promoted ionization. It was not that $LiN_3$ was such an effective trap for $R^+X^-$ ion pairs, but instead it introduced another ionization path conducive to $RN_3$ formation. The $LiN_3$-promoted ionization may be visualized as producing an ion quadruplet[8] which prefers "covalent return" to $RN_3$ rather than RX.

CONTRIBUTION NO. 1686　　　　　　　　　　S. WINSTEIN
DEPARTMENT OF CHEMISTRY　　　　　　BRUCE R. APPEL
UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA 90024
RECEIVED MAY 11, 1964

## Ion Pairs and Dissociated Ions from Trityl Benzoate in Moist Acetone[1]

*Sir:*

Since trityl systems represent rather a structural extreme among possible RX substrates in solvolysis, trityl benzoate provides an important calibration point for our understanding of ion pairs and dissociated ions[2] in solvolysis and the gap between ionization and chemical capture rates.[3]

The behavior of 0.01–0.04 $M$ carbonyl-$^{18}$O-labeled trityl benzoate in 95% acetone is illustrated in Table I.

TABLE I

$^{18}$O EQUILIBRIUM, SOLVOLYSIS, AND AZIDE FORMATION FROM TRITYL BENZOATE IN MOIST ACETONE

| $\Sigma$(Salt),[a] $10^2 M$ | Salt | $10^2 M$ | $10^5 k$ (sec.$^{-1}$) $k_{eq}$ | $k_t$ |
|---|---|---|---|---|
| | | 95% Me$_2$CO; 50.0° | | |
| . . . | . . . | . . . | 0.55 | 2.8 |
| 1.00 | . . . | . . . | 0.57 | 2.9 |
| 6.00 | . . . | . . . | | 3.3 |
| 0.046 | Bu$_4$NOBz | 0.046 | | 0.72 |
| 5.67 | Bu$_4$NOBz | 5.67 | | 0.26 |
| 1.04 | Bu$_4$NN$_3$ | 1.04 | | 0 |
| 6.00 | Bu$_4$NN$_3$ | 1.46 | | 3.3[b] |
| | | 99.2% Me$_2$CO; 75.0° | | |
| . . . | . . . | . . . | 1.9[c] | 0.32[d,e] |
| 1.01 | . . . | . . . | | 0.57[d] |
| 1.02 | Bu$_4$NOBz | 1.02 | | 0.070 |
| 0.99 | Bu$_4$NN$_3$ | 0.99 | 1.5 | 0.61[b,d] |
| 0.98 | LiN$_3$ | 0.98 | 3.3[c] | 6.4[b] |
| 1.03 | LiClO$_4$ | 1.03 | ca. 10[f] | 23.8 |

[a] $\Sigma$(Salt) brought to listed value with Bu$_4$NClO$_4$.　[b] $k_{N_3}$ value.　[c] ±0.3.　[d] ±0.03.　[e] Mean value; rate constant drifts up from ca. 0.24 to 0.36 over first 50% of the reaction, presumably due to benzoic acid catalysis; such catalysis increases with decreasing water content of the solvent.　[f] One point rate.

The $^{18}$O equilibration[3e–g] rate constant ($k_{eq}$) is considerably larger than in dry acetone,[4] but now this rate is much less than the rate of chemical capture represented by the titrimetric rate constant ($k_t$). Solvolysis shows strong common-ion rate depression,[2b] and it is possible to depress $k_t$ to a very small fraction of the undepressed value by inclusion of Bu$_4$NOBz. Inclusion of Bu$_4$NN$_3$ quenches solvolysis essentially quantitatively, the azide-capture rate constant ($k_{N_3}$) being the same as $k_t$ in the

(1) Research sponsored by the National Science Foundation.
(2) S. Winstein, et al.: (a) Chem. Ind. (London), 664 (1954); (b) J. Am. Chem. Soc., **78**, 328 (1956); (c) ibid., **80**, 169 (1958); (d) ibid., **86**, 2072 (1964).
(3) (a) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, ibid., **82**, 1010 (1960); (b) S. Winstein, M. Hojo, and S. Smith, Tetrahedron Letters, **No. 22** 12 (1960); (c) Y. Pocker, Proc. Chem. Soc., 140 (1961); (d) S. Winstein, A. Ledwith, and M. Hojo, Tetrahedron Letters, **No. 10**, 341 (1961); (e) H. L. Goering and J. F. Levy, ibid., **No. 18**, 644 (1961); (f) H. L. Goering, R. G. Boidy, and J. F. Levy, J. Am. Chem. Soc., **85**, 3059 (1963); (g) H. L. Goering and J. F. Levy, ibid., **86**, 120 (1964).
(4) S. Winstein and B. R. Appel, ibid., **86**, 2718 (1964).

presence of an equivalent concentration of "inert" salt, Bu$_4$NClO$_4$. In 97.5% acetone, the solvolysis rate of trityl benzoate is lower, but the common-ion rate depression picture is similar to the one in 95% acetone.

Acetone containing 0.450 $M$ water (99.2% acetone) is a solvent which still provides the simple common ion rate depression criterion for dissociated intermediates.[2b] However, it is not so far removed from dry acetone in ionizing and dissociating power but that it can furnish some insight into the behavior of substrates in the dry solvent. In the 99.2% acetone, $k_{eq}$ is intermediate between the values in 95% and anhydrous acetone[4] solvents. Contrasting with the 95% solvent, $k_{eq}$ is now greater than $k_t$ by a factor of 6. The solvolysis in the 99.2% solvent still shows very strong common-ion rate depression. The inclusion of Bu$_4$NN$_3$ does not suppress $^{18}$O equilibration seriously, but it quenches solvolysis essentially completely. The azide capture rate constant ($k_{N_3}$) is again equal to the appropriate solvolysis rate constant ($k_t$).

In the aqueous acetone solvents, as in anhydrous acetone,[4] we visualize that $^{18}$O equilibration[3e–g] of trityl benzoate proceeds by way of an ion pair intermediate not easily capturable by added salts or water. Chemical capture (solvolysis or azide formation) proceeds very predominantly by way of trityl species which have become dissociated and no longer contain the OBz portion of the original ROBz molecule. If we take ($k_{eq}$ + $k_t$) in the aqueous acetones and $k_{eq}$ in anhydrous acetone as measures of the ionization rate constant[3] at zero or small tetrabutylammonium salt concentrations, we see that rate of chemical capture represents 3%, 14%, and 84% of the ionization rate constant in anhydrous, 99.2%, and 95% acetone solvents, respectively. We see that ion pair return can render an exchange or solvolysis rate of a trityl derivative much smaller than the ionization rate, just as in the case of various benzhydryl derivatives.[3] However, the indications are that ion pair return drops off in importance as water is added to acetone solvent sooner with trityl derivatives than with comparable benzhydryl analogs.

The gap between solvolysis and ionization rates of trityl benzoate is of interest in connection with correlations of solvolysis rates such as the $mY$ correlation. In an earlier discussion[5] we inferred that ion pair return, rendering $k_t$ values smaller than ionization rate constants, was one of the disturbances contributing to dispersion of log $k_t$ vs. $Y$ plots for systems such as α-phenylethyl and benzhydryl. The present observations on trityl benzoate and the earlier gaps between polarimetric $k_\alpha$ or ($k_{eq}$ + $k_t$) values and the corresponding solvolysis rate constants for α-phenylethyl and benzhydryl derivatives[3] confirm the importance of this disturbance.

The effects of LiN$_3$ and LiClO$_4$ on the behavior of trityl benzoate in the 99.2% acetone solvent are of interest in connection with the report of Swain and Tsuchihashi[6] that LiN$_3$ suppresses $^{18}$O equilibration of trityl benzoate in dry acetone with only small rate enhancement. In 99.2% acetone inclusion of 0.01 $M$ LiN$_3$ increases greatly the ionization rate constant, ($k_{eq}$ + $k_{N_3}$) being more than four times as large as the

(5) S. Winstein, A. H. Fainberg, and E. Grunwald, ibid., **79**, 4146 (1957).
(6) C. G. Swain and G. Tsuchihashi, ibid., **84**, 2021 (1962).

$(k_{eq} + k_t)$ value in the absence of salt or the $(k_{eq} + k_{N_3})$ value in the presence of 0.01 $M$ Bu$_4$NN$_3$. Whereas with 0.01 $M$ Bu$_4$NN$_3$ 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.

CONTRIBUTION NO. 1687      S. WINSTEIN
DEPARTMENT OF CHEMISTRY      BRUCE R. APPEL[8]
UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA 90024

## Carbonium Ion Behavior of Nopinyl Derivatives[1]

*Sir:*

Schleyer[2] has informed us that the supposed $\alpha$- and $\beta$-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 $\beta$-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 $\beta$-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).

(2) P. von R. Schleyer, E. W. Watts, and C. Cupas, *J. Am. Chem. Soc.*, **86**, 2722 (1964).

(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.
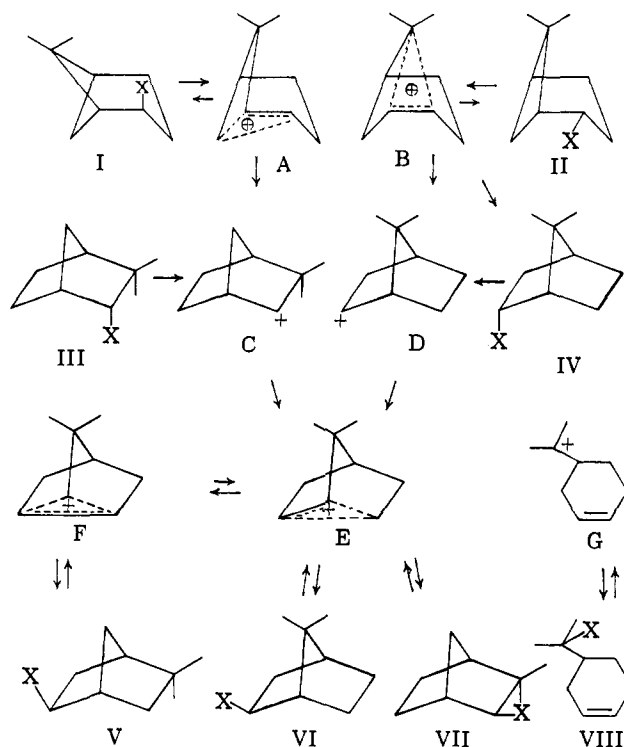


The products of the very fast stage of the acetolysis after lithium aluminum hydride reduction contained norterpineol (VIII-OH), $\beta$-nopinol (II-OH), apoborneol (IV-OH), apoisoborneol (VI-OH), *exo*-camphenilo (VII-OH), and $\beta$-fenchoisocamphorol (V-OH) in the proportions summarized in Table 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 $\beta$-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 $\beta$-NOPINYL-OBs AT 24°

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

Attempts to isolate the apparently more reactive $\alpha$-nopinyl ester I-OBs have so far been unsuccessful. However, the $\alpha$- and $\beta$-nopinols can be compared in rearrangement rates at 75° in 70% aqueous dioxane catalyzed by 0.099 $M$ perchloric acid. Under these conditions $\beta$-nopinol and $\alpha$-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 $\beta$-nopinol (II-OH) contained 37% norterpineol (VIII-OH), 27% apoborneol (IV-OH), 20% apoisoborneol (VI-OH), 5% *exo*-camphenilol