mate the free energy of ionization of the chloromethanes. It would still be necessary that a proportionality exist between the free energies of ionization of the chloromethanes in alcohols and the diarylmethanols in aqueous sulfuric acid.

Resonance Energy of Diaryl- and Triarylmethyl Cations.—Three lines of evidence give an indication that the resonance energy of diaryl- and triarylmethyl cations may be similar. First is the difference between pK_{R^+} for Ar_3C^+ and pK_{R^+} for Ar_2CH^+ where Ar represents a particular substituted phenyl ring. For a limited series it had been noticed that this difference was nearly constant independent of the substituent on the phenyl ring.[10] This series has been extended and revised using the values of pK_{R^+} based on the C_0 scale and the results are summarized in Table VI. This constant difference had been interpreted in terms of a constant difference in the energy term arising from release of steric strain on ionization for the triaryl series as compared with the diaryl series.[10] This interpretation requires that the size of groups around the central carbon be identical throughout the diaryl series and throughout the triaryl series. It thus was expected that the above correlation would not be valid for *ortho* substituents,[10] and this is demonstrated by the data on the 2-methyl derivatives. The data for the 4-dimethylamino derivatives also fail to follow the above relation.

TABLE VI

COMPARISON OF pK_{R^+} FOR Ar_3C^+ AND Ar_2CH^+ WITH IDENTICALLY SUBSTITUTED PHENYL RINGS

Substituent	pK_{R^+} Ar_3C^+	pK_{R^+} Ar_2CH^+	Difference in pK_{R^+}
4-Methoxy	+ 0.82	− 5.71	6.53
4-Methyl	− 3.56	−10.4	6.8
4-*t*-Butyl	− 6.5	−13.2	6.7
Unsubstituted	− 6.63	−13.3	6.7
4-Chloro	− 7.74	−13.96	6.22
3-Chloro	−11.03	−17.3	6.3
4-Dimethylamino	+ 9.36	+ 5.61	3.75
2-Methyl	− 3.38	−12.5	9.1

The second indication is based on a comparison of the value of ρ for the diaryl and triaryl series, −5.63 and −3.98, respectively. A substituent is thus more effective in changing pK_{R^+} in the diaryl series and interestingly, 2ρ for the diaryl series (−11.26) is nearly equal to 3ρ for the triaryl series (−11.94). Thus the total substituent effect is nearly equal in both series.

The final indication is the similarity in absorption spectra between correspondingly substituted diaryl- and triarylmethyl cations. This has been noted previously.[2]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Neighboring Carbon and Hydrogen. XVIII. Solvolysis of the Nopinyl *p*-Bromobenzenesulfonates

BY S. WINSTEIN AND N. J. HOLNESS[1]

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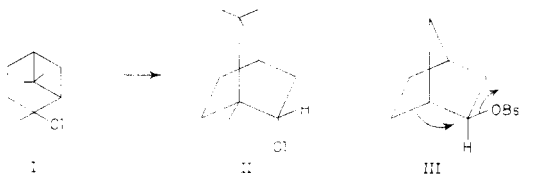
The nopinyl system, a simpler analog of that in pinene hydrochloride, is interesting in connection with carbonium ion behavior. In the present study, the diastereomeric α- and β-nopinols have been prepared and characterized, and the solvolysis of the *p*-bromobenzenesulfonates has been examined. Besides traces of apocyclene, the solvolysis product from the nopinyl *p*-bromobenzenesulfonates in aqueous acetone consisted of 72 ± 4% of highly optically active apoisoborneol, 26 ± 5% of racemic β-fenchoisocamphorol, together with several per cent. of *exo*-camphenilol. No appreciable amounts of norterpineol or *endo* bicyclic alcohols were observed. The rates and products of solvolysis suggest the following description of the solvolysis. Anchimeric acceleration of ionization is at most small. Migration of the migrating group proceeds to completion, a rearranged carbonium ion being formed. This unbridged rearranged carbonium ion immediately is converted to the more stable bridged structure. From the latter arises active apoisoborneol and *exo*-camphenilol. Hydrogen shift of the 1,3-variety (2,6-in bicyclic structures) within the bridged carbonium ion gives rise to new bridged carbonium ions. One of the latter accounts for formation of optically inactive β-fenchoisocamphorol. Another accounts for formation of some enantiomorphic apoisoborneol.

The solvolysis of the nopinyl *p*-bromobenzenesulfonates VI and VII is of some interest, especially in connection with questions regarding anchimeric[2] assistance to ionization and the nature and behavior of carbonium ion intermediates. The nopinyl system is a simpler analog of that in pinene hydrochloride I, whose rearrangement to bornyl chloride II is a classical example of the Wagner–Meerwein rearrangement,[3] and whose high reactivity in solvolysis has been reported by Hughes[4] to appear to provide an example of anchimeric acceleration. Further, the nopinyl system, with its unique geometry, provides an interesting comparison with systems containing the [2,2,1]bicycloheptyl skeleton such as *exo*-norbornyl *p*-bromobenzenesulfonate (III).[5,6] The preparation of the α- and β-nopinols



I II III

(1) Hercules Powder Co. Fellow, 1953–1954.

(2) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

(3) H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922).

(4) E. D. Hughes, *Quart. Revs.*, **5**, 245 (1951); *Bull. soc. chim.*, **18**, 39 (1951).

(5) (a) S. Winstein and D. S. Trifan, THIS JOURNAL, **71**, 2953 (1949); (b) S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952); (c) S. Winstein and D. S. Trifan, *ibid.*, **74**, 1154 (1952).

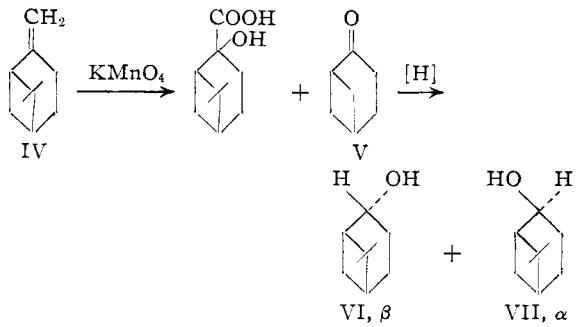
(6) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951).

and an exploratory study of the solvolysis of the corresponding *p*-bromobenzenesulfonates are reported in the present article.

Results

The starting material for the preparation of the nopinols VI and VII was optically active β-pinene (IV). Permanganate oxidation[7] of the latter material gave rise to nopinic acid and nopinone V, reduction of which gave rise to the nopinols VI and VII. According to Wallach,[7] reduction of nopinone with sodium in moist ether gives a mixture of a solid nopinol, m.p. 102°, designated α, and a liquid nopinol, m.p. 5–7°,[8] designated β.

In the present work the α-nopinol, m.p. 102°, was obtained easily by lithium aluminum hydride reduction of nopinone V. The α-isomer is quite predominant in the nopinol mixture and much of it is obtained by direct recrystallization. Further amounts of the α-isomer may be obtained as the acid phthalate.



We could not obtain the β-isomer in pure form from the mixture even as the acid phthalate. Attempted equilibration of the nopinol from lithium aluminum hydride reduction with the aid of sodium and fluorenone still did not permit isolation of pure β-nopinol.

Aluminum isopropoxide reduction of nopinone did give rise to a nopinol mixture containing considerable β-isomer. This was isolated in pure form as the acid phthalate, saponification of which yielded a solid β-nopinol, m.p. 37.0–37.5°. The physical properties of the nopinols and their derivatives are summarized in Table I.

TABLE I

PROPERTIES OF THE NOPINOLS AND DERIVATIVES

Designation	Compound	M.p., or b.p. (mm.), °C. Obsd.	Lit.	[α]D (ether) Obsd.	Lit.
α	Alcohol	101.5–102	102[7]	− 5.55	− 5.32[7]
	Acid phthalate	131–131.5		−47.5	
	p-Bromobenzenesulfonate	93–94		− 6.58	
	Acetate	107 (18)	$n^{25}D$ 1.4627		
β	Alcohol	37.0–37.5	5–7[8]	−18.87	−15.03[7]
	Acid phthalate	155.8–156.2		+ 4.42	
	p-Bromobenzenesulfonate	98.5–99.5			

For possible assistance in deciding the relative configurations of the α- and β-nopinols, they were characterized as to relative rates of oxidation with chromic acid and relative rates of saponification of the acid phthalates. The second order rate constants are summarized in Table II for the oxidation of the nopinols and in Table III for the saponification of the acid phthalates. There is a sufficient difference in rate of saponification of the acid phthalates that the good second order saponification rate constants provide another indication that the α- and β-isomers were obtained as pure diastereomers.

TABLE II

RATES OF CHROMIC ACID OXIDATION OF THE NOPINOLS IN 50% ACETIC ACID

Nopinol	Oxidation normality 10^2[ROH]	10^2[CrO_3]	Temp., °C.	10^2k_2, l. mole^{-1} sec.$^{-1}$
β-	1.152	0.949	49.90	33.8 ± 0.6
α-	1.135	.949	50.08	49.2 ± 1.5

TABLE III

RATES OF SAPONIFICATION OF α- AND β-NOPINYL ACID PHTHALATES IN WATER

Nopinyl phthalate	Temp., °C.	Acid phthalate 10^2 *M*	Excess NaOH 10^2 *M*	10^5k_2, l. mole^{-1} sec.$^{-1}$
α-	50.14	2.61	7.22	20.7 ± 0.8
	50.00[a]			20.5
	75.20	4.32	5.86	156 ± 5
	75.00[a]			153
β-	50.14	3.54	6.29	83.4 ± 1.4
	50.00[a]			82.7
	75.20	4.32	5.86	434 ± 8
	75.00[a]			426

[a] Interpolated or extrapolated from the data at the other temperatures.

Both the α- and β-nopinyl *p*-bromobenzenesulfonates displayed good first order behavior in acetolysis, the pertinent rate constants being summarized in Table IV. Again, there is a substantial difference between the two diastereomers, so that the data provide evidence of diastereomeric purity of the α- and β-materials.

TABLE IV

RATES OF ACETOLYSIS OF α- AND β-NOPINYL *p*-BROMOBENZENESULFONATES

Compound, OBs	Temp., °C.	[ROBs], 10^2 *M*	10^5 *k*, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
α-Nopinyl	25.00[a]		0.00318		
	50.00[a]		0.121		
	75.00	2.50	2.74 ± 0.01	27.2	−1.7
	75.00	2.65	2.73 ± .02		
	99.51	2.39	38.9 ± .4		
	99.51	2.46	38.5 ± .5		
	100.0[a]		40.7		
β-Nopinyl	25.00[a]		0.0188		
	50.52	2.29	.663 ± 0.005		
	50.52	2.23	.659 ± .006		
	50.00[a]		.618		
	75.00	2.24	12.35 ± .04	26.1	−1.8
	75.00	2.03	12.32 ± .04		
	100.0[a]		165		

[a] Extrapolated from data at the other temperatures.

Solvolysis of the α- and β-nopinyl *p*-bromobenzenesulfonates in refluxing 60% aqueous acetone or in aqueous dioxane gave substantially entirely rearranged products, no nopinols being detected in the product. Except for possible traces of apocy-

(7) O. Wallach, *Ann.*, **356**, 227 (1907).

(8) G. Komppa and T. Hasselstrom, *Ann. Acad. Sci. Fennicae*, **A30**, No. 14 (1929).

clene XXIV, the whole of the product was composed of alcohols which yielded acid phthalate on treatment with phthalic anhydride in pyridine. The monocyclic alcohol, norterpineol (analogous to terpineol from pinene), a specimen of which was prepared for comparison purposes, does not yield an acid phthalate under the standard conditions employed; therefore, it was not present in substantial amount in the solvolysis product.

The alcohol product contained large amounts of apoisoborneol (XXII) and β-fenchoisocamphorol (XXV), both of which could be isolated in essentially pure condition and characterized. Infrared spectral data indicated the presence of small amounts of *exo*-camphenilol (XXIII), which, however, was not isolated separately. For semi-quantitative estimation of the composition of the alcohol product mixture, a large fraction of the apoisoborneol was removed by chromatography on alumina, the apoisoborneol being eluted easily. The residual alcohol was acetylated to a liquid acetate mixture whose composition was estimated from the infrared spectrum using samples and spectra available from other work on apoisobornyl, *exo*-camphenilyl and β-fenchoisocamphoryl derivatives.[9]

The apoisoborneol (XXII) was obtained highly optically active and somewhat variable in m.p. between 131–132° and 141°, possibly due to variation in optical purity and extent of slight contamination with *exo*-camphenilol. The apoisoborneol also was obtained as the acid phthalate, m.p. 173–174°. An independent characterization of the apoisoborneol could be based on the behavior in acetolysis of its *p*-bromobenzenesulfonate. In other work[9] it has been found that the apoisobornyl, *exo*-camphenilyl and β-fenchoisocamphoryl *p*-bromobenzenesulfonates are very much more reactive than the *endo* isomers. Further, of the three reactive *exo* isomers, the apoisobornyl derivative is substantially more reactive than the other two, and it is unique in displaying a rapidly downward drifting first-order acetolysis rate constant because of internal return to the *exo*-camphenilyl isomer. Different samples of apoisoborneol isolated from solvolysis of nopinyl derivatives, with either the lower or higher melting points, gave *p*-bromobenzenesulfonates which behaved quantitatively as apoisobornyl *p*-bromobenzenesulfonate in acetolysis.

The β-fenchoisocamphorol (XXV) was isolated by saponification of the acetate mixture after infrared analysis and careful chromatographic separation of the derived alcohol. There was obtained apoisoborneol (XXII) in the expected amount, and finally the β-fenchoisocamphorol (XXV), optically inactive, m.p. 54–58°, m.p. of acid phthalate, 129–131°.

The over-all composition of alcohol product from hydrolysis of the α- and β-nopinyl *p*-bromobenzenesulfonates may be summarized as 72 ± 4% apoisoborneol (XXII), 26 ± 5% β-fenchoisocamphorol (XXV), together with several per cent. of *exo*-camphenilol (XXIII). The present procedure was not sufficiently precise to guarantee a definite agreement or difference between the product compositions from the two isomeric starting materials.

One of the two nopinyl *p*-bromobenzenesulfonates, the α-isomer, was solvolyzed also in acetic acid at 100°. The products were similar to those in aqueous acetone, except that a substantial amount of apocyclene (XXIV), *ca.* 13% of the product, was isolated, and the proportion of β-fenchoisocamphorol in the alcohol from saponification of the acetate was substantially higher.

Discussion

In considering the configurations of the nopinols, reference to models shows that the addition of a 1,3-methylene bridge to a cyclohexane skeleton to produce the [3,1,1]bicycloheptyl skeleton gives rise to a system which can be described as containing both an approximate chair and an approximate boat form of cyclohexane, each somewhat strained and deformed. This is illustrated in structures VIII, IX and X. Either a methylene group (VIII or X) or the isopropylidene group (IX) can constitute the head of the boat. The hydroxyl group can occupy an equatorial (e) position as in VIII and IX or an axial[10] (a) position as in X. In formulating probable conformations of the different diastereomeric nopinols, we take into account the greater repulsion between non-bonded atoms associated with the presence of the isopropylidene group at the head of the boat (extra boat strain) and with the axial position for an hydroxyl or other group (axial strain).

The conformation of the nopinol diastereomer with the hydroxyl group *trans* to the isopropylidene bridge (VI) can be written as in VIII quite unambiguously. In VIII both the extra boat and axial strains are avoided. The alternative conformation would have the isopropylidene bridge in the boat and the hydroxyl group axial, and it would thus be very poorly populated. In the case of the nopinol diastereomer with the hydroxyl group *cis* to the isopropylidene bridge (VII), either the isopropylidene bridge is in the boat position, the hydroxyl group being equatorial (IX), or the isopropylidene group is chair with the hydroxyl group axial (X). The axial strain in the latter case is unusually large because of the axial position for one of the methyl groups.

From the present work, the nearest to an unambiguous configurational assignment to the nopinols may be based on the relative rates of saponification of the acid phthalates. As is summarized in Table V, the rate of saponification of the β-nopinyl acid phthalate is 4.0 times as large as that of the α-isomer. Further, the rate (10^5k_2 = 82.7) is nearly as large as that of the acid phthalate of *trans*-4-*t*-butylcyclohexanol[11] which has the hydroxyl group purely equatorial because of the *t*-butyl group which is constrained to the equatorial position. On this basis β-nopinol is diastereomer VI, with isopropylidene and hydroxyl groups *trans* to each other, and with the preferred conformation as in VIII (Table V).

It follows that the α-nopinol is the diastereomer VII with isopropylidene and hydroxyl *cis*. The rate of saponification of the α-nopinyl acid phthalate (10^5k_2 = 20.5) is too high for an entirely axial

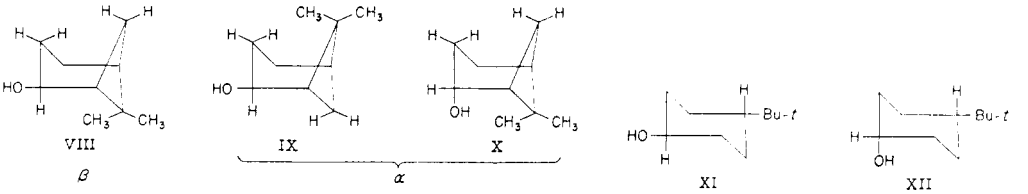
(9) N. J. Holness and A. Colter, unpublished work.

(10) D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Nature*, **172**, 1096 (1953).

(11) N. J. Holness, unpublished work.

TABLE V

COMPARISON OF RATES OF NOPINYL AND 4-*t*-BUTYLCYCLOHEXYL DERIVATIVES

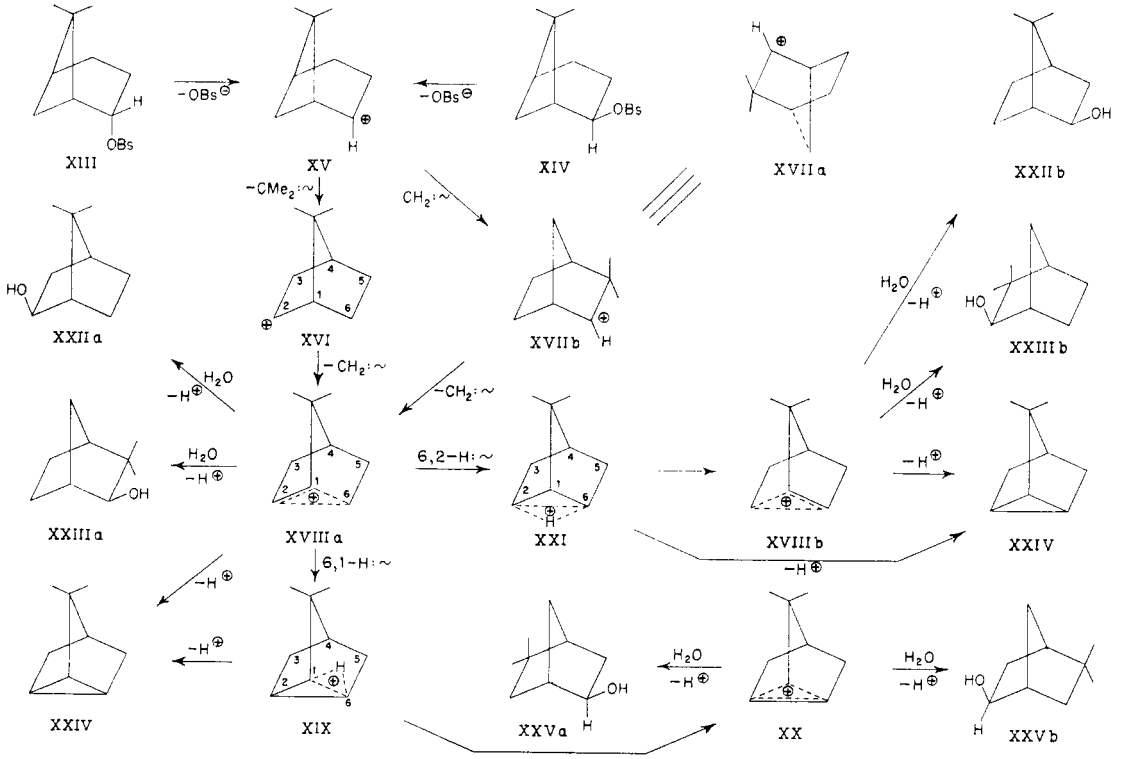


Sapn. of acid phthalates at 50° $10^5 k_2$	82.7		20.5		118		13.0
Rel. rate	4.0	>	1.0				
Rel. rate of oxidn. of ROH by CrO_3 in 50% AcOH at 50°	1.0	<	1.5	>	0.1[a]	<	0.2[a]
Rel. rate of acetolysis of *p*-bromobenzenesulfonates at 75.00°	4.5	>	1.0	<	4.1[b]	<	11.2[b]

[a] Estimated from the rate constants in 75% acetic acid[11] by dividing by the approximate factor 10 which is derived from comparison of 50% acetic acid with 75% as solvent for oxidation of cyclohexanol[11,12] and several substituted cyclohexanols.[12] [b] Based on three times the measured rates of acetolysis of the *p*-toluenesulfonates.[11]

position for the ester group as is depicted for the hydroxyl group in X. Even for the acid phthalate of *cis*-4-*t*-butylcyclohexanol[11] (XII), with saponification hindered by the compelled axial position of the ester group, the rate is about one-tenth of that of the equatorial isomer ($10^5 k_2$ = 13.0). The rate of saponification of X-acid phthalate would be expected to be very much smaller than that of XII. If one assumes the rate of IX-acid phthalate is the same as that of VIII-acid phthalate ($10^5 k_2$ = 82.7) and $10^5 k_2$ for X-acid phthalate is between 13 and 0, then the observed $10^5 k_2$ of 20.5 for α-nopinyl acid phthalate leads to the estimate that α-acid phthalate is between 11 and 25% in the conformation shown for alcohol IX (OH equatorial) and the rest in the conformation shown for alcohol X (OH axial).

The relative rates of oxidation of the two nopinols may be said to support the above configurational assignment since the α-nopinol is more rapid than the β- by a factor of 1.5. This factor may be compared with that observed with the 4-*t*-butylcyclohexanols,[11] the factor between the axial (XII) and equatorial (XI) alcohols being 2.5. However, the rates of the nopinols were about one power of ten faster than cyclohexanols XI and XII. Until the reaction and the high rate level here and in other cases observed by Vavon[12] are better understood,

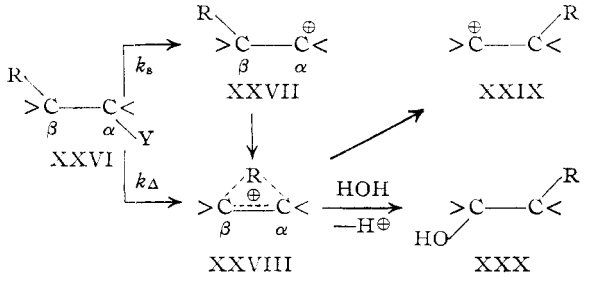


(12) G. Vavon and C. Zaremba, *Bull. soc. chim.*, **49**, 1853 (1931).

relative oxidation rates are a much less reliable guide to configuration than saponification rate.

Considering the behavior of the nopinyl *p*-bromobenzenesulfonates in solvolysis, it is interesting how very high is the predominance of rearrangement, no nopinols being detected. Essentially the whole product involves expansion of the 4-ring to a 5-ring, the [3,1,1]bicycloheptyl system going to [2,2,1]bicycloheptyl.

If this rearrangement is symbolized by formulas XXVI → XXX for simplicity, the present results with the nopinyl systems do not allow a decision to be made between migration of isopropylidene

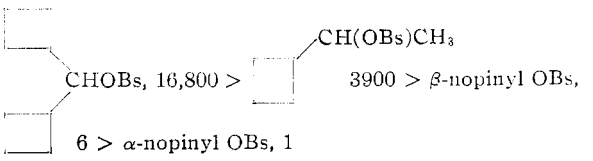


and methylene since, as will become obvious later, both stereoisomeric systems could lead to the same intermediate ion XVIIIa by either migration. Again if the rearrangement is considered from the point of view of substitution at C_α, it is of importance to decide whether part of or the entire ionization of either one or both of the nopinyl *p*-bromobenzenesulfonates XIII and XIV is anchimerically assisted. The assisted ionization, process[13] Δ^R involving participation of R, is symbolized by XXVI → XXVIII, the rate constant being k_Δ. The unassisted ionization, process[13] S, is symbolized by XXVI → XXVII, the rate constant being k_s. A high ratio of Δ^R to S is recognized most easily by an accelerated solvolysis rate relative to a comparison compound where only S occurs.

In the case of the α- and β-nopinyl *p*-bromobenzenesulfonates, solvolysis rates do not reveal any acceleration. As is summarized in Table V, the β-nopinyl *p*-bromobenzenesulfonate is more reactive than the α-nopinyl isomer in acetolysis at 75° by a factor of 4.5. However, even the more reactive β-nopinyl ester, with the equatorial leaving group, is no more reactive than the *trans*-4-*t*-butylcyclohexyl derivative[11] which also has an equatorial leaving group. Further, it is slightly less reactive than the *endo*-norbornyl[5b] or bornyl[5b] derivatives. Also, it is nearly exactly as reactive as the isopropyl[14] derivative. Thus no acceleration is visible over rates of available comparison compounds. Unassisted ionization, S, may dominate over the assisted variety, Δ^R, and the ionization of β- and α-nopinyl ester XIII and XIV, respectively, would then give ordinary ion XV which rearranges further.

There is one difficulty with the rate comparisons just discussed. The comparison compounds do not simulate the unique geometry of the nopinyl skeleton. It is possible that k_s for the nopinyl derivatives is sufficiently reduced by the effect of the unique geometry on such assisting features as hyperconjugation and solvation that k_Δ/k_s is actually substantial in spite of the present apparent lack of rate enhancement. There are a couple of indications that this may be the situation. First is the fact that the β-nopinyl OBs (XIII) with the equatorial OBs group (see VIII) is 4.5 times as rapid in acetolysis as the α-isomer XIV, which we would judge to have mainly an axial OBs group (see X). With the model 4-*t*-butylcyclohexyl derivatives,[11] the axial isomer is three times as reactive as the equatorial. This supports the possibility that at least the β-nopinyl ester and possibly both the β- and α-derivatives are anchimerically accelerated. The more rapid rate of the β-nopinol ester would be due to the greater amount of anchimeric assistance associated with isopropylidene participation rather than methylene. The other indication in favor of anchimerically assisted ionization of the nopinyl esters is the insignificant amount of unrearranged substitution product in the alcohol from hydrolysis. In the case of *endo*-norbornyl *p*-bromobenzenesulfonate[15] hydrolysis in aqueous acetone, where ionization is by the S process and where there is a large tendency for rearrangement of the cation XXVII, the product contains 15% of the inverted unrearranged *exo*-norborneol.

Whether the nopinyl derivatives ionize largely by the S or Δ^R process, it is clear that the rate of any Δ^R ionization measured by k_Δ must be much smaller than it is for comparable monocyclic materials containing the participating 4-ring. The rates of acetolysis of dicyclobutylcarbinyl and cyclobutylmethylcarbinyl *p*-bromobenzenesulfonates, measured in another investigation,[16] are much accelerated, and compared with those of the nopinyl derivatives, they give the following rate sequence at 25°



Certainly an important contributing factor to the difference between the bicyclic derivatives and the monocyclics is that the 4 → 5-ring expansion in the bicyclic cases gives a still highly strained bicycloheptyl skeleton. Thus the relief of strain attending migration of carbon is much smaller than in the monocyclic cases.

The reaction scheme, XXVI → XXX, should still be considered from the point of view of the remaining stage of the reaction, *viz.* substitution at C_β. If substitution by solvent at C_β is involved in the completion of the migration of R from C_β to C_α, symbolized by XXVIII → XXX, inversion at C_β would be the result. If R is isopropylidene, apoborneol (XXXI) would result, and, if R is methylene, *endo*-camphenilol (XXXII) would result. These materials were not found in any appreciable quantity. Instead, the *exo*-isomers, apoisoborneol-

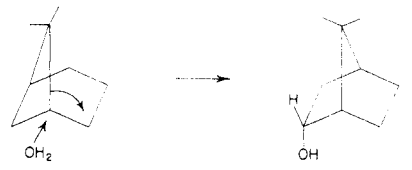
(13) S. Winstein and L. L. Ingraham, THIS JOURNAL, **77**, 1738 (1955).

(14) S. Winstein, *et al.*, *ibid.*, **74**, 1113, 1120 (1952).

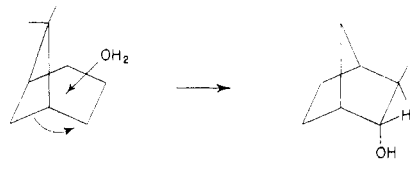
(15) E. Clippinger, unpublished work.

(16) N. J. Holness, unpublished work.

(XXII) and *exo*-camphenilol (XXIII), together with another *exo*-material, β-fenchoisocampherol (XXV) were obtained.



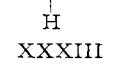
XXXI



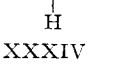
XXXII

The simplest mechanism to account for the observed results involves the complete migration of R in XXVII and XXVIII to form rearranged ion XXIX. Particularized for the nopinyl situation, ion XVI or XVII is formed either through XV or more directly. Then, by immediate carbon bridging, these ions form the more stable bridged[5] carbonium ion species XVIIIa. The prior formation of the bridged species XVIIIa provides the simplest explanation of the essentially exclusive *exo* configuration[5] of the apobornyl and camphenilyl alcohol products XXII and XXIII.

The β-fenchoisocamphorol must owe its formation to a 1,3-type of hydrogen shift (2,6-shift[5c,6,17-20] in bicycloheptyl derivatives). The present evidence[5c,6,9,20] with bicycloheptyl derivatives suggests that such hydrogen shift is subsequent to carbon participation in solvolysis of bromobenzenesulfonates or ionization of chlorosulfinates (XXXIII). If carbon bridging precedes hydrogen shift in a preformed carbonium ion (XXXIV), then bridged species XVIIIa also provides the way to discuss formation of β-fenchoisocamphorol. 6,1-Hydrogen shift within XVIIIa, through a possible interme-



XXXIII



XXXIV

diate XIX, would give XX, an internally compensated bridged ion analogous to the norbornyl cation,[5] which should give racemic β-fenchoisocamphorol (XXVab), in exact accord with experiment.

To the extent 6,2-hydrogen shift occurs in XVIIIa, mirror image XVIIIb will be formed and thus the apoisoborneol will not be entirely XXIIa but partly XXIIb and therefore partly racemic. Apocyclene XXIV arises from loss of a proton from carbonium ion species, but the exact mechanism is not known.[5c] In the present scheme, apocyclene is arbitrarily shown arising from both the XVIII and XIX or XXI variety of bridged species.

The above reaction scheme predicts the formation of highly active apoisoborneol (XXII) and *exo*-camphenilol (XXIII) and racemic β-fenchoisocamphorol (XXV) in the same proportions from either nopinyl ester XIII or XIV. This is approximately what is observed, and a more accurate study will be necessary to show if any differences exist which will require some modifications of the scheme. The product composition also corresponds quite well to that obtained in solvolysis of apoisobornyl *p*-bromobenzenesulfonate in aqueous media.[9] The greater proportion of β-fenchoisocamphorol in the product of acetolysis of α-nopinyl *p*-bromobenzenesulfonate is in line with the greater importance of 2,6-type hydrogen shift in acetic acid[6,9] than in aqueous acetone.

In the present solvolyses of the nopinyl derivatives, two types of products have not proved important. These are monocyclic[21] materials, such as norterpineol, and *endo* rearranged bicyclic substitution products. These types of products become very important in various reactions of the analogous tertiary system (*e.g.*, I) containing an additional α-methyl group. Thus substantial or predominant amounts of bornyl chloride or bornyl esters and of monocyclics may all be derived from various liquid phase reactions of pinene or methylnopinol.[3,7,22] The factors involved in controlling products, such as carbonium ion lifetime, ion pair return,[23] etc., are not yet understood.

The extra α-methyl group in the pinene-hydro system undoubtedly has an important influence, for example in affecting the importance of an ion of the type XXVIII, but the tertiary and secondary systems cannot be well compared until more reaction conditions have been explored with the nopinyl derivatives.

Experimental

Nopinone.—To a solution of 100 g. of β-pinene,[24] $n^{25}D$ 1.4759, $[\alpha]^{24}D$ −19.95° (αD −17.27°, 1 dm.) (reported[25] $n^{22}D$ 1.4724, d^{22}_4 0.8660, $[\alpha]D$ −22.2°; reported,[26] $n^{20.5}D$ 1.4773), in 100 ml. of dry pyridine was added a warm (60°) solution of 235 g. of potassium permanganate in two l. of water over a period of about five hours. The reaction flask was cooled in ice and left overnight. The manganese dioxide was filtered off, and the pyridine solution was acidified with 6 *N* hydrochloric acid. This solution was extracted six times with 100-ml. portions of ether, and the ethereal solution was shaken with 2 *N* sodium bicarbonate solution to give the insoluble salt of nopinic acid. Three such runs were combined, giving rise to 133 g. of the sodium salt. The oil from the neutral fraction was distilled under reduced pressure to give the fractions: (1) 4 g., b.p. 75–77° (8 mm.), $n^{25}D$ 1.4761; (2) 51 g., b.p. 77–78.5° (8 mm.), $n^{25}D$ 1.4769, $[\alpha]^{24}D$ 16.64° (αD 16.29°, 1 dm.); (3) 13 g., b.p. 78.5–81° (8 mm.), $n^{25}D$ 1.4786, $[\alpha]^{24}D$ 14.92° (αD 14.62, 1 dm.); (4) residue, 26 g.; (reported[7] for nopinone, $n^{20}D$ 1.4787, $[\alpha]D$ 18.48°).

(17) H. Meerwein and F. Montfort, *Ann.*, **435**, 207 (1924).

(18) W. E. Doering and A. P. Wolf, XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., Sept. 10–18, 1951, page 437 of Abstracts.

(19) S. Beckmann and R. Bamberger, *Ann.*, **574**, (a) 65, (b) 76 (1951).

(20) S. Winstein, "1,2- and 1,3-Hydrogen Shift," Symposium on Molecular Rearrangements, Queen Mary College, University of London, April 6, 1954.

(21) Heating nopinone V with dilute sulfuric acid does lead to opening of the cyclobutane ring with formation of 4-isopropylcyclohex-2-enone.

(22) *E.g.*, O. Wallach, *Ann.*, **360**, 82 (1908); W. Hückel, *Nachr. Akad. Wiss. Göttingen, Math.-physik. Klasse*, 59 (1941); *C. A.*, **37**, 3074 (1943); M. S. Kharasch and W. B. Reynolds, *J. Org. Chem.*, **9**, 148 (1944); W. A. Mosher, THIS JOURNAL, **69**, 2139 (1947).

(23) *E. g.*, S. Winstein and K. C. Schreiber, THIS JOURNAL, **74**, 2165 (1952).

(24) We are indebted to Dr. J. P. Bain of the Naval Stores Division of the Glidden Co. for this material.

(25) O. Wallach, *Ann.*, **357**, 49 (1907); **363**, 9 (1908).

(26) P. Lipp, *Ber.*, **63**, 411 (1930).

The nopinone yielded a semicarbazone, m.p. 184–186° without recrystallization (reported[7] for nopinone semicarbazone, m.p. 188°).

Reduction of Nopinone with Lithium Aluminum Hydride.—A solution of 55 g. of nopinone in 100 ml. of dry ether was added dropwise to a stirred suspension of 4.0 g. of lithium aluminum hydride in 60 ml. of dry ether. After a further 0.5 hour at room temperature excess reagent was decomposed by cautious addition of ethyl acetate. The solution was acidified with dilute sulfuric acid and extracted four times with 100-ml. portions of ether. The combined ether solutions were washed with water and dried over anhydrous potassium carbonate. Removal of the ether through a Vigreux column gave 25 g. of α-nopinol, crystallized from pentane with a trace of ethyl acetate as long needles, m.p. 101.5–102°, $[\alpha]^{23}D$ −5.55° (*c* 10.62, ether, α −0.589°, 1 dm.) (reported[7] m.p. 102°, $[\alpha]D$ −5.32° (*c* 12.53, ether)]. A 7.3-g. second crop of α-nopinol with the same melting point was obtained.

The acid phthalate of the remaining alcohol mixture was crystallized from ethyl acetate–pentane to give 25 g. of material, m.p. 122–125°. After three recrystallizations from the same solvent, there was obtained 18 g. of α-nopinol acid phthalate, m.p. 128–130°, undepressed on admixture with authentic material.

Another crop of acid phthalate, m.p. 133–135°, was obtained. This crop, after three recrystallizations from ethyl acetate–pentane, yielded 1.2 g. of acid phthalate, m.p. 136.6–137.5°, $[\alpha]D$ −15.73 (ether, *c* 11.95), still a mixture of α- and β-nopinol acid phthalates. Saponification of this acid phthalate yielded a solid alcohol, m.p. 88–93°.

α-Nopinol Esters.—A solution of 1 g. of α-nopinol and 1 g. of phthalic anhydride in 10 ml. of dry pyridine was heated at 100° for 2 hours, and then worked up in the customary manner. Crystallization from ethyl acetate–pentane gave plates, m.p. 129.5–131°. Another recrystallization yielded α-nopinol acid phthalate, m.p. 131–131.5°, $[\alpha]^{23}D$ −47.46° (*c* 10.79, ether, α −5.121°, 1 dm.).

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.51; H, 6.68.

A solution of 15 g. of α-nopinol and 27.8 g. of *p*-bromobenzenesulfonyl chloride in pyridine was left at room temperature for 22 hours. There was obtained 11.5 g. of α-nopinol *p*-bromobenzenesulfonate, m.p. 93.5–94°, and a further 7 g. of material, m.p. 92–93°. The first crop had $[\alpha]D$ −6.58° (*c* 11.19, ether, α −0.736°, 1 dm.).

Anal. Calcd. for $C_{15}H_{19}O_3BrS$: C, 50.14; H, 5.33. Found: C, 50.29; H, 5.59.

A solution of 8 g. of α-nopinol and 15 ml. of acetic anhydride in 25 ml. of dry pyridine was heated for one hour at 100°. The reaction mixture was worked up in the usual way and distilled to give an initial 0.2-g. fraction, b.p. 106–107° (18 mm.), $n^{25}D$ 1.4627, and then 8.5 g. (82%) of α-nopinyl acetate, b.p. 107–107.1° (18 mm.), $n^{25}D$ 1.4627.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.48; H, 9.95. Found: C, 72.61; H, 9.96.

Preparation of β-Nopinol.—This was attempted through equilibration of α-nopinol with sodium and fluorenone. A solution of 45 g. of the alcohol obtained by lithium aluminum hydride reduction of nopinone in 60 ml. of toluene was refluxed with 0.3 g. of sodium and 6 g. of fluorenone. Working up in the conventional manner and steam distillation gave a toluene distillate containing crystals of α-nopinol. Filtration yielded 15 g. of material, m.p. 100–101°. The residual alcohol yielded 19 g. of an acid phthalate, with m.p. 136.5–137.5°, after crystallization from ethyl acetate–pentane. This acid phthalate was the same difficultly separable mixture mentioned above in the case of the product from reduction of nopinone with lithium aluminum hydride.

A solution of 50 g. of nopinone in 950 ml. of a *ca.* 1 *M* solution of aluminum isopropoxide in isopropyl alcohol was refluxed for four hours while 600 ml. of isopropyl alcohol was distilled off. The reaction mixture was cooled, acidified with 2 *N* hydrochloric acid, diluted to two l. and extracted five times with 150-ml. portions of pentane. The combined extracts were washed three times with water, once with sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Evaporation of the pentane afforded an oil $[\alpha]D$ −11° (c 14, ether).

The oil was dissolved in 30 ml. of dry pyridine and heated for one hour at 100° with 50 g. of phthalic anhydride. Treatment in the conventional manner gave an acid phthalate, m.p. 151–154.5°. Two crystallizations from ethyl acetate–pentane gave 21 g. of β-nopinol acid phthalate, m.p. 155.8–156.2°, $[\alpha]D$ 4.42° (*c* 6.36 in ether, α −0.281°, 1 dm.). Additional crops (23.7 g.) had melting points about 155–156°.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.77; H, 6.86.

β-Nopinol and the *p*-Bromobenzenesulfonate.—Steam distillation of 19 g. of β-nopinol acid phthalate from 25% aqueous potassium hydroxide afforded the free alcohol. This was extracted from the distillate with pentane in the customary way. Evaporation of the solvent through a Vigreux column afforded 8.8 g. of β-nopinol, m.p. 37.0–37.5°, $[\alpha]D$ −18.87° (*c* 12.21, ether, α −2.304, 1 dm.).

The *p*-bromobenzenesulfonate was prepared as described for α-nopinol *p*-bromobenzenesulfonate. Crystallization of the product from pentane afforded β-nopinol *p*-bromobenzenesulfonate, m.p. 98.5–99.5°.

Anal. Calcd. for $C_{15}H_{19}O_3BrS$: C, 50.14; H, 5.33. Found: C, 49.85; H, 5.28.

Norterpineol.—A mixture of 10 g. of butadiene and 8.5 g. of methyl acrylate was heated in a sealed tube at 140° for 3 hours and then cooled. The colorless product was washed out with pentane and then distilled under reduced pressure to give 10 g. of methyl Δ^3-tetrahydrobenzoate, b.p. 68.5–69.0° (12 mm.), $n^{25}D$ 1.4583 (reported[27] b.p. 70° (13 mm.)).

To the Grignard reagent prepared from 14.2 g. of methyl iodide, 2.5 g. of magnesium turnings and 100 ml. of dry ether was added 5.7 g. of methyl Δ^3-tetrahydrobenzoate in 50 ml. of dry ether over a period of 30 minutes. The product was poured onto a mixture of ice and ammonium chloride and then extracted into ether in the usual way. Removal of the ether through a Vigreux column and then distillation of the residual oil under reduced pressure afforded 3.30 g. of norterpineol, b.p. 86–88° (12 mm.), $n^{25}D$ 1.4787 (reported[27] b.p. 90° (13 mm.)). A 1.40-g. initial fraction, b.p. up to 86° (12 mm.), had $n^{25}D$ 1.4736.

A solution of 1.1 g. of norterpineol in 5 ml. of dry pyridine was heated for 3 hours at 100° with 1.1 g. of phthalic anhydride. Working up in the usual way gave about 50 mg. of an acid, m.p. 200° dec., undepressed in m.p. on mixing with authentic phthalic acid.

Oxidation of the Nopinols.—To a solution of 0.55 g. of chromium trioxide in 150 ml. of 50% acetic acid was added 1 g. of α-nopinol. The solution was kept at 50° for two hours, diluted to 1 l., saturated with sodium chloride and extracted four times with 150-ml. portions of pentane. Treatment by the customary procedure gave an oil which was chromatographed to give 735 mg. of nopinone, $n^{25}D$ 1.4754, semicarbazone m.p. 184–186°, undepressed on admixture with authentic semicarbazone.

The kinetics of oxidation of the nopinols by chromium trioxide in 50% acetic acid (1 volume acetic acid:1 volume water) were followed by the method used in the case of the 4-*t*-butylcyclohexanols.[11] Second-order constants were first evaluated employing oxidation–reduction normalities for the concentrations of alcohol and chromium trioxide, and then the constants were multiplied by the factor 3. The corrected constants are given in Table II.

Kinetics of Saponification of Acid Phthalates.—The measurements were carried out as described for the 4-*t*-butylcyclohexyl acid phthalates.

Rates were followed to 70 or 80% completion, good infinity titers also being observed.

Rates of Acetolysis.—The rates of acetolysis of the α- and β-nopinyl *p*-bromobenzenesulfonates in anhydrous acetic acid were measured by the usual method. Rates were followed to *ca.* 90% completion, and the infinity titers were 99–100% of theoretical.

Solvolysis of α-Nopinol *p*-Bromobenzenesulfonate in 60% Acetone.—A solution of 22.5 g. of *p*-bromobenzenesulfonate, m.p. 92–93°, in 700 ml. of 60% acetone was refluxed with 15 g. of calcium carbonate for 100 hours. The acetone solution was diluted with water to a volume of 5 l., and then the mixture was extracted 7 times with 100-ml. portions of pentane. After removal of the solvent, the residue was chromatographed over 250 g. of alumina. A small low-melting fraction smelling of apocyclene was obtained first. Then there was obtained 4.02 g. of apoisoborneol, m.p. 131 ·

(27) K. Alder and W. Vogt, *Ann.*, **564**, 109 (1949).

132°, $[\alpha]_D$ +10.27° (*c* 8.45, EtOH), +10.64° (*c* 8.96, EtOH). The melting point was unchanged on repeated chromatography.

The remaining 3.44 g. of alcohol product was converted to acid phthalate in the conventional manner. Crystallization from ethyl acetate–pentane gave 0.51 g. of apoisobornyl acid phthalate, m.p. 173–174°, m.p. reported[19] for *dl*-acid phthalate, 174–175°. The remainder of the acid phthalate was saponified and converted to acetate; 3.05 g., b.p. 109° (25 mm.), n^{25}D 1.4597.

Inspection of the infrared spectrum of the acetate showed a similarity with the spectra of mixtures of apoisobornyl, *exo*-camphenilyl and β-fenchoisocamphoryl acetates.[9] The absence of α-nopinyl acetate was indicated by the absence of characteristic absorption peaks at 8.9, 9.35, 10.2 and 10.8 μ. The infrared spectrum of the acetate was compared with a mixture, 49.7% apoisobornyl and 50.3% β-fenchoisocamphoryl acetate, and with a mixture, 76.2% β-fenchoisocamphoryl, 19.1% apoisobornyl and 3.4% *exo*-camphenilyl acetate, these mixtures being available from other work.[9] By comparison of optical densities at 8.7 and 9.3 μ, an estimate of the composition of the acetate mixture was reached. This was 50% β-fenchoisocamphoryl, 43% apoisobornyl and 7% *exo*-camphenilyl acetates. On this basis, the calculated[9] n^{25}D is 1.4598, compared to the observed n^{25}D 1.4597.

Saponification of 2.67 g. of the acetate mixture and careful chromatography of the alcohol afforded 1.015 g. (45%) of apoisoborneol, m.p. 131–132°, $[\alpha]_D$ +13.44° (*c* 8.60, EtOH). Further elution with pentane and pentane–10% ether gave 1.250 g. of a low-melting alcohol, m.p. 54–58°, $[\alpha]_D$ +0.18° (*c* 7.73, EtOH). The *dl*-β-fenchoisocamphorol has[9,28] m.p. 60–61°.

Preparation of an acid phthalate from 0.965 g. of the alcohol, m.p. 54–58°, gave 1.43 g. of β-fenchoisocamphoryl acid phthalate, m.p. 129–131° (m.p.[19] of *dl*-β-fenchoisocamphoryl acid phthalate 130–131°).

An earlier solvolysis of α-nopinyl *p*-bromobenzenesulfonate in 80% aqueous dioxane gave rise to a product which was converted directly to acid phthalate, m.p. 154–156°, markedly depressed by admixture of β-nopinyl acid phthalate, m.p. 156°. No appreciable quantity of neutral material remained after the conversion to acid phthalate. Saponification of the acid phthalate and chromatography gave alcohol fractions, m.p. 133–134° and m.p. 141°. Conversion of some of the 133–134° alcohol fraction to *p*-bromobenzenesulfonate gave rise to a material which behaved in acetolysis identically with apoisobornyl *p*-bromobenzenesulfonate.[9] The integrated rate constant for acetolysis at 25° fell from 6.0×10^{-4} sec.$^{-1}$ to 3.4×10^{-5} sec.$^{-1}$ between 36 and 92% solvolysis, 24% being the zero point for the run.

Solvolysis of β-Nopinyl *p*-Bromobenzenesulfonate in 60% Acetone.—A solution of 9.3 g. of β-nopinyl *p*-bromobenzenesulfonate in 300 ml. of 60% acetone was refluxed for 30 hours with 7 g. of calcium carbonate. The product was worked up as in the case of the α-nopinyl *p*-bromobenzenesulfonate, and then it was chromatographed. Elution with pentane gave initially a small fraction which may have contained apocyclene. Elution with pentane–10% ether gave 1.634 g. of pure apoisoborneol, m.p. 139–141°, $[\alpha]_D$ +14.12° (*c* 8.44, EtOH), m.p. unchanged on repeated chromatography, m.p. on admixture with the apoisoborneol from the α-nopinyl *p*-bromobenzenesulfonate, 132–134°.

The remaining alcohol was acetylated to give 0.95 g. of the acetate, b.p. 109° (25 mm.), n^{25}D 1.4594. Examination of the infrared absorption spectra of the acetate mixture and that of the acetate from the solvolysis of α-nopinyl *p*-bromobenzenesulfonate, and comparison of the peak intensities at 8.65, 8.85 and 9.25 μ led to an estimate of 68% β-fenchoisocamphoryl, 30% apoisobornyl and 2% *exo*-camphenilyl acetates in the mixture. This leads to a calculated n^{25}D 1.4592.

Conversion of some of the 139–141° alcohol to *p*-bromobenzenesulfonate gave rise to a material which behaved just as does apoisobornyl *p*-bromobenzenesulfonate in acetolysis.

Acetolysis of α-Nopinyl *p*-Bromobenzenesulfonate.—A solution of 8.5 g. of α-nopinyl *p*-bromobenzenesulfonate in 450 ml. of 0.1 *N* sodium acetate in acetic acid was heated at 100° for 7 hours. The acetate, after pentane extraction, was reduced with lithium aluminum hydride in ether in the usual way, and the alcohol was chromatographed.

The first two pentane fractions contained 221 mg. of apocyclene, identified[9] by the infrared absorption of its carbon disulfide solution by means of the characteristic absorption peak at 12.4 μ. Further elution with pentane yielded 1.068 g. of apoisoborneol, m.p. 139–141°. Elution with pentane and pentane–10% ether then gave 610 mg. of the oily alcohol, very predominantly β-fenchoisocamphorol.

(28) G. Komppa and S. Beckmann, *Ann.*, **537**, 140 (1939).

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXIV. The Reaction of Trimethylamine with α-Methylallyl Chloride[1a,b]

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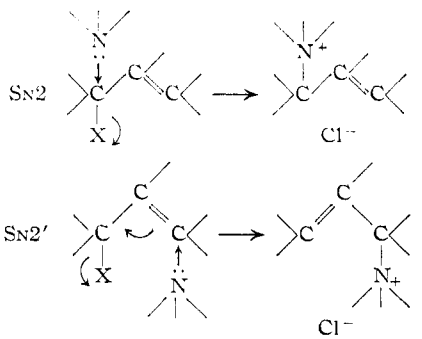
A study has been made of the bimolecular displacement reaction between trimethylamine and α-methylallyl chloride in acetone solution. The reaction was found to consist of simultaneous SN2 and SN2′ displacements. Reaction rates and thermodynamic functions of activation for the two modes of displacement are presented.

Introduction

Bimolecular nucleophilic displacement upon an allylic system may proceed by two mechanisms: normal displacement, SN2, and abnormal displacement, SN2′, as illustrated below for the general case with an unspecified nucleophile, N, and an unspecified leaving group, X. The possibility of SN2′ displacement upon allylic systems was recognized,[2] on theoretical grounds, prior to conclusive experimental demonstration. Experimental validation of the theory first was provided when it was



(1) (a) A preliminary report of this work appeared in *Science*, **115**, 488 (1952); (b) acknowledgment is made of the partial support of this research by a National Science Foundation Grant; (c) Standard Oil Company of California, Research Fellow, 1952.

(2) (a) E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938); (b) S. Winstein, Ph.D. Dissertation, California Institute of Technology, 1938.