(k_{eq} + k_t) value in the absence of salt or the (k_{eq} + k_{N_3}) value in the presence of 0.01 M Bu_4NN_3. Whereas with 0.01 M Bu_4NN_3 the rate of chemical capture (k_{N_3}) is only *ca.* 30% of the ionization rate, the corresponding figure with 0.01 M LiN_3 is over 65%. The large accelerating effect of lithium salts on ionization rate is illustrated by the effect of 0.01 M $LiClO_4$ which increases (k_{eq} + k_t) by a factor of 15. In 99.2% acetone, as in the anhydrous solvent,[4] lithium salts tend to introduce specific salt-promoted ionization.[7] The latter tends to give larger fractions of chemical capture than the ordinary salt-unassisted ionization.

(7) (a) S. Winstein, S. Smith, and D. Darwish, *J. Am. Chem. Soc.*, **81**, 5511 (1959); (b) S. Winstein, E. Friedrich, and S. Smith, *ibid.*, **86**, 305 (1964).

(8) U. S. Rubber Company Foundation Postgraduate Fellow in Physical and Engineering Science for 1962–1963.

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Carbonium Ion Behavior of Nopinyl Derivatives[1]

Sir:

Schleyer[2] has informed us that the supposed α- and β-nopinyl *p*-bromobenzenesulfonates (I-OBs and II-OBs) reported by Winstein and Holness[3] some years ago were actually the corresponding rearranged *endo*-camphenilyl and apobornyl esters III-OBs and IV-OBs. We have confirmed this by examination of samples of the esters still available from the former investigation. The nopinyl derivatives prove to be extremely reactive in ionization reactions and the formerly isolated bromobenzenesulfonates were the products of ionization and "internal return" to rearranged derivatives, a phenomenon discovered in these laboratories and illustrated with a number of examples.

In spite of its enormous reactivity we have been able to prepare and isolate β-nopinyl bromobenzenesulfonate (II-OBs), m.p. 46° dec., by a low temperature technique developed for very reactive esters by Carter in these laboratories. This material shows a correct C and H analysis and appropriate infrared and n.m.r. spectra distinctly different from those of the isomeric IV-OBs.

A solution of II-OBs (*ca.* 0.01 M) in acetic acid, 0.02 M in sodium acetate, proceeds to a fast infinity titer of 32% solvolysis with a first-order rate constant of 2.6 ± 0.1 × 10^{-2} sec.$^{-1}$ at 23.5°. Then solvolysis proceeds to *ca.* 57% at a rate level corresponding to the apoisobornyl (VI), *exo*-camphenilyl (VII), and β-fenchoisocamphoryl (V) esters. The kinetic behavior[3,4] indicates a substantial proportion of the more reactive apoisobornyl ester in the mixed esters solvolyzing in this stage of the acetolysis. The residual ester (43%) proved to be the apobornyl derivative IV-OBs by m.p. and infrared and n.m.r. spectra. In 70% aqueous acetone, 33% of the apobornyl ester is formed.

(1) Research sponsored by the U. S. Army Research Office (Durham).

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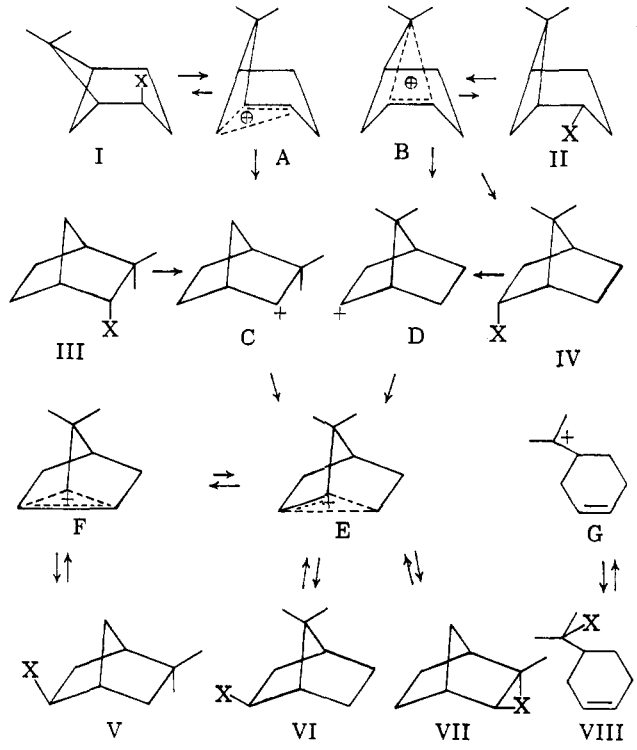
(3) S. Winstein and N. J. Holness, *ibid.*, **77**, 3054 (1955).

(4) (a) S. Winstein, *Experientia Suppl. II*, 137 (1955); (b) A. Colter, Ph.D. Thesis, U.C.L.A., 1956; (c) S. Winstein, Abstracts of 15th National Organic Chemistry Symposium of the American Chemical Society, Rochester, N. Y., June 17–20, 1957, p. 29.



The products of the very fast stage of the acetolysis after lithium aluminum hydride reduction contained norterpineol (VIII-OH), β-nopinol (II-OH), apoborneol (IV-OH), apoisoborneol (VI-OH), *exo*-camphenilol (VII-OH), and β-fenchoisocamphorol (V-OH) in the proportions summarized in Table I. At 57% solvolysis the proportion of the three *exo*-alcohols had increased from 57% to 83% (Table I). In aqueous acetone the proportion of norterpineol was considerably increased and that of β-fenchoisocamphorol was substantially reduced. The various products were identified by v.p.c. retention times on two different columns and by actual isolation in the case of norterpineol.[3]

TABLE I

PERCENTAGES OF PRODUCTS OF SOLVOLYSIS FROM β-NOPINYL-OBs AT 24°

	AcOH 32% ∞	AcOH 57% ∞	70% aceton 67% ∞
Norterpineol (VIII)	15	7	37
β-Nopinol (II)	3	1.6	1
Apoborneol (IV)	25	9	10
Apoisoborneol (VI)	27	38	37
exo-Camphenilol (VII)	4	4	6
β-Fenchoisocamphorol (V)	26	41	9

Attempts to isolate the apparently more reactive α-nopinyl ester I-OBs have so far been unsuccessful. However, the α- and β-nopinols can be compared in rearrangement rates at 75° in 70% aqueous dioxane catalyzed by 0.099 M perchloric acid. Under these conditions β-nopinol and α-nopinol disappear with first-order rate constants of 1.4 ± 0.1 × 10^{-5} sec.$^{-1}$ and 1.5 ± 0.1 × 10^{-4} sec.$^{-1}$, respectively. At 74% conversion, the alcohol mixture from β-nopinol (II-OH) contained 37% norterpineol (VIII-OH), 27% apoborneol (IV-OH), 20% apoisoborneol (VI-OH), 5% *exo*-camphenilol

(VII-OH), and 11% β-fenchoisocamphorol (V-OH). At 95% conversion, the alcohol product from α-nopinol (I–OH) contained 59% *endo*-camphenilol (III-OH), 26% VI-OH, 4% VII-OH, and 11% V-OH.

In the prior work[3] it was not clear whether ionization of the nopinyl derivatives was anchimerically assisted or not and also which group (methylene or isopropylidene) migrated. The rearranged classical ions C or D were regarded as intermediates and leakage from these cations to the nonclassical ion E and thence to the β-fenchoisocamphoryl nonclassical ion F by 6 → 1 hydrogen shift was evident. The observed[3] mixture of the three *exo*-alcohols arose from these nonclassical cations. The present work shows that ionization of the nopinyl derivatives is very strongly anchimerically assisted. Thus, the β-nopinyl II-OBs acetolyzes more rapidly than its apobornyl isomer IV-OBs by a factor greater than 10^5. Apparently, α-nopinyl derivatives (I) are even more reactive, presumably predominantly because of extra steric acceleration of ionization. The present observations are best accounted for with the aid of the nonclassical bridged ions A and B from I-X and II-X, respectively, preceding the rearranged classical ions C and D. Ion A would appear to account for at least the bulk of the *endo*-camphenilol (III-OH) from I-OH, and ion B the β-nopinol (II-OH), apobornel (IV-OH), and norterpineol (VIII-OH) from β-nopinol II-OBs.[5] It seems plausible that norterpineol formation may involve prior formation of the open norterpinyl cation G, but this is not clear.

The *exo*-alcohols from the nopinyl derivatives are formed in relative proportions essentially identical with those observed in solvolysis of the apoisobornyl and *exo*-camphenilyl VI-OBs and VII-OBs esters in another study.[4] Thus, at the first infinity in acetolysis of II-OBs the VI:V:VII ratios in the product are 47:46:7 compared to 47:49:5 from earlier infrared analysis[4b] of the products of acetolysis of VI-OBs or VII-OBs. These products must arise from nonclassical ions[3,4] E and F. Leakage from E to F by 6 → 1 hydrogen shift is more important in acetic acid than in aqueous acetone or aqueous dioxane.[3,4]

It is interesting how much ion pair return to rearranged products accompanies solvolysis of β-nopinyl II-OBs. Thus, in acetolysis 43% of apobornyl IV-OBs is formed, and even after the relevant cations have attained the E or F structure, ion pair return accounts for the formation of 25% of *exo*-bromobenzenesulfonates. It is also interesting how much leakage occurs from the original bridged ions A or B to C or D and on to E. In acetolysis of β-nopinyl II-OBs, if all the apobornyl IV-OBs formation is depicted as arising from B, the amount of leakage is estimated at 45%. In aqueous acetone the corresponding figure is 35%. In acid-catalyzed rearrangement of the nopinols it is *ca.* 36–41%.

(5) The conversion of A or B to *endo* derivatives III and IV is apparently essentially irreversible, since solvolysis of III-OBs and IV-OBs gave no detectable nopinol or norterpineol product.[3,4] Such solvolysis of III-OBs and IV-OBs also gave no detectable *endo*-III-OH or IV-OH, leakage of the corresponding C or D ions to E being very efficient.

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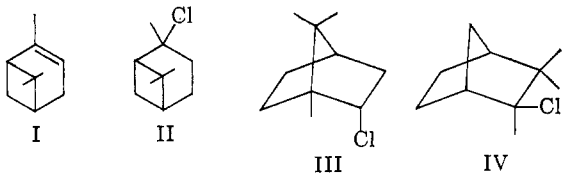
Estimation of Nonassisted Solvolysis Rates. The Structures of the "Nopinyl *p*-Bromobenzenesulfonates"

Sir:

In 1899 Wagner[1] made the then revolutionary suggestion that α-pinene (I) and its major product of reaction with HCl, bornyl chloride (III), did not possess the same carbon skeleton. The pronounced tendency of compounds of the pinane series to undergo cationic rearrangement and ring opening, which so bedeviled the early terpene chemists,[2] has provided a subject for detailed mechanistic and stereochemical studies.[3–7] Pinene hydrochloride (II), intermediate in the conversion of I into III, is even more reactive than camphene hydrochloride (IV).[3,8] The stereospecific and very



I II III IV

rapid transformation of pinane derivatives into 2-*endo*-bicyclo[2.2.1]heptane analogs, such as III, is usually interpreted in terms of nonclassical carbonium ion theory.[3] Relief of four-membered ring strain provides a considerable driving force for anchimeric assistance. The stereochemistry of the rearrangement can be accounted for in terms of a bridged intermediate or transition state (nucleophilic attack concomitant with rearrangement).[3]

Participation effects should be more pronounced in secondary than in tertiary carbonium ions, since the latter are inherently more stable and would be expected to benefit less from anchimeric assistance.[9] A test of this hypothesis—a key tenet of nonclassical carbonium theory—in the pinane series apparently has failed.[4] Conversion of the stereoisomeric secondary alcohols, α-nopinol (VI) and β-nopinol (V), to *p*-bromobenzenesulfonates by the usual method (*p*-bromobenzenesulfonyl chloride in pyridine) gave compounds whose solvolytic reactivities, comparable to cyclohexyl brosylate, showed no evidence of rate enhancement. Based on the behavior of tertiary pinyl derivatives, solvolysis rates many powers of ten in excess of the reported values might reasonably have been anticipated. Not only the reported reaction rates but also the solvolysis products were peculiar. There was no evidence of ring opening and, although conversion to the bicyclo[2.2.1]heptane ring system was complete, the products

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