(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), apoborneol (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
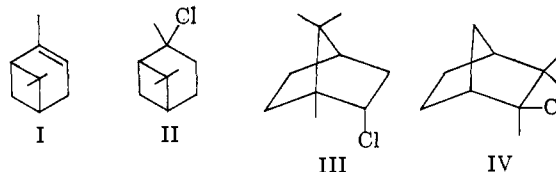
I    II    III    IV

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

(1) G. Wagner, J. Russ. Phys. Chem. Soc., 31, 680 (1899).

(2) J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. II, 2nd Ed., Cambridge University Press, Cambridge, 1949.

(3) J. A. Berson in P. de Mayo, Ed., "Molecular Rearrangements," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 183–187, and references therein cited.

(4) S. Winstein and N. J. Holness, J. Am. Chem. Soc., 77, 3054 (1955).

(5) W. D. Burrows and R. H. Eastman, ibid., 81, 245 (1959).

(6) W. Hückel and E. Gelchsheimer, Ann., 625, 12 (1959).

(7) (a) N. A. Abraham and M. Vilkas, Bull. soc. chim. France, 1450 (1960); (b) Y. Chrétien-Bessière and J.-P. Monthéard, Compt. rend., 258, 937 (1964).

(8) H. Meerwein and H. van Emster, Ber., 55, 2500 (1922); K. Meerwein and J. Vorster, J. prakt. Chem., 147, 83 (1936); E. D. Hughes, Quart. Rev. (London), 5, 245 (1951); Bull. soc. chim. France, C-39 (1951); W. A. Mosher and I. L. Gelb, Abstracts, First Delaware Valley Regional Meeting, American Chemical Society, Philadelphia, Pa., Feb., 1956, p. 57; H. C. Brown and F. J. Chloupek, J. Am. Chem. Soc., 85, 2322 (1963); P. Beltrame, C. A. Bunton, A. Dunlop, and D. Whittaker, J. Chem. Soc., 658 (1964).

(9) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., New York, N. Y., 1962; Chem. Rev., 56, 571 (1956).

(VII–IX) had the *exo* and not the expected *endo* orientation. In addition, no significant difference in product spectrum was detected between "α-" and "β-nopinyl brosylates," whereas the tertiary methylnopinols gave different bicyclic rearranged products.[5,7a]
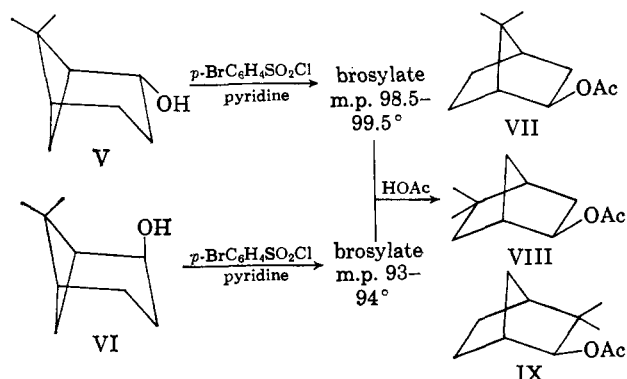


To explain these unusual results, a classical nopinyl carbonium ion was postulated *ad hoc* to be the initial solvolysis intermediate. This classical ion was pictured to rearrange to classical dimethylnorbornyl cations and thence to nonclassical species, wherefrom *exo* products VII–IX were said to form.[4] These results and their interpretation have been accepted in reviews on the subject,[3,9] but no convincing explanation for the formation of classical and not nonclassical intermediates in these solvolyses has been offered.

The reported results, which do not conform with expectations based on nonclassical carbonium ion theory, do not conform with classical carbonium ion theory either.

A scheme has been devised for estimating acetolysis rates of secondary arenesulfonate esters in cases where anchimeric assistance is absent.[10] For most compounds this scheme is quite accurate,[10] but when it is applied to the nopinyl brosylates there are major discrepancies between the calculated and the reported rates, especially for the α-isomer. Based on the observed carbonyl frequency of nopinone (1717 cm.$^{-1}$),[11] dihedral angles of 40 and 45° estimated from models, and the relief of about 0.7 kcal. of nonbonded repulsion strain on ionization of α-nopinyl brosylate, a rate of $10^{1.5}$ relative to cyclohexyl brosylate is calculated.[10] The rate of the compound reported to be "α-nopinyl brosylate" is $10^{-0.74}$.[4,11] No other compound yet investigated has proven to have a rate significantly slower than that predicted by this scheme.[10,11] Our confidence in the accuracy of this nonassisted solvolysis rate estimation method[10] has led us to reinvestigate this problem.

There is a simple explanation capable of resolving all these discrepancies, which explanation we have verified experimentally. The reaction of α-nopinol (VI) with *p*-bromobenzenesulfonyl chloride in pyridine in the cold did not give "α-nopinyl brosylate," but, by internal return even under those mild conditions, *endo*-camphenilyl brosylate (X). Likewise, brosylation of β-nopinol (V) produced apobornyl brosylate (XI). *endo*-Camphenilyl brosylate (X) is a known compound[12]

(10) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854, 1856 (1964); also see ref. 11.

(11) C. S. Foote, *ibid.*, **86**, 1853 (1964).

(12) A. Colter, Ph.D. Thesis, University of California, Los Angeles,

whose recorded properties (m.p. 94–95°, $k_1$ (HOAc, 75.45°) = 2.90 × $10^{-5}$ sec.$^{-1}$)[12] correspond closely to those reported for "α-nopinyl brosylate" (m.p. 93.5–94°, $k_1$ (HOAc, 75.00°) = 2.74 × $10^{-5}$ sec.$^{-1}$).[4] In our hands brosylates prepared from both α-nopinol (VI, m.p. 93–94°) and from *endo*-camphenilol (XII) (m.p. 93–94°) were identical (m.m.p. 93–94°, superposable infrared and n.m.r. spectra of even crude, unrecrystallized material). The n.m.r. spectrum confirmed the assigned structures. The CHOR protons in only the *endo*-camphenilyl series (X and XII) appear as the expected clean doublets, with $J \cong 5$ c.p.s.[13] Similarly, conversion of apoborneol (XIII)[14] to brosylate gave a substance identical with that prepared from β-nopinol (V). Both α-nopinol and β-nopinol can be converted to *p*-nitrobenzoate esters without rearrangement, and we plan to study the rates of solvolysis of these compounds. The amazing rearrangement propensity of these secondary nopinyl derivatives—now revealed—was further demonstrated in the following way: refluxing α-nopinol (VI) for 24 hr. with 6 N HCl caused substantial conversion to *endo*-camphenilol (XII). Under the same conditions, β-nopinol (V) gave mostly olefinic products.
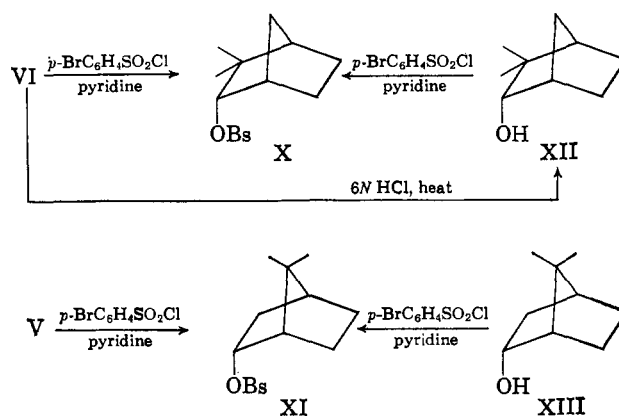


The revised structures for "α-nopinyl brosylate" (actually X) and for "β-nopinyl brosylate" (actually XI) require reinterpretation of their solvolyses. There is nothing unexpected in the behavior of these materials.[3,4,12] The very high reactivity and stereospecificity of rearrangement of authentic α- and β-nopinyl derivatives, inferred from the present findings, are consistent with participation theory. Further exemplified is the effectiveness of the method for estimating nonassisted solvolysis rates which we have proposed.[10]

1956; S. Winstein, XIVth International Congress of Pure and Applied Chemistry, Zurich, July, 1955; *Experientia Suppl. II*, 137 (1955).

(13) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964), and references therein cited.

(14) G. Komppa and S. Beckmann, *Ann.*, **522**, 137 (1936).

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