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THE EFFECT OF THE LEAVING GROUP ON ORIENTATION IN E2 ELIMINATION REACTIONS[1]

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The widely-accepted belief that the Hofmann rule is the consequence of polar effects[2] has recently been challenged by Brown,[3] who points out that the proportion of the less-alkylated olefin increases as the steric requirements of the leaving group increase. In most of his examples, an explanation based on the ease of heterolysis of the C-X bond and the inductive effect of X predicts the same trend. When X is halogen the predicted trends for the steric *vs*. the polar explanations are not parallel, but in several instances Brown[3] reports no sig-

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[2] (a) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.* 2093 (1948);

(b) W. Hanhart and C. K. Ingold, *ibid.* 997 (1927).

[3] (a) H. C. Brown and O. H. Wheeler, *J. Amer. Chem. Soc.* **78**, 2199 (1956);

(b) H. C. Brown and I. Moritani, *ibid.* **78**, 2203 (1956);

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

nificant effect on olefin proportions of changing the halogen.

We have now studied eliminations from 2-pentyl and 2-methyl-2-butyl halides using gas chromatography (a technique not available at the time of Brown's work) to determine product compositions. Separation of 1-olefin from 2-olefin in both series was effected by di-n-decyl phthalate as stationary phase. Eliminations were run at reflux in absolute ethanol with 1.0-1.5 M halide and 1.0-3.3 M potassium or sodium ethoxide.

With 2-methyl-2-butyl, the proportion of 2-methyl-1-butene was 43.1% from the chloride and 33.5%[4] from the bromide. With 2-pentyl, the proportion of 1-pentene ran: Chloride, 36.8%; bromide, 24.7%; and iodide, 19.6%.[5] All percentages are averages from three or more runs and average deviations were less than 2%. Purity of starting materials was established by gas chromatography and infrared spectra. We determined that solvolytic (E1) eliminations made negligible contributions in all reactions studied.

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[4] H. C. Brown, I. Moritani and M. Nakagawa, J. Amer. Chem. Soc. 78, 2191 (1956) report 30% 1-olefin from the bromide.

[5] Ref. 3a reports 31% 1-pentene from the bromide and 30% 1-pentene from the iodide. We have no good explanation of the discrepancies between these infrared analyses and our gas-chromatographic analyses.

Clearly, the results are in the wrong order for the steric explanation. The order of increasing ease of heterolysis of the C-X bond is Cl $<$ Br $<$ I, however, so one might expect double-bond character in the transition state to increase in the same order. Thus the tendency for the more stable olefin to predominate should be greatest for the iodide and least for the chloride, in agreement with our results. The change in inductive effect with changing halogen is probably of minor importance, but also predicts the observed order.

Our results do not, of course, prove that steric effects are unimportant with bulky leaving groups such as trialkylammonium. Obviously further work is necessary, but until more definitive evidence is available it seems unwise to assume that the steric requirements of the leaving group have any important effect on the olefin proportions in E2 eliminations.