Further applications of radical bridging to the control of the stereochemistry of substitution reactions are under active investigation. For example, *cis*-4-*t*-butyl cyclohexyl bromide (axial bromine) is considerably more reactive than is *trans*-4-*t*-butyl cyclohexyl bromide (equatorial bromine).

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(8) Ethyl Corporation Fellow, 1962–1963.

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The Mechanism of Aliphatic Bromination by N-Bromosuccinimide

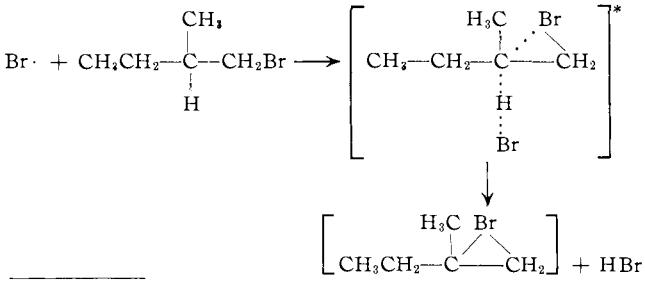
Sir:

The following results demonstrate that in radical-chain bromination with N-bromosuccinimide (NBS), the intermediate alkyl radical does not react with NBS to complete the bromination.

Recent investigations of the H abstraction step of radical-chain benzylic bromination by NBS raised serious doubt about the validity of the previously accepted[1] mechanism, which assumed hydrogen abstraction by the N-succinimidyl radical. The $\sigma^+\rho$ correlation for the reaction of substituted toluenes with bromine, NBS, N-bromotetrafluorosuccinimide, and N-bromotetramethylsuccinimide exhibit identical values of ρ.[2] Hydrocarbons exhibit the same relative reactivities toward benzylic substitution by molecular bromine or NBS.[3] Primary deuterium isotope effects in photobromination and bromination with NBS are nearly identical.[4] These data suggest that the abstracting specie in benzylic bromination by NBS is the bromine atom. NBS merely furnishes a low concentration of molecular bromine, presumably *via* its rapid ionic reaction with HBr.

This mechanism, originally suggested by Goldfinger[5] in connection with studies of the analogous chlorination with N-chlorosuccinimide, is supported by the observation of McGrath and Tedder[6] that at low molecular bromine concentration, allylic substitution predominates over addition to a double bond.

Radical chain bromination of (+)-1-bromo-2-methylbutane, α^{27}_{obsd} +4.89°, with molecular bromine is a highly selective reaction leading to (−)-1,2-dibromo-2-methylbutane, α^{27}_{obsd} −2.86°, of high optical purity.[7] The high selectivity of hydrogen abstraction by the bromine atom is attributed to bridging in the intermediate complex, leading to the formation of a bridged radical.



This behavior is contrasted by the low selectivity demonstrated in hydrogen abstraction by a chlorine atom or *t*-butoxy radical, in which bridging is relatively unimportant. The high degree of optical purity of 1,2-dibromo-2-methylbutane obtained in bromination with molecular bromine suggests that the second step in photohalogenation, the reaction of the radical with bromine, is also very rapid. Low concentration of bromine, or a less reactive halogenation agent, such as *t*-butyl hypochlorite, will not trap the bridged radical before it has undergone racemization.

These considerations suggested that it might be possible to elucidate the details of the mechanism of NBS brominative substitution of aliphatic compounds.

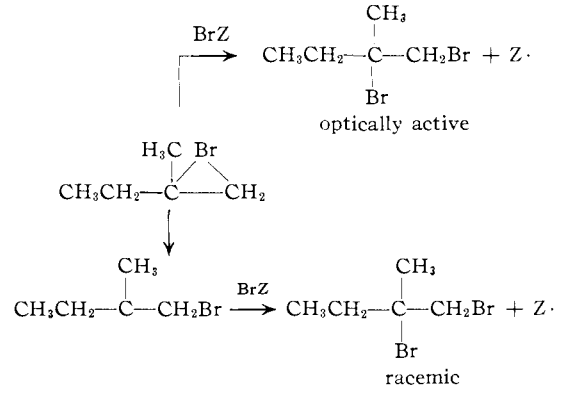
The photobromination of (+)-1-bromo-2-methylbutane (+4.89°) with NBS was studied under the conditions listed in Table I. In each case the selectivity was identical with that observed in reaction with molecular bromine; 1,2-dibromo-2-methylbutane was the only dibromide produced.

TABLE I

Solvent	Temp., °C.	Solubility of NBS (mole/l.)	α_{obsd} (temp., °C.)[a]
$CFCl_3$	25	0.0006	−0.25 (28)
CH_2Cl_2	40	0.29	−0.30 (25)
CCl_4[b]	76	0.006	−0.06 (35)

[a] Observed rotation of the 1,2-dibromo-2-methylbutane produced. [b] Photoinitiation and thermal initiation give identical results.

The preservation of optical activity in the 1,2-dibromo-2-methylbutane indicates that the reaction proceeds through a bridged radical.[7] Two major pathways are available to the bridged radical: reaction with a brominating agent, BrZ, to yield optically active dibromide; or ring opening and racemization, followed by reaction with the brominating agent.



Since a 500-fold change in the concentration of NBS produces only a small change in the rotation of the final product, *the reagent BrZ cannot be NBS.* Presumably, the radical reacts with molecular bromine at low concentration. Similar racemizations are observed when (+)-1-bromo-2-methylbutane is brominated with molecular bromine under high dilution conditions. The slow addition of bromine to an irradiated, refluxing solution of (+)-1-bromo-2-methylbutane in $CFCl_3$ produced (−)-1,2-dibromo-2-methylbutane, α^{29}_{obsd} −0.80°. The decreased concentration of bromine effectively increases the lifetime of the intermediate radical and allows partial racemization. The concentration of molecular bromine in the reaction of the active monobromide with NBS is less than that which may be mechanically maintained, and the observed rotation of the 1,2-dibromo-2-methylbutane produced is therefore quite small. We attribute the

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nearly total racemization in refluxing CCl_4–NBS to the effect of temperature observed in reactions of (+)-1-bromo-2-methylbutane with molecular bromine.[7]

Earlier work[1-6] implied that Br· 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 Br_2 present in steady low concentration.

$$Br\cdot + RH \longrightarrow HBr + R\cdot$$
$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot$$
$$NBS + HBr \longrightarrow Br_2 + \text{succinimide}$$

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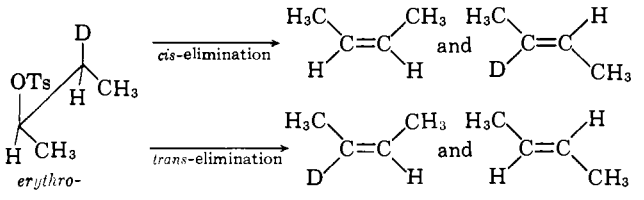
Importance of "Gegenion" in Electrophilic Processes. *cis* and *trans* E1 Reaction Conditions

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 (SN1). 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.[1] 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.[2,3] Recently, attention has been sharply focused on this subject by Cram and Sahyun,[4] and Winstein and Cocivera.[5] 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 intercontamination. The results of these experiments are summarized in Tables I and II.

TABLE I

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

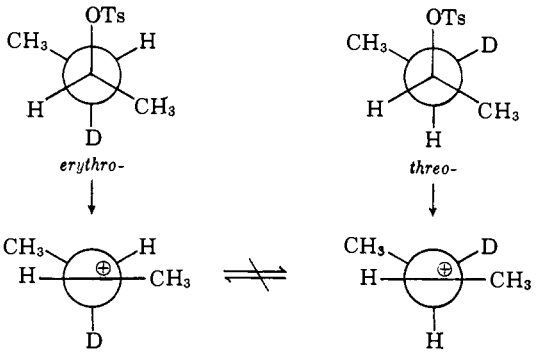
Solvent	Solvent pK_a	Tosylate isomer	*trans*-2-Butene, %	*cis*-2-Butene, %
Nitrobenzene	−11.3	*erythro*-	98 ± 2	95 ± 2
Nitrobenzene	−11.3	*threo*-	89 ± 2	99 ± 2
Glacial acetic acid	−6.1	*erythro*-	82 ± 2	65 ± 2

TABLE II

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

Solvent	Solvent pK_a	Tosylate isomer	*trans*-2-Butene, %	*cis*-2-Butene, %
$^-$OEt in ethanol	...	*erythro*-	100	100
Acetamide	0.0	*threo*-	92 ± 2	69 ± 2
Acetamide	0.0	*erythro*-	81 ± 2	91 ± 2
80% aqueous ethanol	~−2	*erythro*-	66 ± 2	84 ± 2

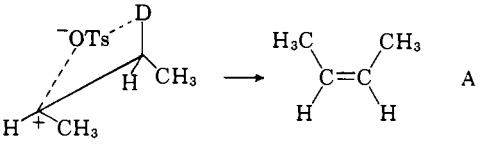
Ionization of the tosylate group and movement of a hydrogen atom through a 60° clockwise arc would produce the same carbonium ion from both *threo*- and *erythro*-tosylates. However, in solvolytic eliminations



(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 α-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,[6] the less basic solvents favoring *cis*- and the more basic solvents *trans*-eliminations.

The *cis*-elimination is rationalized by removal of the β-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

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