**Tetrahedron Letters No.45, pp. 3363-3365, 1964. Pergamon Press Ltd.
Printed in Great Britain.**

ACETOLYSIS OF *exo*-NORBORNYL p-TRIFLUOROMETHYLTHIONBENZOATE

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(Received 9 September 1964)

The effect of the nature of the leaving group on ionization rates (3), solvolysis rates (3), and products (3,4,5) in the solvolysis of *exo*-norbornyl derivatives is of considerable interest because of the information which is provided on the nature and behavior of ionic intermediates. Arenesulfonate esters (3,4) give racemic products indicative of symmetrical intermediates with, for the p-bromobenzenesulfonate ester (3), the rate of ionization exceeding the rate of acetolysis by a factor of 3.5 at 25.0°. The products from deamination of the corresponding amine (4,5), however, retain some asymmetry. In this Communication data on the acetolysis of *exo*-norbornyl p-trifluoromethylthionbenzoate, I, are presented which indicate that the first capturable intermediate in this solvolysis is symmetrical.

The yellow *exo*-norbornyl p-trifluoromethylthionbenzoate (6), λ_{max} 420 mμ (ϵ 110, HOAc), was prepared (7) from the lithium salt of *exo*-norborneol and p-trifluoromethylthiobenzoyl chloride (6) in tetrahydrofuran solvent at 0°. Using *exo*-norborneol, $[\alpha]_D$ - 1.72° (c 9.9, $CHCl_3$), a thion ester was obtained with $[\alpha]_D^{29}$ + 8.18° (c 10.3, $CHCl_3$).

Acetolysis of the thion ester I at 140.0°, followed by the disappearance of the absorption at 420 mμ, gave good kinetics with a first order rate constant, k_A, of $(1.48 \pm 0.03) \times 10^{-5}$ sec.$^{-1}$. With optically active *exo*-norbornyl p-trifluoromethylthionbenzoate both the rate of racemization and the rate of disappearance of thion ester were measured. As illustrated in

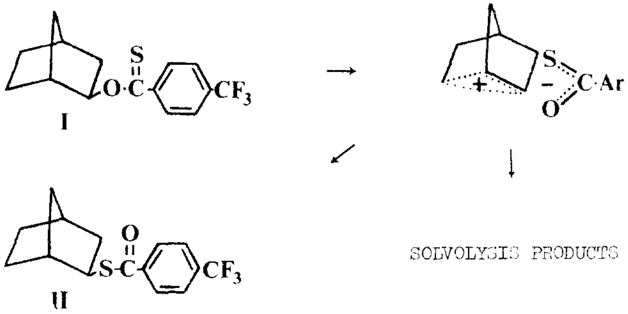

Table I the rate of racemization is equal to the rate of disappearance of thion ester. Apparently ion pair return to form racemic thion ester is not important under these conditions.

TABLE I

Rate of Solvolysis and Rate of Racemization of
Optically Active exo-Norbornyl p-Trifluoromethylthionbenzoate
in Acetic Acid at 140.0°

Time, 10^{-4}sec.	A^a	α^b	$10^5 k_A$, sec.$^{-1}$	k_A/k_α
-	0.492	+1.43	-	-
3.45	.312	1.00	1.52	1.01
6.9	.214	0.69	1.43	1.01
10.6	.133	.43	1.56	1.00
49.0	.047	.00		

[a] Absorbance at 420 mμ with 2 mm. path length.
[b] Optical rotation at the sodium D line in a 1 dcm. tube.

Products from the solvolysis of thion ester, I, in acetic acid at 140° determined by v.p.c. and isolation were found to be exo-norbornyl p-trifluoromethylthiolbenzoate (6), II, (m.p. 46 - 47°) 16% and exo-norbornyl acetate, 73% with ca. 10% of more volatile material. When optically active thion ester was solvolysed the thiol ester, II, isolated had $[\alpha]_D$ 0.00 ± 0.02° corresponding to at least 98% racemization. Optically active thiol ester, II, $[\alpha]_D^{24}$ + 9.83° (c 6.0, HOAc) is stable under the reaction conditions.

These data are consistent with ionization to an ion pair in which the sulfur atom of the anion is symmetrical with respect to two centers of the cation. Since the nucleophilic p-trifluoromethylthiobenzoate anion presumably requires little movement to be properly orientated for ion pair return on sulfur, it is unlikely that unsymmetrical (8) norbornyl cations are involved in this reaction.

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