(16) Empirical force field calculations on the corresponding two rotamers in trineopentylbenzene itself, using the STRAIN program developed at Princeton University,[7,8,17] gave values of −1.05 and −0.14 kcal/mol for rotamers D and A, B and C, respectively. The difference of 0.91 kcal/mol is of interest in comparison with the $\Delta G°$ value of 0.49 kcal/mol estimated in connection with a band shape analysis of the methylene proton spectrum of the tribromo compound at 100 MHz (see subsequent text). The details of the molecular mechanics calculations will be described in a later paper.[18]
(17) The STRAIN program was placed at our disposal through the kind generosity of Professor Kurt Mislow.
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(19) A modified version of a program described in detail by Wennerbeck and Sandström.[20]
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Steric Effects. IV. E1 and E2 Eliminations

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Abstract: Rate constants for E2 elimination of β-substituted 'onium compounds and orientation data for E2 and E1 eliminations taken from the literature give significant correlations in nine out of ten sets studied with the modified Taft equation, $Q_X = \psi \upsilon_X + h$. The effect of β-alkyl groups on rates and orientation in E2 elimination reactions and on orientation in E1 elimination reactions can be quantitatively described by steric effects.

There is considerable controversy in the literature regarding the explanation of the effect of alkyl groups on reaction rates and orientation in E1 and E2 eliminations.[1] In the case of E2 eliminations, Banthorpe, Hughes, and Ingold[2] made the statement that, "the inductive and electromeric effects dominate the picture of eliminations down to the simplest examples of Hofmann and Saytzeff". These authors regard steric effects as insignificant except in the case of very large alkyl groups. Brown and his coworkers,[3] on the other hand, have proposed that steric effects are the cause of the observed effect of alkyl groups on the orientation in both E1 and E2 reactions. It seemed of interest to examine the available data quantitatively by means of correlations with the modified Taft equation

$$Q_X = \psi \upsilon_X + h \tag{1}$$

where Q is the quantity to be correlated, and υ is the steric parameter we have defined in the first paper of this series,[4] from the esterification of carboxylic acids. Some of the data have been correlated with the equation

$$Q_X = \alpha \sigma_{IX} + \beta \sigma_{RX} + \psi \upsilon_X + h \tag{2}$$

to detect the presence of significant electrical effects. In this equation, σ_I and σ_R are substituent constants representative of the localized and delocalized electrical effects, respectively. Values of σ_I are taken from our compilation,[5] values of σ_R are from the equation

$$\sigma_R = \sigma_p - \sigma_I \tag{3}$$

The σ_p values are taken from the compilation of McDaniel and Brown.[6] The data were also correlated with the equation

$$Q_X = \psi' \upsilon'_X + h \tag{4}$$

where υ' represents the steric parameter defined from nucleophilic substitution of substituted alkyl bromides as described in the third paper of this series.[7]

The data sets studied fall into two groups, rate constants for the E2 elimination reactions of 'onium ions bearing β-alkyl substituents (sets 1–4) and ratios of percent 1-olefin formed to percent 2-olefin formed, or similar quantities, for elimination reactions involving compounds that can produce more than one elimination product (sets 5–10). When two or more products are formed, the overall rate constant k_T is given by

$$k_T = k_1 + k_2 + \ldots + k_n \tag{5}$$

where $k_1, k_2, \ldots k_n$ are the rate constants for the formation of products 1, 2, ... n. For these rate constants, we may write

$$k_1 = p_1 k_T, k_2 = p_2 k_T, \ldots k_n = p_n k_T \tag{6}$$

where $p_1, p_2, \ldots p_n$ denote the percents formed of products, 1, 2, ... n. Thus, applying the modified Taft equation we may obtain

$$\log k_1 = \log p_1 k_T = \psi_1 \upsilon_X + h_1 \tag{7}$$

$$\log k_2 = \log p_2 k_T = \psi_2 \upsilon_X + h_2 \tag{8}$$

$$\log p_1 k_T - \log p_2 k_T = \log (p_1/p_2) = \psi_1 \upsilon_X + h_1 - (\psi_2 \upsilon_X + h_2) = \log r_{12} \tag{9}$$

$$\log r_{12} = \psi_{12} \upsilon_X + h_{12} \tag{10}$$

The data for sets 5–10 were also correlated with the equation

$$\log r_{12} = \psi \upsilon_{12} \upsilon'_X + h'_{12} \tag{11}$$

The data used in the correlations are presented in Table I.

Results

The results of the correlation of sets 1–4 (sets labeled A) with eq 2 are set forth in Table II. Only set 2 gave significant results. In this set, the values of α and β were not significant, whereas the value of ψ was significant, as deter-

Table I. Data Used in Correlations

1	10^5k_2, $XCH_2CH_2NMe_3^+ + EtO^-$ in EtOH at 104.22°[a] H, 71.3; Me, 5.16; Et, 2.82; $Bu(CH_2)_4$, 2.60; *i*-Pr, 1.06; *t*-Bu, 0.084
2	10^5k_2, $XCH_2CH_2NMe_3^+ + t\text{-BuO}^-$ in *t*-BuOH at 72.85°[a] H, 30,100; Me, 373; Et, 87.7; *i*-Pr, 22.5; *t*-Bu, 0.72
3	10^5k_2, $XCH_2CH_2SMe_2^+ + EtO^-$ in EtOH at 64.08°[a] H, 79; Me, 29; Et, 21; *i*-Pr, 16; *t*-Bu, 0.43
4	10^5k_2, $XCH_2CH_2SMe_2^+ + t\text{-BuO}^-$ in *t*-BuOH at 34.86°[a] H, 271; Me, 33; Et, 19; *i*-Pr, 7.9; *t*-Bu, 3.2
5	r_{12}, XCH_2CBrMe_2 + pyridine in EtOH at about 70°[b] Me, 0.33; Et, 0.47; *i*-Pr, 0.81; *t*-Bu, 2.33
6	r_{12}, $XCH_2CBrMe_2 + EtO^-$ in EtOH at about 70°[b] Me, 0.43; Et, 1.00; *i*-Pr, 1.17; *t*-Bu, 6.14
7	r_{12}, XCH_2CMe_2Br, solvolysis in 85% butyl Cellosolve at 25°[c] Me, 0.27; Et, 0.41; *i*-Pr, 0.70; *t*-Bu, 4.3
8	r_{tc}, $XCH_2CHOBsMe$, solvolysis in AcOH at 70°[d] Me,[e] 1.08; Et, 1.39; *i*-Pr, 1.94; *t*-Bu, 84
9	r_{1c}, $XCH_2CHOBsMe$, solvolysis in AcOH at 70°[d] Me,[e] 0.23; Et, 0.45; *i*-Pr, 0.74; *t*-Bu, 27.2
10	r_{1t}, $XCH_2CHOBsMe$, solvolysis in AcOH at 70°[d] Me,[e] 0.21; Et, 0.33; *i*-Pr, 0.38; *t*-Bu, 0.32

[a] Reference 2. [b] H. C. Brown, I. Moritani, and M. Nakagawa, *J. Am. Chem. Soc.*, 78, 2190 (1956). [c] H. C. Brown and M. Nakagawa, *ibid.*, 77, 3610 (1955). [d] H. C. Brown and M. Nakagawa, *ibid.*, 77, 3614 (1955). [e] Data for tosylate.

mined by the "Student t" test. It would seem that electrical effects of the alkyl substituents are either negligible or approximately constant.

The results of the correlation of all sets with eq 1 and 4 (sets labeled B) and with eq 10 and 11 (sets labeled C) are set forth in Table III. With eq 1, the rate constants for elimination of the 'onium ions (sets 1-4) gave generally better results than with eq 4. Thus, with eq 1 three sets gave excellent results and one set gave fair results, as determined by the confidence levels for the significance of the regression analysis. With eq 4, two sets gave excellent, one gave good, and one gave fair results.

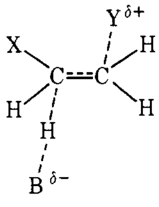
Correlation of product ratios for E2 eliminations, sets 5 and 6, gave good and fair results with both eq 10 and eq 11. Correlations were slightly better with eq 10.

Correlation of product ratios for E1 eliminations, sets 7-10, was slightly better with eq 10 than with eq 11; thus one set gave excellent, two gave good, and one did not give significant results with eq 10; while one set gave very good, two gave good, and one did not give significant results with eq 11.

Discussion

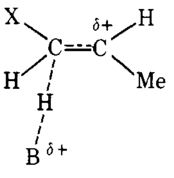
Our results clearly show that the effect of alkyl substituents upon the rates of E2 elimination of 'onium ions and upon orientation in E1 and E2 eliminations can be accounted for entirely by steric effects. Thus our findings refute the conclusions of Banthorpe, Hughes, and Ingold[2] and support the conclusions of Brown and his coworkers.[3] We do not in any way wish to imply that electrical effects are negligible in these reactions. We believe, rather, that the electrical effect of alkyl groups is essentially constant. In that event, eq 2 becomes equivalent to eq 1.

We have noted above that correlation with the υ values which relate to the esterification of carboxylic acids gives generally better results than does correlation with the υ' values which were obtained from bimolecular nucleophilic substitution. The transition states for the elimination reactions (I and II) must, in so far as steric effects are concerned, bear a closer relationship to the transition state for esterification (III) than they do to the transition state for bimolecular nucleophilic substitution (IV).



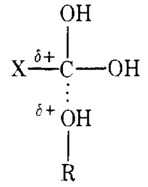
I

E2 elimination



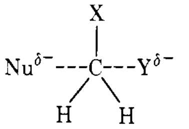
II

E1 elimination



III

esterification

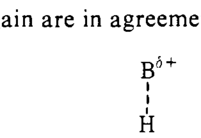


IV

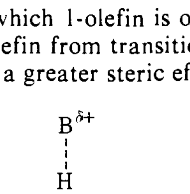
S_N2 substitution

In the rates of elimination, the sign of ψ indicates steric retardation, as expected for these reactions. The magnitude of ψ is comparable to that observed in acid catalyzed hydrolysis of esters,[4] esterification,[4] and base catalyzed hydrolysis of esters.[8] It is interesting that ψ is greater for NMe_3^+ as the leaving group than for SMe_2^+. This agrees with the fact that the NMe_3^+ group, for which υ is 1.22, is larger than the SMe_2^+ group, which should be approximately the size of the isopropyl group for which υ is 0.76. As to the effect of base size, the larger $t\text{-BuO}^-$ ion gives a greater ψ value in the case of the NMe_3^+ leaving group while, for the SMe_2^+ leaving group, there does not seem to be any significant difference in ψ. As the temperatures and solvents are not the same in the sets being compared (sets 3 and 4), no definitive conclusion can be drawn.

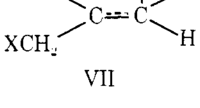
Assuming that, as in the other sets studied, the steric effect is also one of retardation then, in all of these cases, ψ_1 and ψ_2 should be negative. As in all of the sets, 5-10, the ψ_{12} values obtained are positive, it follows that, while both ψ_1 and ψ_2 are negative, the absolute value of ψ_2 is greater than the absolute value of ψ_1. Thus the steric effect is greater for elimination leading to 2-olefin than it is for elimination leading to 1-olefin in sets 5, 6, and 7. Consider the transition states leading to 1-olefin and 2-olefin for sets 5 and 6, both of which involve E2 elimination. They are V and VI, respectively. Comparison of transition states V and VI suggests that steric effects for V should be considerably less than those for VI, in agreement with the observed ψ_{12} values. The results for set 7, for which 1-olefin is obtained from transition state VII and 2-olefin from transition state VIII, again are in agreement with a greater steric effect ex-



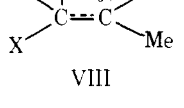
V



VI



VII



VIII

Table II. Results of Correlation with Equation 2

Set	α	β	ψ	h	R^{a}	F^{b}	$r_{12}{}^{c}$	$r_{13}{}^{c}$	$r_{23}{}^{c}$
1A	0.970	−1.49	−2.47	1.83	0.966	89.60^{j}	0.842	0.851	0.838
2A	−2.85	2.98	−3.59	4.42	0.993	22.82^{m}	0.863	0.853	0.846
3A	11.2	−12.3	−2.48	1.92	0.996	41.64^{m}	0.863	0.853	0.846
4A	−6.40	4.96	−1.41	2.40	0.989	15.54^{m}	0.863	0.853	0.846

Set	$s_{est}{}^{d}$	$s_{\alpha}{}^{d}$	$s_{\beta}{}^{d}$	$s_{\psi}{}^{d}$	$s_{h}{}^{d}$	n^{e}
1A	0.129	5.21^{q}	2.42^{p}	0.304^{i}	0.128^{h}	6
2A	0.406	17.1^{q}	8.24^{p}	0.955^{n}	0.402^{l}	5
3A	0.154	6.46^{o}	3.12^{n}	0.362^{l}	0.152^{l}	5
4A	0.211	8.86^{p}	4.28^{o}	0.496^{o}	0.209^{l}	5

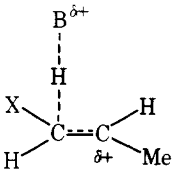
Confidence levels of F and of "Student t" tests on s_{α}, s_{β}, s_{ψ}, and s_{h} are given as superscripts. [a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of σ_{I} on σ_{R}, σ_{I} on ν, σ_{R} on ν. [d] Standard errors of the estimate, ψ, and h. [e] Number of points in the set. [f] 99.9% confidence level (CL). [g] 99.5% CL. [h] 99.0% CL. [i] 98.0% CL. [j] 97.5% CL. [k] 95.0% CL. [l] 90.0% CL. [m] <90.0% CL. [n] 80.0% CL. [o] 50.0% CL. [p] 20.0% CL. [q] <20.0% CL.

Table III. Results of Correlation with Equations 1, 4, 10 and 11

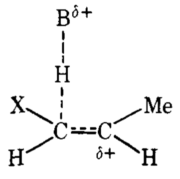
Set	ψ	h	r^{a}	F^{b}	$s_{est}{}^{c}$	$s_{\psi}{}^{c}$	$s_{h}{}^{c}$	n^{d}
1B	−2.36	1.88	0.996	448.8^{e}	0.100	0.111^{e}	0.0809^{e}	6
1C	−2.28	1.57	0.979	68.44^{f}	0.252	0.276^{g}	0.182^{g}	5
2B	−3.75	4.35	0.992	181.2^{e}	0.250	0.279^{e}	0.205^{e}	5
2C	−3.56	3.88	0.958	33.90^{i}	0.558	0.611^{h}	0.402^{g}	5
3B	−1.79	2.21	0.931	19.49^{j}	0.364	0.406^{j}	0.299^{g}	5
3C	−1.85	2.06	0.977	61.93^{f}	0.214	0.235^{g}	0.154^{e}	5
4B	−1.59	2.30	0.975	57.33^{f}	0.188	0.209^{g}	0.154^{e}	5
4C	−1.47	2.09	0.923	17.31^{j}	0.323	0.354^{j}	0.233^{g}	5
5B	1.11	−0.986	0.988	82.71^{i}	0.0697	0.122^{h}	0.100^{h}	4
5C	0.892	−0.709	0.983	58.82^{i}	0.0823	0.116^{h}	0.0856^{h}	4
6B	1.41	−0.962	0.963	25.78^{j}	0.159	0.277^{j}	0.228^{k}	4
6C	1.13	−0.609	0.959	22.90^{j}	0.168	0.237^{j}	0.174^{k}	4
7B	1.60	−1.35	0.996	224.0^{f}	0.0610	0.107^{g}	0.0876^{g}	4
7C	1.29	−0.951	0.994	162.8^{g}	0.0715	0.101^{g}	0.0743^{g}	4
8B	2.63	−1.43	0.977	42.58^{i}	0.231	0.404^{j}	0.332^{j}	4
8C	2.14	−0.784	0.981	51.84^{i}	0.210	0.297^{h}	0.219^{k}	4
9B	2.77	−2.05	0.988	82.57^{i}	0.175	0.305^{h}	0.251^{h}	4
9C	2.24	−1.37	0.989	88.40^{i}	0.169	0.239^{h}	0.176^{h}	4
10B	0.129	−0.618	0.383	0.345^{l}	0.126	0.219^{o}	0.180^{k}	4
10C	0.0971	−0.581	0.357	0.292^{l}	0.127	0.180^{o}	0.132^{j}	4

Confidence levels of F and of "Student t" test of s_{ψ} and s_{h} are indicated by superscripts. [a] Correlation coefficient. [b] F test for significance of regression. [c] Standard errors of estimate, ψ, and h. [d] Number of points in set. [e] 99.9% confidence level (CL). [f] 99.5% CL. [g] 99.0% CL. [h] 98.0% CL. [i] 97.5% CL. [j] 95.0% CL. [k] 90.0% CL. [l] <90.0% CL. [m] 80.0% CL. [n] 50.0% CL. [o] 20.0% CL. [p] <20.0% CL.

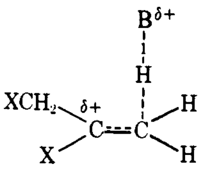
erted in the case of transition state VIII than in the case of transition state VII. In the case of set 8, transition state IX leads to *trans*-2-olefin and transition state X leads to *cis*-2-olefin. Obviously, steric effects should be greater in X than in IX, in agreement with our observations. In the case of set 9, transition state XI leads to 1-olefin and transition state X leads to *cis*-2-olefin. Comparison of these transition states indicates that steric effects should be greater in X than in XI again in agreement with our results. The failure of set 10 to give good correlation may possibly be due to a small difference in the magnitude of steric effects between transition state XI and transition state IX.



IX



X



XI

In conclusion, we find that the effect of alkyl groups on rates and orientation in E2 elimination reactions and on orientation in E1 elimination reactions can be quantitatively described by steric effects. This conclusion agrees with the discussion of Pankova and Zavada[9] for the case of the syn elimination of $RCH_2CH(NMe_3{}^{+}Cl^{-})CH_2Bu$ leading to trans $RCH_2CH{=}HCBu$.

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