fluorine shift is equivalent to +59.1 p.p.m. from internal tetrachlorotetrafluorocyclobutane.<sup>22</sup>

## Experimental

*2-Chloropentane* was prepared by the method of Whitmore and Karnatz<sup>24</sup> from 2-pentanol, pyridine, and thionyl chloride. The reaction mixture was cooled in an ice-salt bath during addition of the thionyl chloride. It was then left at room temperature for 1 hr. and in a 30–50° water bath for 2 hr. before pouring onto cracked ice. The organic layer was washed with 10% sodium carbonate, dried, and then distilled to convert the chlorosulfonic ester to the chloride. A final distillation gave material of b.p. 94.5–96°,  $n_{D}^{20}$  1.4058 (lit.<sup>24</sup> b.p. 96.5°,  $n_{D}^{20}$  1.4068). The distillations were somewhat erratic, and occasionally material containing appreciable amounts of 3-chloropentane was obtained. Only batches shown to contain less than 1% of 3-chloropentane were used in elimination reactions.

*3-Chloropentane* for gas chromatographic comparisons was prepared in the same manner as 2-chloropentane, b.p. 94–95°.

*2-Bromopentane* was obtained from K & K Laboratories, b.p. 115–116°,  $n_{D}^{20}$  1.4380 (lit.<sup>25</sup> b.p. 117.2°,  $n_{D}^{19.8}$  1.4401). The infrared spectrum was identical with that reported for pure 2-bromopentane, though gas chromatographic analysis of some batches on a 15-ft. column of 20% Apiezon L revealed a trace of 3-bromopentane.

(21) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963), report +18 p.p.m. for *t*-butyl fluoride.

(22) No secondary fluorides seem to have been reported previously, but with tertiary fluorides running around +20 p.p.m. and primary fluorides around 100 p.p.m. (ref. 21 and 23), this figure seems reasonable.

(23) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(24) F. C. Whitmore and F. A. Karnatz, *J. Am. Chem. Soc.*, **60**, 2536 (1938).

(25) H. Pines, A. Rudin, and V. N. Ipatieff, *ibid.*, **74**, 4063 (1952).

2-Pentyl *p*-toluenesulfonate was prepared as described by Pines.<sup>25</sup> The liquid sulfonate was used without distillation.

3-Pentyl *p*-toluenesulfonate was prepared in the same manner. The product had m.p. 45° (lit.<sup>25</sup> m.p. 43–43.5°).

2-Iodopentane was obtained from the *p*-toluenesulfonate as described by Brown and Wheeler.<sup>5</sup> Each batch was shown to be free of 3-iodopentane by gas chromatography or infrared spectrum. The material used was distilled at 57° (50 mm.), as some decomposition occurred at atmospheric pressure.

3-Iodopentane was prepared in the same manner as 2-iodopentane and had b.p. 62–64° (48 mm.),  $n_D^{24}$  1.4955.

2-Fluoropentane was made from 2-pentyl *p*-toluenesulfonate by the procedure of Edgell and Parts.<sup>26</sup> The reaction mixture was heated to 90° under 500 mm., and the products were collected in a trap cooled by Dry Ice and acetone. The temperature was raised to 120° for 24 hr. before discontinuing the reaction. The distillate, which contained considerable olefin, was dried over potassium carbonate. Olefin was removed by cooling in an ice-salt bath and rapidly adding bromine with stirring until the color persisted. The mixture was washed with sodium bisulfite and dried over potassium carbonate and magnesium sulfate. Distillation was from a flask cooled in ice and salt to a receiver cooled in Dry Ice and acetone. Pressure started at 70 and was gradually lowered to 30 mm. The yield was poor (5–10%), but gas chromatographic analysis on a 20-ft. column of adiponitrile on Chromosorb P showed no trace of olefin. The micro boiling point was 56–57° (lit.<sup>17</sup> 56° for “*sec*-amyl fluoride”).

2- and 3-Fluoropentane were also prepared by treating the corresponding alcohols with 50% aqueous hydrofluoric acid in a Teflon bottle at 135° and collecting the product in a polypropylene bottle. Olefin was removed as above. The yields were superior to those from the *p*-toluenesulfonate, but isomerization was shown by the presence of 1-pentene in the product from treatment of the “3-fluoropentane” with sodium ethoxide in ethanol. 2- and 3-Fluoropentane had identical retention times on several gas chromatographic columns.

2-Chloro-2-methylbutane was Eastman Kodak White Label grade. The material used had b.p. 83–84°,  $n_D^{20}$  1.4039 (lit.<sup>27</sup> 84.3–85°,  $n_D^{20}$  1.4036). Gas chromatographic analysis gave a single major peak with ca. 0.2% of an impurity with lower retention time, presumably olefin.

2-Bromo-2-methylbutane was obtained by treatment of 2-methyl-2-butanol with 48% hydrobromic acid.<sup>28</sup> The product had b.p. 104.5–105°,  $n_D^{20}$  1.4402 (lit.<sup>29</sup> b.p. 103.5–104°,  $n_D^{20}$  1.4410, 1.4421).

2-Fluoro-2-methylbutane was prepared by treating 2-methyl-2-butanol with 48% aqueous hydrogen fluoride in a Teflon bottle at 70–75° and distilling the product

as formed into a polypropylene bottle cooled in ice water. The procedure was adapted from one used for *t*-butyl fluoride.<sup>30</sup> Olefin was removed by treatment with bromine followed by low-temperature distillation as in the 2-fluoropentane preparation. The yield was ca. 10% of material containing, as the only apparent impurity, less than 0.3% of 2-methylbutenes, as shown by gas chromatography. Efforts to obtain a micro boiling point were frustrated by decomposition.

*Elimination Reactions of Pentyl Chlorides, Bromides, and Iodides.* Absolute ethanol was prepared by the method of Lund and Bjerrum.<sup>31</sup> Potassium and sodium ethoxide solutions were prepared by dissolving the clean metal in cold absolute ethanol. Concentration was usually checked by titration and the solutions were used the same day they were prepared.

The procedure was similar to that of Brown and Wheeler.<sup>5</sup> Reaction mixtures containing the 2-pentyl halides were refluxed for 6–16 hr. under a condenser containing water at 38–52°, while reaction mixtures containing the 2-methyl-2-butyl halides were kept at total reflux for 10 hr. In each case the olefin in the reaction mixture was then distilled, followed by distillation of a few milliliters of ethanol to ensure complete removal of olefin. The olefin was collected in a trap cooled in Dry Ice and acetone. Reactions with sodium thiophenoxide were refluxed for 1.5 hr. and then treated in the same manner. In early work the products were washed and dried over Drierite, but later it was found that the crude original distillate could be analyzed directly by gas chromatography. Any unreacted halide present was shown not to interfere.

*Elimination Reactions of Pentyl Fluorides.* A quantity of the alkyl fluoride (generally 0.5–2.0 g.), sufficient to give a solution of the desired concentration, was dissolved in 12–25 ml. of the sodium ethoxide solution, and the mixture was sealed in a Pyrex tube. The tube was heated in a furnace at 120 ± 5° for times ranging from 13 to 104 hr. (mostly near 100 hr.) for the *t*-pentyl fluoride and 70 to 80 hr. for the 2-pentyl fluoride. The tube was cooled in acetone and Dry Ice, and opened, and gas chromatographic analysis was performed directly on the whole reaction mixture. Since unreacted alkyl fluoride remained in each reaction mixture (48–92% of the sum of alkyl fluoride + olefin), the alkyl fluoride was subjected to the conditions of the analysis and found to undergo no elimination.

*Control Experiments.* Samples of 1- and 2-pentene were subjected separately to the conditions of the elimination reactions. Analysis by gas chromatography showed that neither underwent isomerization. A known mixture of 2-methyl-1-butene and 2-methyl-2-butene was subjected to the reaction conditions and recovered in more than 90% yield with no change in composition. A known mixture of the same two olefins was also unchanged by the conditions used for the elimination reactions of the alkyl fluorides.

*Gas chromatographic analyses* were performed on the Aerograph Model A-110-C or Aerograph Hy-Fi instruments (Wilkins Instrument and Research, Inc.), except

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for the early work on the 2-methylbutenes, which was done on a Perkin-Elmer instrument. The solid support was Chromosorb, and columns were 0.25 in. in diameter (0.125 in. for those on the Hy-Fi). The 2-methylbutenes were separated at room temperature on a 15-ft. didecyl phthalate column or on two 1-m. columns in series packed with didecyl and dinonyl phthalate, respectively. Originally, 1- and 2-pentene were separated on a 25-ft. didecyl phthalate column at 15°. This column failed to separate *cis*- and *trans*-2-pentene, but a 15-ft. column of ethylene glycol saturated with silver nitrate accomplished the job at room temperature with slight overlap of the 1-pentene and *cis*-2-pentene peaks. In addition, product mixtures from 2-pentyl chloride had to be redistilled to remove unreacted chloride, since it would react with the silver nitrate. In later work the 1-pentene and *cis*- and *trans*-2-pentene were determined simultaneously on a 20-ft. adiponitrile column at room temperature. None of the column materials had any effect on unreacted alkyl halide under the analytical conditions except for the ethylene glycol-silver nitrate mixture noted above.

The 2- and 3-chloropentanes were separated on a 15-ft. Apiezon-L column at 67°. The same column at 103° separated the 2- and 3-iodopentanes, and at 110° the 2- and 3-bromopentanes. Separation of the 2- and 3-fluoropentanes could not be accomplished under any conditions tried.

*Base-Promoted Elimination vs. Solvolysis.* Rough kinetics on the second-order reaction with ethoxide ion and the first-order reaction with ethanol were run on most of the halides used in this investigation. Runs were in the refluxing solvent and no particular effort to attain precision was made. Concentrations similar to those of the preparative runs were used, and three to five points were determined per run by titration of chilled aliquots with sodium hydroxide (in the solvolyses) or hydrochloric acid (in the second-order reactions). The rate constants are useful only as orders of magnitude, and will not be tabulated.

The qualitative conclusions are as follows. 2-Pentyl iodide and bromide had  $k_2 > 500k_1$ . 2-Pentyl chloride underwent less than 0.25% solvolysis in 22 hr., which is longer than the time of the preparative run. 2-Methyl-2-butyl fluoride when heated in ethanol at 120° for 85 hr. with a slight excess of sodium acetate (to prevent acid-catalyzed solvolysis) produced less than 1.7% olefin. From this result it was assumed that solvolysis would also be negligible with 2-pentyl fluoride. 2-Methyl-2-butyl chloride had  $k_2 \sim 3k_1$ , and the bromide had  $k_2 \sim 5k_1$  (no correction applied for solvolysis accompanying the second-order reaction). These figures indicate that as much as 10–20% solvolysis may accompany the preparative elimination reactions of these two compounds under the conditions used.

## Mechanisms of Photochemical Reactions in Solution. XXXI. Activation and Deactivation of Conjugated Dienes by Energy Transfer

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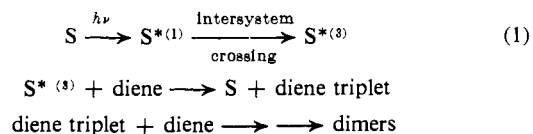
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The photosensitized dimerizations of isoprene and butadiene have been studied in detail. Similar variations in the composition of the product mixtures are observed as the excitation energies of the triplet states of the sensitizers are varied. The results suggest that excitation of *s-cis*-dienes to triplet states requires less excitation energy than is needed to excite *s-trans* forms. *cis* triplets added to dienes give much larger yields of cyclohexene derivatives than are obtained from *trans* triplets. Other quantitative studies of the reaction of isoprene included: (1) measurement of quantum yields, (2) dependence of quantum yields on isoprene concentration; and (3) the influence of an added quencher (azulene). The results are all consistent with a mechanism in which the diene is activated by transfer of triplet excitation from a sensitizer to a diene molecule.

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Earlier reports<sup>3–6</sup> have shown that irradiation of solutions containing conjugated dienes and various photosensitizers, with light absorbed only by the latter, leads to formation of dimers of the dienes. The following mechanism has been suggested.



It has further been inferred that stereoisomeric triplets of the dienes are formed in varying amounts in the presence of different sensitizers.<sup>5</sup> This paper will

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