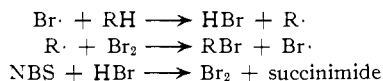


nearly total racemization in refluxing  $\text{CCl}_4\text{-NBS}$  to the effect of temperature observed in reactions of (+)-1-bromo-2-methylbutane with molecular bromine.<sup>7</sup>

Earlier work<sup>1-6</sup> implied that  $\text{Br}\cdot$  rather than succinimidyl radical abstracted a hydrogen atom from the substrate. The present study indicates that the alkyl radical intermediate is not brominated by NBS, but presumably by molecular  $\text{Br}_2$  present in steady low concentration.



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(8) Ethyl Corporation Fellow, 1962-1963.

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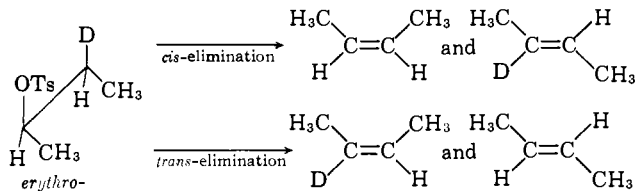
RECEIVED JUNE 24, 1963

### Importance of "Gegenion" in Electrophilic Processes. *cis* and *trans* E1 Reaction Conditions

Sir:

Studies of the solvolyses of alkyl halides, tosylates, and sulfonium ion salts in aqueous ethanol led to the concept of electrophilic processes in which solvent-aided ionizations yield carbonium ions which are partitioned among the available reaction routes, such as ejection of a proton to produce olefin (E1), or addition of a nucleophile ( $\text{S}_{\text{N}}1$ ). The choice between these paths was considered to be independent of the method of generating the carbonium ion. Re-examination of the data employed to support this position shows deviations from this generalization.<sup>1</sup> Again and again instances have been reported which indicate that the composition of the products in these processes are strongly dependent upon the nature of the leaving group and solvent.<sup>2,3</sup> Recently, attention has been sharply focused on this subject by Cram and Sahyun,<sup>4</sup> and Winstein and Cocivera.<sup>5</sup> Both groups suggest that the "gegenions" play an important role in determining the products from these processes.

A study of solvolytic elimination reactions in the 3-deuterio-2-butyl tosylate system has helped to elucidate the role of both solvent and "gegenion." This system is convenient for studying the stereochemistry, since *trans*-elimination yields, in the case of *erythro*-3-deuterio-2-butyl tosylate, deuterated *cis*-2-butene and undeuterated *trans*-2-butene. The stereochemical purity of the tosylates was demonstrated to be better than 95% by examination of the butenes obtained by reaction with potassium ethoxide in ethanol. The extent of *cis*- or *trans*-elimination is



known by separating the butene product mixture into its components and assaying their deuterium content by mass spectrometry, correcting for the small amounts of

(1) K. A. Cooper, E. D. Hughes, C. K. Ingold, and B. J. MacNulty, *J. Chem. Soc.*, 2038 (1948).

(2) M. S. Silver, *J. Am. Chem. Soc.*, **83**, 3482 (1961).

(3) W. B. Smith and W. H. Watson, Jr., *ibid.*, **84**, 3174 (1962).

(4) D. J. Cram and M. R. V. Sahyun, *ibid.*, **85**, 1257 (1963).

(5) S. Winstein and M. Cocivera, *ibid.*, **85**, 1702 (1963).

TABLE I  
PERCENT OLEFIN FORMED BY *cis*-ELIMINATION (MECHANISM A)

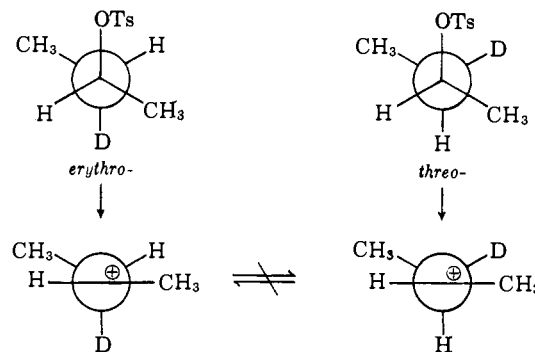
Solvent	Solvent $\text{p}K_{\text{a}}$	Tosylate isomer	<i>trans</i> -2-Butene, %	<i>cis</i> -2-Butene, %
Nitrobenzene	-11.3	<i>erythro</i> -	98 $\pm$ 2	95 $\pm$ 2
Nitrobenzene	-11.3	<i>threo</i> -	89 $\pm$ 2	99 $\pm$ 2
Glacial acetic acid	-6.1	<i>erythro</i> -	82 $\pm$ 2	65 $\pm$ 2

TABLE II  
PER CENT OLEFIN FORMED BY *trans*-ELIMINATION (MECHANISM B)

Solvent	Solvent $\text{p}K_{\text{a}}$	Tosylate isomer	<i>trans</i> -2-Butene, %	<i>cis</i> -2-Butene, %
$\text{-OEt}$ in ethanol	...	<i>erythro</i> -	100	100
Acetamide	0.0	<i>threo</i> -	92 $\pm$ 2	69 $\pm$ 2
Acetamide	0.0	<i>erythro</i> -	81 $\pm$ 2	91 $\pm$ 2
80% aqueous ethanol	$\sim$ -2	<i>erythro</i> -	66 $\pm$ 2	84 $\pm$ 2

intercontamination. The results of these experiments are summarized in Tables I and II.

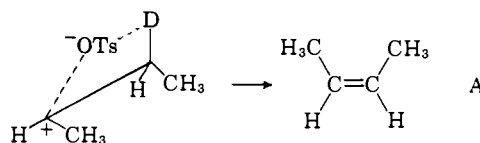
Ionization of the tosylate group and movement of a hydrogen atom through a 60° clockwise arc would produce the same carbonium ion from both *threo*- and *erythro*-tosylates. However, in solvolytic eliminations



(80% aqueous ethanol, anhydrous acetamide, glacial acetic acid, 90% formic acid, and nitrobenzene) these isomeric tosylates yield olefins with widely differing extents of deuteration. These large differences suggest that these tosylates *do not react through a common intermediate*. This leaves as the only alternative the conclusion that the product precursor has the tosylate group intimately associated with the same face of the  $\alpha$ -carbon atom to which it was attached in the starting ester.

In nitrobenzene olefin is produced by a nearly stereospecific *cis*-elimination, whereas in acetamide or aqueous ethanol the reaction follows a predominantly *trans* path. This alteration of mechanism from one extreme to another can be correlated with the basicities of the solvents,<sup>6</sup> the less basic solvents favoring *cis*- and the more basic solvents *trans*-eliminations.

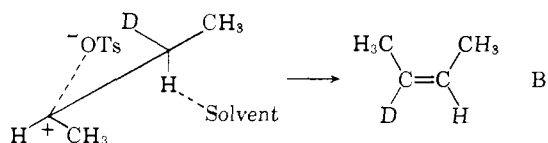
The *cis*-elimination is rationalized by removal of the  $\beta$ -proton by the parting tosylate group which must remain on the same face of the carbonium ion until it has removed a proton from an adjacent carbon atom.



By contrast, *trans*-eliminations, which occur in the more basic solvents, require attack by the solvent from

(6) E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. 1, S. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, New York, N. Y., in press.

the antiperiplanar position, essentially as in the concerted E2 elimination. Thus, the difference between E2 and E1 in basic solvents may only be a matter of degree



of polarization of the bond between the leaving group and the  $\alpha$ -carbon.

Although it is not possible completely to rule out gegenion free carbonium ions in each of the solvents, it is clear that they do not play a major role in these solvolytic eliminations. Streitwieser and Walsh<sup>7</sup> have demonstrated that the solvolytic displacement of tosylate by acetate group in the 2-octyl system occurs with 100% inversion in glacial acetic acid. *All of these results are best accommodated by rejection of the idea that in these solvolytic processes the fate of the carbonium ion is independent of its origin.*

**Acknowledgment.**—This work was supported by the U. S. Army Research Office (Durham).

(7) A. Streitwieser, Jr., and T. D. Walsh, *Tetrahedron Letters*, 27 (1963).

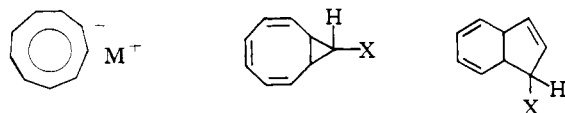
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RECEIVED JULY 3, 1963

### The Cyclononatetraenyl Anion

Sir:

The cyclononatetraenyl anion I should have a closed shell configuration of 10  $\pi$  electrons and should be highly resonance stabilized.<sup>1</sup> That it should be aromatic is, however, questionable for two reasons: (1) The energy required to distort the angles of its bonds might be excessively large<sup>2</sup> and (2) the nine-membered ring might valence tautomerize<sup>3</sup> spontaneously to form a single bond at the expense of a double. Nevertheless, the cyclononatetraenyl anion does appear to be aromatic. Its synthesis is the subject of this report.



Ia,  $M^+ = Li^+$   
b,  $M^+ = K^+$

IIa, X = Cl  
b, X = OCH<sub>3</sub>  
c, X = H

IIIa, X = Cl  
b, X = OCH<sub>3</sub>  
c, X = H

Cold chloroform reacts with dipotassium cyclononatetraenide<sup>4</sup> in tetrahydrofuran (THF) to yield, after aqueous work-up, 9-chlorobicyclo[6.1.0]nonatriene (IIa), b.p. 28–32° (0.2 mm.), in 52% yield;  $\lambda_{max}^{EtOH}$  248  $\mu$  ( $\log \epsilon$  3.57). *Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>Cl: C, 70.82; H, 5.94; Cl, 23.23. Found: C, 71.06; H, 6.06; Cl, 23.42. Similarly, dichloromethyl methyl ether reacts to yield 9-methoxybicyclo[6.1.0]nonatriene (IIb) in 26% yield; b.p. 54–56° (1.1 mm.);  $\lambda_{max}^{EtOH}$  255  $\mu$  ( $\log \epsilon$  3.69). *Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>O: C, 81.09; H, 8.11. Found: C, 80.89; H, 8.18. Methylene chloride yields bicyclo[6.1.0]nonatriene<sup>5</sup> (IIc) in 45% yield.

IIa was identified by its ultraviolet spectrum and by its n.m.r. spectrum. The latter exhibited a multiplet

(1) Its Hückel molecular orbital delocalization energy is 3.5  $\beta$ .

(2) The compressional barrier is, however, overcome by its next lower homolog, the cyclooctatetraenyl dianion [T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962), and references therein].

(3) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

(4) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).

(5) E. Vogel, *Angew. Chem.*, **73**, 548 (1961), and private communication.

at 4.1 (rel. int. 6) and a coupled ( $J = 4$  c.p.s.) triplet at 7.54 (rel. int. 1) and doublet at 8.14  $\tau$  (rel. int. 2). IIb exhibited a similar n.m.r. spectrum: a multiplet at 4.2 (rel. int. 6), a singlet at 6.70 (rel. int. 3), and a coupled ( $J = 4$  c.p.s.) triplet at 7.40 (rel. int. 1) and doublet at 8.40  $\tau$  (rel. int. 2). Only the *anti* isomers appear to be found, in striking contrast to the formation of mixtures of comparable amounts of *syn* and *anti* isomers, the former predominating, when chloro-<sup>6</sup> and methoxycarbene<sup>7</sup> are added to other olefins.<sup>8</sup>

Heating IIa to 70° yields 1-chloro-8,9-dihydroindene (IIIa; *Anal.* Found: C, 71.03; H, 6.01; Cl, 23.24), identified by its ultraviolet spectrum [ $\lambda_{max}^{EtOH}$  262 (3.52), 270  $\mu$  ( $\log \epsilon$  3.44)] and its n.m.r. spectrum (4.2, 5.27, 6.6  $\tau$ , rel. int. 6:1:2, all multiplets). Lithium aluminum hydride reduces IIIa to 8,9-dihydroindene<sup>9</sup> (IIIc) [ $\lambda_{max}^{EtOH}$  262 (3.57), 271  $\mu$  ( $\log \epsilon$  3.51), maleic anhydride adduct, m.p. 141.5°], which was identical with that obtained by heating IIIc.<sup>5</sup>

IIa reacts with lithium in THF to give lithium cyclononatetraenide (Ia). On quenching with H<sub>2</sub>O, IIIc is formed, and on quenching with D<sub>2</sub>O, it is formed (24% yield) with the incorporation of 1 atom of deuterium.<sup>10</sup> Similarly, IIb reacts with potassium to give potassium cyclononatetraenide (IIb), which, on quenching with D<sub>2</sub>O, yields monodeuterated IIIc.<sup>11</sup>

The n.m.r. spectra of potassium and of lithium cyclononatetraenide in completely deuterated THF consist of only one single very sharp peak at 2.96 and 3.15  $\tau$ , respectively.<sup>12</sup> These spectra show that the cyclononatetraenyl anion is aromatic.<sup>13</sup> If the cyclononatetraenyl anion and the cyclooctatetraenyl dianion are compared, their ring currents<sup>14</sup> should be similar,<sup>15</sup> but the protons in the former should be less shielded than in the latter because the negative charge density associated with each carbon atom is  $1/9$  rather than  $2/8$ . That is, the cyclononatetraenyl anion's proton n.m.r. should<sup>16,17</sup> appear  $(1/4 - 1/9) \times 10 = 1.4$  p.p.m. to lower fields than the resonance (4.3  $\tau$ ) of the cyclooctatetraenyl dianion.<sup>4</sup> The agreement with the observed chemical shift is excellent.

The ultraviolet spectra of Ia [ $\lambda_{max}^{THF}$  252  $\mu$  (5.0), 318  $\mu$  (3.9), 325  $\mu$  ( $\log \epsilon$  3.9)] and Ib are similar.<sup>18</sup>

It is remarkable that the cyclononatetraenyl anion has the all-*cis* stereochemistry.

(6) (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960); (b) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962).

(7) V. Schöllkopf, A. Lerch, and W. Pitteroff, *Tetrahedron Letters*, 241 (1962); cf. V. Schöllkopf and G. J. Lehman, *ibid.*, 165 (1962); V. Schöllkopf and H. Kuppers, *ibid.*, 105 (1963).

(8) The stereochemical assignment is based on the assumption that the small size of the spin-spin coupling constant implies the *anti* stereochemistry (after Closs, ref. 6b). The presence of a trace of the other isomer in samples of IIb is indicated by a small second methoxyl peak 0.05 p.p.m. above the main peak.

(9) K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

(10) Found: 9.40; 9.60; 9.38; atom % excess D. (Falling drop analyses by Josef Nemeth, Urbana, Ill.)

(11) 9.46 atom % excess D.

(12) Measured using the trace protonated solvent peaks as internal standards.

(13) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 180 ff.

(15) The point dipole approximation of Pople<sup>14</sup> leads to the prediction that the protons in cyclononatetraenide should be more shielded than those in cyclooctatetraenide by 0.02 p.p.m.

(16) (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (b) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(17) If the proportionality constant is 10.7<sup>15b</sup> the shift should be 1.5 p.p.m.

(18) The spectra are in agreement with that reported for tetraethylammonium cyclononatetraenide, synthesized independently by E. A. Lalancette and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2853 (1963). We thank these authors for communicating this result to us prior to publication.