

to the anisotropy of carbon-carbon and carbon-hydrogen bonds can be expressed with the following approximate expression<sup>3</sup>

$$\Delta\delta = (\Delta\chi/3R^3)(1 - 3\cos^2\theta) \quad (2)$$

where the difference in the magnetic susceptibilities parallel and perpendicular to the bond axis is given by  $\Delta\chi$ ,  $R$  is the distance to the anisotropic center, and  $\theta$  is the angle between the vector describing this distance and the bond axis. The  $1/R^3$  dependence of eq. 2 would seem to explain the leveling off of the substituent values for the larger radicals

The discontinuity between the ethyl value and those of the larger radicals possibly can be explained in terms of the hydrocarbon chain coiling back on itself. The angle  $\theta$  in eq. 2 is such that the  $\alpha,\beta$ -carbon-carbon bond makes a paramagnetic correction, while the  $\beta,\gamma$ -carbon-carbon bond gives a diamagnetic term providing the two *gauche* forms contribute to any appreciable extent. Only for substituents larger than the ethyl radical is this type of conformational coiling possible. Furthermore, for radicals larger than propyl the extension of the carbon chain is in a direction away from the substituted carbon, and a rapid leveling off in the substituent effect is expected.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF UTAH  
SALT LAKE CITY 12, UTAH

EDWARD G. PAUL  
DAVID M. GRANT

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#### ION PAIRS IN ELIMINATION<sup>1</sup>

Sir:

Before the distinction between ionization and dissociation was well recognized and the important role of ion pairs in carbonium ion reactions was clear, the proportions of substitution and elimination from unimolecular solvolysis were supposed to be independent of the nature of the leaving group, X, in the organic substrate, RX. Thus, in their classic work with *t*-Bu and *t*-Am systems in 80% aqueous ethanol as solvent, Hughes and Ingold<sup>2</sup> observed only minor variation of the proportions of elimination and substitution as X varied through the sequence: Cl, Br, I, +SMe<sub>2</sub>. Since rate of reaction was sensitive to leaving group, but product composition was not, this provided support for their SN1-EI formulation. The present communication reports the striking variation of the elimination:substitution ratio in solvolysis of *t*-Bu and *t*-Am substrates with solvent and leaving group.

Using the highly dissociating solvent, water, as a point of departure, we see in Table I that the per cent olefin from *t*-BuX is small and also equal within experimental error for all four leaving groups, Cl, Br, I and +SMe<sub>2</sub>. Further, this per cent olefin is not far from the value for the carbonium ion arising from *t*-BuO+H<sub>2</sub>, calculated from reported<sup>3a</sup> acid-catalyzed <sup>18</sup>O-exchange and dehydration rate constants of *t*-BuOH on the assumption that the carbonium ion loses the originally formed water molecule from its solvation shell. With *t*-AmX in water, the agreement between per cent olefin observed from *t*-AmCl and that calculated from *t*-AmO+H<sub>2</sub> is even better.

The change of solvent from water to less dissociating ethanol produces not only an increase in the fraction of elimination, but also considerable variation with leaving group. The fraction of elimination decreases in the order: Cl > Br > I > +SMe<sub>2</sub>. The further change to the still less dissociating and also less nucleophilic sol-

(1) Research supported by the National Science Foundation.

(2) E. D. Hughes, C. K. Ingold, *et al.*, *J. Chem. Soc.*, 1280, 1283 (1937); 2038 (1948).

(3) (a) I. Dostrovsky and F. S. Klein, *ibid.*, 791 (1955); (b) R. Boyd, R. Taft, Jr., A. Wolf and D. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).

TABLE I  
MOLE PER CENT OF OLEFIN FROM SOLVOLYSIS IN SEVERAL SOLVENTS

MOLE PER CENT OF OLEFIN FROM SOLVOLYSIS IN SEVERAL SOLVENTS	X	H <sub>2</sub> O <sup>b</sup>	H <sub>2</sub> O <sup>b</sup>	EtOH <sup>b</sup>	AcOH <sup>c</sup>
		25.0°	75.0°	75.0°	75.0°
<i>t</i> -BuX <sup>a</sup>	Cl	5.0 ± 1.0	7.6 ± 1.0	44.2 ± 1.0	73 ± 2 <sup>d</sup>
	Br	5.0 ± 1.0	6.6 ± 1.0	36.0 ± 1.0	69.5 <sup>d</sup>
	I	4.0 ± 1.0	6.0 ± 1.0	32.3 ± 1.0	...
	+SMe <sub>2</sub> ClO <sub>4</sub> <sup>-</sup>	...	6.5 ± 1.0	17.8 ± 1.4	11.7 ± 1.0
	+OH <sub>2</sub>	3	4.7	...	...
<i>t</i> -AmX <sup>a</sup>	Cl	8.9 ± 0.4			85 <sup>e</sup>
	+OH <sub>2</sub>	8.8			

<sup>a</sup> Ca. 0.04 M. <sup>b</sup> 0.07–0.14 M 2,6-lutidine. <sup>c</sup> 0.025–0.103 M NaOAc. <sup>d</sup> These figures reflect a small correction for addition of acetic acid to olefin subsequent to its formation. <sup>e</sup> Ca. 0.1 M *t*-AmCl, 0.25 M NaOAc [see J. Takahashi, Thesis, U.C.L.A., 1960, and S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958)].

vent, acetic acid, produces a larger dependence of fraction elimination on leaving group. In this solvent, per cent olefin at 75° varies greatly, ranging from 12% with *t*-Bu+SMe<sub>2</sub> ClO<sub>4</sub><sup>-</sup> to ca. 70% with *t*-BuBr and *t*-BuCl. Obviously, the composition of the solvolysis product from the *t*-Bu system depends markedly on the nature of the leaving group as well as the solvent.

Since there are strong arguments in favor of R-X ionization preceding both substitution and elimination in the solvents being considered, the contrast between elimination proportions from *t*-BuS+Me<sub>2</sub> and the *t*-butyl halides must be ascribed to the proximity of the counter halide ion. How much of the observed elimination involves the counter ion may be gaged roughly by using the results with *t*-BuS+Me<sub>2</sub> ClO<sub>4</sub><sup>-</sup> as a guide to the behavior of the dissociated *t*-butyl cation.<sup>4</sup> On this basis, at least 73% of the elimination from *t*-BuCl in ethanol involves the counter chloride ion, and this figure is at least 95% in acetic acid solvent.

Thus, most, or even all, of the elimination occurring in acetolysis of *t*-BuCl takes place from trimethylcarbonium chloride ion pairs. Further, it is clear that a negligible fraction of these ion pairs can become dissociated and then re-formed.<sup>5</sup> This is shown<sup>6</sup> by the virtual absence of radiochlorine exchange during acetolysis of 0.06 M *t*-BuCl at 50° in the presence of 0.07 M 2,6-lutidine and 0.002 M radio-labeled *n*-Bu<sub>4</sub>NCl. Under these conditions the first-order exchange rate constant,  $k_e$ , is  $3 \times 10^{-8}$  sec.<sup>-1</sup>, smaller than the titrimetric solvolysis rate constant,<sup>8</sup>  $k_t$ , by a factor greater than 10<sup>2</sup>.

The structure of the carbonium chloride ion pair giving elimination is not known in detail, so it is difficult to specify whether the proton is removed by a solvent molecule influenced by the counter chloride ion or whether it is removed by the chloride ion itself. The latter represents the simpler interpretation. However, both descriptions are consistent with the observed order of efficiency of the halide ions in this solvolytic elimination, namely: Cl > Br > I.

It would appear that elimination is another general reaction which may proceed in solvolytic and other

(4) This measure of the behavior of the dissociated carbonium ion is not ideal, since it neglects the possible effect of the departing dimethyl sulfide. Also, the sulfonium perchlorate salt very probably begins to react at least partially as associated ion pairs in the less dissociating solvents. [See, *e.g.*, J. B. Hyne and J. W. Abrell, *Can. J. Chem.*, **39**, 1657 (1961).] Therefore, some effect of the perchlorate counter ion may be present.

(5) (a) S. Winstein, *et al.*, *Chem. Ind.* (London), 664 (1954); (b) *J. Am. Chem. Soc.*, **78**, 328 (1956).

(6) This argument presupposes that ion pair return<sup>5</sup> re-forms covalent *t*-BuCl. That this does occur is indicated, *e.g.*, by the fact that kinetic control of products from the second-order reaction of isobutene with hydrogen chloride in acetic acid solvent leads to extensive formation of *t*-BuCl as well as *t*-BuOAc.<sup>7</sup>

(7) Y. Pocker and Y. V. S. Devi, private communication.

(8) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957).

media, e.g., acetone,<sup>9</sup> by way of undissociated ion pairs,<sup>10</sup> just as do many racemizations, exchanges and a great variety of rearrangements.

By microscopic reversibility, the present type of elimination is related to the reverse reaction of addition of hydrogen halide to certain olefins, carbonium chloride ion pairs being common intermediates. Pertinent cases in acetic acid solvent would appear to be the addition of hydrogen chloride to isobutylene<sup>7</sup> and the mainly *cis* addition of hydrogen chloride and hydrogen bromide to acenaphthylene.<sup>11</sup>

(9) It seems likely that the essentially quantitative first-order elimination which *t*-BuBr undergoes in solvent acetone is of this same type. [See S. Winstein, S. Smith and D. Darwish, *Tetrahedron Letters*, No. 16, 24 (1959).]

(10) See, also, S. Winstein, E. Vogelfanger, K. C. Pande and H. F. Ebel, *J. Am. Chem. Soc.*, **84**, 4993 (1962), for elimination from norbornyl ion pairs.

(11) M. J. S. Dewar and R. C. Fahey, Abstracts, American Chemical Society National Meeting, Los Angeles, California, April 1-5, 1963, p. 51M.

(12) National Science Foundation Predoctoral Fellow, 1959-1963.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CALIFORNIA  
LOS ANGELES 24, CALIFORNIA

M. COCIVERA<sup>12</sup>  
S. WINSTEIN

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### SUBSTITUENT EFFECTS ON *anti*-7-BENZONORBORNENYL BROSYLATE SOLVOLYSES

Sir:

Interest in substituent effects on a reaction site not in the same plane as the benzene ring led us to study the acetylation of substituted *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonates. We wish to report promptly the strikingly large substituent effect observed on a carbonium ion reaction in this rigid homobenzylic<sup>1</sup> system.

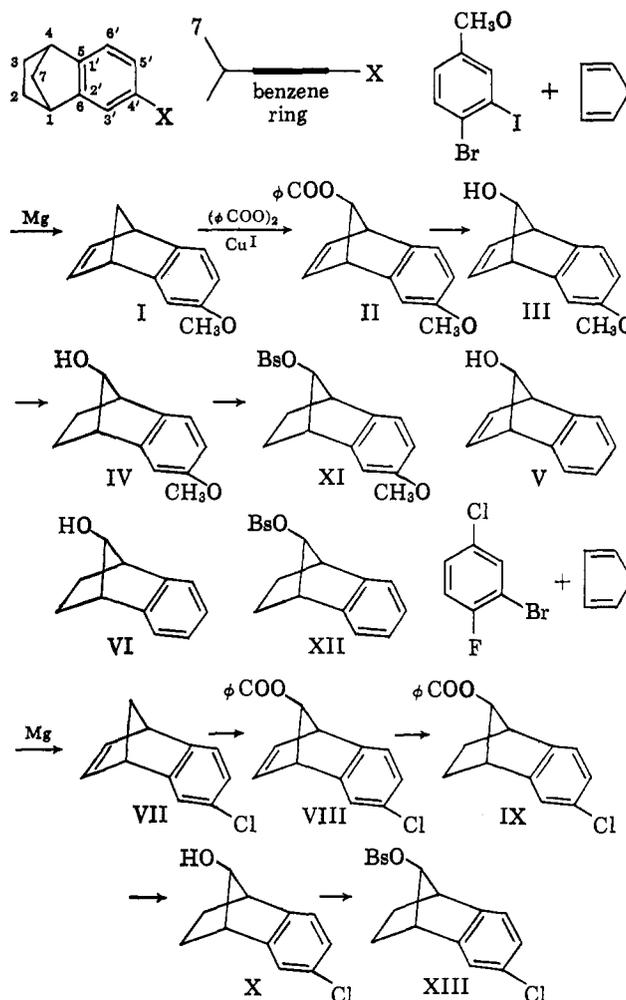
Wittig's procedure<sup>2</sup> for the addition of benzyne to cyclopentadiene and our stereospecific benzyloxylation<sup>3</sup> of the 7-position of benzenorbornadienes were used to synthesize the desired compounds. The cycloaddition was successfully carried out with cyclopentadiene, magnesium and 4-bromo-3-iodoanisole,<sup>4</sup> b.p. 124-126° (2 mm.),  $n_D^{26}$  1.6493, (prepared from 6-bromo-*m*-anisidine by the Sandmeyer reaction) yielding racemic 4'-methoxybenzenorbornadiene (I) in 40% yield, b.p. 99-100° (4 mm.),  $n_D^{23}$  1.5642,  $\lambda_{max}^{cyclohexane}$  249 m $\mu$  (log  $\epsilon$  3.35), 284 m $\mu$  (log  $\epsilon$  3.26), 290 m $\mu$  (log  $\epsilon$  3.23). Copper salt-catalyzed reaction of I with benzoyl peroxide yielded *anti*-7-benzoyloxy-4'-methoxybenzenorbornadiene (II), m.p. 90.5-91°. Reaction of II with methylmagnesium iodide gave *anti*-4'-methoxybenzenorbornadien-7-ol (III), m.p. 68.5-70°, which on catalytic reduction over palladium-charcoal afforded quantitatively *anti*-4'-methoxybenzenorbornen-7-ol (IV), m.p. 78-78.5°. *anti*-7-Benzenorbornadienol (V) and *anti*-7-benzenorbornenol (VI) were prepared by a similar sequence, and their structures were confirmed by independent syntheses.<sup>1</sup> Benzyne reaction of 2-bromo-4-chlorofluorobenzene, b.p. 90° (30 mm.),  $n_D^{19}$  1.5549 (obtained by the Schiemann reaction on 2-bromo-4-chloroaniline) with cyclopentadiene gave 4'-chlorobenzonorbornadiene (VII), b.p. 112-112.5° (10 mm.),  $n_D^{21}$  1.5763,  $\lambda_{max}^{cyclohexane}$  241 m $\mu$  (log  $\epsilon$  3.28), 269 m $\mu$  (log  $\epsilon$  2.83), 276 m $\mu$  (log  $\epsilon$  2.92), 284 m $\mu$  (log  $\epsilon$  2.89), in 55.6% yield. Benzyloxylation afforded *anti*-7-benzoyloxy-4'-chlorobenzonorbornadiene (VIII), m.p. 124-124.5°. Catalytic reduction of VIII gave *anti*-7-benzoyloxy-4'-chlorobenzonorbornene (IX), m.p. 124.5-125°, which was transformed by lithium aluminum hydride into *anti*-4'-chlorobenzonorbornen-7-ol (X), m.p. 114°, in good yield.

(1) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

(2) G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

(3) H. Tanida and T. Tsuji, *Chem. Ind. (London)*, 211 (1963).

(4) Satisfactory analyses were obtained for all compounds described.



The benzyloxylation reaction gave only *anti*-products, with no evidence of the epimers. Their orientations were established by comparison of the infrared spectra of IV, VI and X with III and V; the latter showed clearly an internal interaction between the hydroxyl group and the  $\pi$ -electrons of the double bond,<sup>5</sup> the  $\nu_{OH}$  absorptions of IV, VI and X appearing at 2.75  $\mu$ ,<sup>6</sup> whereas those of III and V were at 2.81  $\mu$ .<sup>7</sup> The formation of 2-methoxynaphthalene in high yield by the Oppenauer oxidation of III established unequivocally that the position of the methoxy group was originally 4'. Brosylates of the *anti*-alcohols were prepared in a standard method, *anti*-4'-methoxybenzenorbornen-7-ol *p*-bromobenzenesulfonate (XI), m.p. 94-95°, *anti*-benzenorbornen-7-ol *p*-bromobenzenesulfonate (XII), m.p. 132.5-133.5°, *anti*-4'-chlorobenzonorbornen-7-ol *p*-bromobenzenesulfonate (XIII), m.p. 91-92°.

Solvolysis of the three brosylates in glacial acetic acid containing equivalent sodium acetate<sup>8</sup> yielded the *anti*-7-acetates in quantitative yield. There was no

(5) Cf. P. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958); M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 306 (1959).

(6) The measurements were carried out using Perkin-Elmer Model 12c, LiF prism, 20-mm. cell in carbon tetrachloride solution.

(7) Further support was obtained by behavior of the hydrogen at the 7-position in the n.m.r. spectra, due to diamagnetic anisotropy effects of the double bond: K. Tori, R. Muneyuki, T. Tsuji, Y. Hata and H. Tanida, to be published (presented at the 16th Annual Meeting of the Chemical Society of Japan in Tokyo, April, 1963). Hydrogenation of the double bond causes an upfield shift of the *anti*-7-hydrogen of about 0.15-0.25 p.p.m. Also, cf. R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(8) E.g., S. Winstein, C. Hanson and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).