ture did not exceed 10°. Continuing the reaction for 20 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by addition of 10 ml. of 10% potassium hydroxide, by means of a syringe, at such a rate that the temperature did not exceed 5°. (*Caution!* The first few drops of base should be added slowly because a considerable exotherm develops.) Then refluxing the reaction mixture for 1 hr., extracting with pentane for 90 hr., removing the solvent in a nitrogen stream, and subliming the residue at 60° (0.1 mm.) gave 1.16 g. (50.3%) of **N-cyclohexylhydroxylamine**, m.p. 140°.

Similarly, treating 3.34 g. (20 mmoles) of potassium cyclohexanenitronate with 28 ml. (130.2 mequiv. of hydride ion) of a borane–THF solution and keeping the reaction mixture for 20 hr. at ambient temperature resulted in the evolution of 1.8 mmoles of hydrogen.

Hydrolyzing the reaction mixture at 0° with 3 ml. of water, which was added slowly by means of a syringe, and then refluxing for 30 min. gave 63.0 mmoles of hydrogen. Removing THF *in vacuo*, adding 10 ml. of 10% potassium hydroxide at 0° to the residue, and refluxing for 1 hr. gave no more hydrogen. The total amount of hydrogen evolved was 64.8 mmoles, indicating that 3.2 equiv. of hydride was consumed in the reaction.

N-Benzylhydroxylamine.—To 3.50 g. (20 mmoles) of potassium phenylmethanenitronate at 0° was introduced by means of a hypodermic syringe 14 ml. of a 1.7 *M* solution of borane in THF at such a rate that the temperature did not exceed 10°. Continuing the reaction for 24 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by the addition of 10 ml. of 20% hydrochloric acid by means of a syringe, at such a rate that the temperature did not exceed 5°. The reaction mixture was refluxed for 1 hr. while maintaining pH 1, made basic with 10% potassium hydroxide at 0°, and extracted with pentane for 72 hr. Removing the solvent in a nitrogen stream and subliming the residue at room temperature (0.2 mm.) gave 1.18 g. (48.1%) of **N-benzylhydroxylamine**, m.p. 57°.

Reduction of Potassium Fluorenitronate.—To 4.98 g. (20 mmoles) of potassium fluorenenitronate at 0° was introduced by means of a hypodermic syringe 27 ml. of a 1.86 *M* solution of borane in THF at such a rate that the temperature did not exceed 10°. Continuing the reaction for 12 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by the addition of 10 ml. of 10% potassium hydroxide by means of a syringe, at such a rate that the temperature did not exceed 5°. Then refluxing the reaction mixture for 1 hr., extracting with pentane for 72 hr., removing the solvent in a nitrogen stream, and subliming the residue at 80° (0.2 mm.) gave 1.53 g. (39.2%) of **fluorenone oxime**, m.p. 195°. A mixture melting point determination with an authentic sample of fluorenone oxime showed no depression.

Acidification of the alkaline aqueous reaction mixture at 0° with 10% sulfuric acid and fitration of the precipitate gave 1.71 g. (40.6%) of **9,9′-dinitro-9,9′-bifluorene:** m.p. 163°; after recrystallization from absolute ethanol, m.p. 180° (lit.[12] m.p. 184°); $\lambda_{\max}^{\text{Nujol}}$ 6.4 μ (NO_2).

Acknowledgment.—We wish to thank the Office of Naval Research for financial support of this work.

(12) C. D. Nenitzescu, *Ber.*, **62**, 2669 (1929).

Solvolysis of *exo*-Norbornyl *p*-Trifluoromethylthionbenzoate

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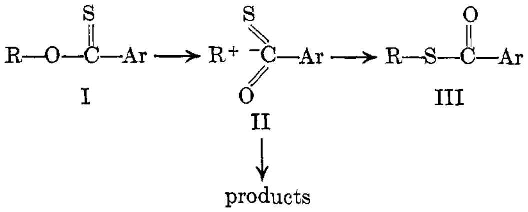
The rates of solvolysis of *exo*-norbornyl *p*-trifluoromethylthionbenzoate in acetic acid and aqueous ethanol were measured. It was found that in acetic acid at 140.0° the rate of loss of optical activity was the same as the rate of disappearance of the thion ester indicating that ion-pair return by oxygen to carbon 1 is not important with this system. The thiol ester produced in 16% yield was found to be at least 97% racemic indicating that the *exo*-norbornyl cation is symmetrical toward ion-pair return on sulfur.

Ionization rates often exceed the rate of formation of products in limiting solvolysis reactions because ion-pair return regenerates the starting material.[3] An understanding of structural effects on reactivity requires methods of measuring ionization rates in addition to total solvolysis rates.

Rate constants corresponding to ionization have been determined for systems in which heterolysis produces a carbonium ion in which two centers are made equivalent by participation[4,5] or where the first carbonium ion formed has rearranged[6] so that ion-pair return gives a new species of markedly different reactivity from the starting material.

With one-center carbonium ions in nonrearranging systems, scrambling of centers in the leaving group has recently been used as a measure of the lower limit to the ionization rate. For example, Goering,[7] Winstein,[8] and Swain[9] have used the scrambling of ^{18}O-labeled carbonyl and acyl oxygens in benzoate esters to estimate ionization rates. Darwish[10a] and co-workers have employed the reaction of sulfinate esters to give sulfones and solvolysis products, and Fava has studied the isomerization of thiocyanates to isothiocyanates.[10b]

We have used thion esters[11,12] I in studying solvolysis reactions since ionization would initially form an ion pair such as II in which it would be expected that ion-pair return would occur predominately on sulfur to produce the relatively stable thiol ester[11] III. With benz-



$$\underset{\mathrm{I}}{\mathrm{R{-}O{-}\overset{\overset{S}{\|}}{C}{-}Ar}} \longrightarrow \underset{\mathrm{II}}{\mathrm{R^{+}\ {}^{-}\overset{S}{\underset{O}{C}}{-}Ar}} \longrightarrow \underset{\mathrm{III}}{\mathrm{R{-}S{-}\overset{\overset{O}{\|}}{C}{-}Ar}}$$

$$\mathrm{II} \downarrow \text{products}$$

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[1] Alfred P. Sloan Fellow.

[2] National Science Foundation Predoctoral Fellow.

(3) See, *e.g.*, A. Streitwieser, Jr. "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(4) D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964).

(5) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965).

(6) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).

(7) H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964).

(8) S. Winstein and B. R. Appel, *ibid.*, **86**, 2718 (1964).

(9) C. G. Swain and G. Tsuchihashi, *ibid.*, **84**, 2021 (1962).

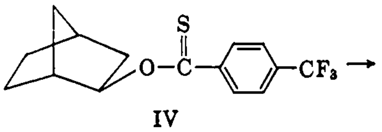
(10) (a) D. Darwish and E. A. Preston, *Tetrahedron Letters*, **No. 2**, 113 (1964). (b) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Am. Chem. Soc.*, **87**, 1045 (1965).

(11) S. G. Smith, *Tetrahedron Letters*, **No. 21**, 979 (1962).

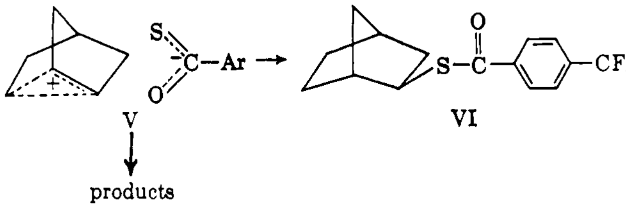
(12) Part of this work has appeared in preliminary form: S. G. Smith and J. P. Petrovich, *ibid.*, **No. 45**, 3363 (1964).

hydryl thionbenzoate, for example, in ethanol at 100.0°, 83% thiol ester was detected from ion-pair return.[11]

In this paper a study of the solvolysis of *exo*-norbornyl *p*-trifluoromethylthionbenzoate[12] is presented. This is an informative system with regard to the use of the thion ester leaving group as a probe for measuring rates of ionization since heterolysis would produce a symmetrical nonclassical norbornyl cation[13] and a thiobenzoate anion, V. By use of the optically active ester the rate of ionization as given by the rate of scrambling of carbons 1 and 2 in the two-center cation, measured by the rate of loss of optical activity, can be compared with the rate of ionization as assessed by the rate of disappearance of the thion ester group.



IV



Results and Discussion

Preparation of Materials.—*p*-Trifluoromethylthiobenzoyl chloride was prepared in *ca.* 20% yield by the addition of the lithium reagent from *p*-bromobenzotrifluoride to an excess of carbon disulfide maintained at −40 to −30° to form the dithio acid followed by treatment with thionyl chloride to give the purple acid chloride.

The thion ester of *exo*-norborneol, IV, was obtained as a yellow oil, λ_{max} 420 mμ (ϵ 110), from the reaction of the lithium alcoholate in tetrahydrofuran at 0° with *p*-trifluoromethylthiobenzoyl chloride in 50-60% yield after purification by chromatography on alumina. Using *exo*-norborneol[14] with $[\alpha]^{25}\text{D}$ −1.72° (*c* 9.92, $CHCl_3$) gave a thion ester with $[\alpha]^{26}\text{D}$ +8.18° (*c* 10.3, $CHCl_3$).

The corresponding thiol ester, *exo*-norbornyl *p*-trifluoromethylthiobenzoate (VI) was most easily obtained by the reaction of *endo*-norbornyl *p*-bromobenzenesulfonate with potassium *p*-trifluoromethylthiobenzoate in acetonitrile solvent. Using *endo*-bromobenzenesulfonate ester with $[\alpha]^{24}\text{D}$ −9.90 (*c* 9.96, $CHCl_3$) gave a thiol ester with $[\alpha]^{25}\text{D}$ +9.83° (*c* 6.0, HOAc).

Rate Measurements.—The solvolysis of *exo*-norbornyl *p*-trifluoromethylthionbenzoate (IV) is conveniently followed by measuring the absorbance at 420 mμ of aliquots taken at appropriate times. As illustrated in Table I for the acetolysis at 125.0°, satisfactory first-order rate constants were observed. First-order rate constants, k_a, calculated from a weighted least-squares slope of a plot of log ($A - A_\infty$) *vs.* time for runs in acetic acid, acetic acid plus various salts, and aqueous ethanols are summarized in Tables II and III. Because of a side reaction which results in a slow color formation in the no-salt runs in acetic acid at 125°, the values reported under these conditions correspond to initial rate constants.

Table I

Acetolysis of *exo*-Norbornyl *p*-Trifluoromethylthionbenzoate[a] with Lithium Perchlorate[b,c]

Time, 10^{-3} sec.	A^d	% reaction	$10^4 k$, sec.$^{-1}$
...	1.020	...	...
1.67	0.789	24.3	1.64
2.63	0.690	34.8	1.59
3.84	0.570	47.3	1.64
4.16	0.559	48.6	1.57
4.53	0.507	54.0	1.68
4.81	0.490	55.8	1.66
5.22	0.479	57.0	1.59
6.01	0.438	61.3	1.55
7.07	0.387	67.5	1.53
37.0	0.071		
67.6	0.069		
		Least-squares rate constant	1.61

[a] 0.0100 *M*. [b] 0.0207 *M*. [c] At 125.0° [d] Absorbance in a 1-cm. cell at 420 mμ.

Table II

Summary of Reaction Rate Constants for *exo*-Norbornyl *p*-Trifluoromethylthionbenzoate in Acetic Acid

10^2 ester, *M*	10^2 $LiClO_4$, *M*	Temp., °C.	$10^4 k$, sec.$^{-1}$
1.00	...	140.0	1.48 ± 0.05[a]
1.06	...	125.0	0.033 ± 0.001[a]
1.06	0.19	125.0	0.37 ± 0.01
1.02	1.02	125.0	1.02 ± 0.01
1.00	2.07	125.0	1.61 ± 0.03
1.10	4.14	125.0	2.50 ± 0.01
1.06	5.15	125.0	3.21 ± 0.06
1.05	0.21[b]	125.0	0.38 ± 0.01

[a] Calculated $\Delta H^* = 31.7$ kcal./mole and ΔS^* (125°) = −3.9 e.u. [b] With 0.01 *M* LiOAc added.

Table III

Summary of Reaction Rate Constants for *exo*-Norbornyl *p*-Trifluoromethylthionbenzoate[a]

Solvent, % ethanol	Ester, 10^2 *M*	$10^4 k$, sec.$^{-1}$
70	1.12	1.76 ± 0.01
75	1.00	1.26 ± 0.02
85	5.06	0.598 ± 0.007

[a] In aqueous ethanol at 125.0°.

As illustrated in Table III the rate of solvolysis of the thion ester IV is strongly dependent on the ionizing power of the solvent. A change from 70% aqueous ethanol to 85% aqueous ethanol reduces the rate by a factor of 3. Correlating the rates in aqueous ethanol with Winstein *Y* values[15] gives an *m* of 0.45, a value consistant with an ionization process for this reaction.[16]

The addition of lithium perchlorate or lithium perchlorate plus lithium acetate increases the rate of acetolysis markedly (Table II). Although a plot of k_a *vs.* concentration of lithium perchlorate curves down slightly, an approximate fit to the linear salt effect equation gives a *b* of 1800. Apparently thion esters, like carboxylic esters,[17] are much more sensitive to salt-

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(13) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).

(14) Optically pure *exo*-norborneol has $[\alpha]\text{D}$ 2.85–3.02° (neat, 1 dm.): J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

(15) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(16) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).

(17) S. Winstein, E. C. Friedrich, and S. Smith, *ibid.*, **86**, 305 (1964).

promoted ionization than arenesulfonate esters which gave b values in the range of 10 to 20 in acetic acid.[18] The large salt effect observed with the thion ester IV supports the thesis that the acetolysis is limiting in character.

Products.—The products from the solvolysis of the thion ester IV were examined by vapor phase chromatography and identified by retention time and collection from the column followed by comparison of physical properties with samples prepared by independent routes. An internal standard added before running the v.p.c. analysis allowed the calculation of absolute yields.

As summarized in Table IV, at 140° in acetic acid 16% of thiol ester VI and 73% of *exo*-norbornyl acetate are formed. More volatile material (*ca.* 10%) is also formed in this reaction. In addition to markedly increasing the reaction rate lithium perchlorate changed the nature of the products. In the presence of 0.05 M lithium perchlorate no thiol ester was detected; instead 98% *exo*-norbornyl acetate was found (Table IV). Changes in the amount of ion-pair return and the nature of the products formed in salt-promoted reactions have been noted previously by Winstein and co-workers.[17]

TABLE IV

PRODUCTS FROM THE SOLVOLYSIS OF *exo*-NORBORNYL *p*-TRIFLUOROMETHYLTHIONBENZOATE IN ACETIC ACID AND AQUEOUS ETHANOL

Solvent	Temp., °C.	% thiol ester	% acetate ester
Acetic acid	140.0	16	73
Acetic acid	140.0	15.5[a]	74[a]
Acetic acid	125.0	<1	98[b]
85% ethanol	125.0	12	. . .
70% ethanol	125.0	14	. . .

[a] With added 0.01 M lithium acetate. [b] With added 0.05 M lithium perchlorate.

TABLE V

COMPARISON OF RATE OF RACEMIZATION AND RATE OF SOLVOLYSIS OF *exo*-NORBORNYL *p*-TRIFLUOROMETHYLTHIONBENZOATE[a,b]

Time, 10^{-4} sec.	A[c]	α[d]	$10^5\,k$, sec.$^{-1}$	$k_a/k\alpha$
. . .	0.492	1.43	. . .	. . .
3.45	0.312	1.00	1.52	1.01
6.90	0.214	0.69	1.43	1.01
10.60	0.133	0.43	1.56	1.00
49.00	0.047	0.00		
		Av.	1.50	1.01

[a] 0.102 M. [b] In acetic acid at 140.0°. [c] Absorbance in a 2-mm. cell at 420 mμ. [d] Rotation in a 1-dm. tube at the sodium D line.

Comparison of Racemization and Solvolysis Rates.—The rate of acetolysis, k_a, and the rate of racemization, k_α, of optically active *exo*-norbornyl *p*-trifluoromethylthionbenzoate were determined simultaneously by following the absorbance at 420 mμ and the optical activity on each aliquot in a kinetic run. As illustrated in Table V the rate of disappearance of thion ester is equal to the rate of racemization. Apparently ion-pair return on oxygen to form racemic thion ester, analogous to the behavior of the bromobenzenesulfonate ester,[5] is not important under these conditions.

These data indicate that the rate of disappearance of the thion ester grouping is a good measure of the rate of ionization with this system.

Stereochemistry of Product Formation.—The final rotation in kinetic runs was 0.00 ± 0.02° corresponding to essentially complete racemization of the products. Isolation of the thiol ester by preparative v.p.c. and direct examination of it for optical activity gave a rotation of 0.00 ± 0.02° corresponding to at least 97% racemization. Optically active thiol ester is stable to the reaction conditions (see Experimental).

The nucleophilic sulfur atom of the anion is apparently unable to distinguish between the two centers of the norbornyl cation. Corey, *et al.*,[19] were also unable to capture an unsymmetrical norbornyl cation within an ion pair using a *m*-carboxybenzenesulfonate anion. These data are most easily accommodated by a symmetrical cation intermediate.

Racemic thiol ester would also be obtained if the reaction proceeded by way of a Chugaev-like elimination to give norbornene and thiobenzoic acid followed by addition of thiobenzoic acid to the olefin to yield thiol ester. Aside from differences in polar character, this route can be distinguished from ionization processes since the ion-pair route equilibrates carbons 1 and 2 while the elimination–readdition route would tend to equilibrate carbons 2 and 3. Carbons 1 and 2 were labeled by reduction of norcamphor with lithium aluminum deuteride to 2-*d*-*endo*-norborneol followed by solvolysis of the corresponding *p*-bromobenzenesulfonate ester in aqueous acetone to give *exo*-norborneol containing 0.94 atom % deuterium by combustion analysis. The n.m.r. spectrum of the thion ester prepared from this labeled *exo*-norborneol indicated 0.28 atom % deuterium at carbon 1 and 0.66 atom % deuterium at carbon 2. The isolated thiol ester from the acetolysis of the deuterated thion ester and 0.48 atoms of deuterium in the 2-*endo* position by n.m.r. This corresponds to complete equilibration of the 1 and 2 positions but essentially no equilibration of the 2 and 3 positions. This is the result expected for ionization to a symmetrical cation followed by ion-pair return on sulfur to form thiol ester.

It is interesting to note that the deuterium in the 2-*endo* position in the isolated thiol ester is not diluted with hydrogen from 6,2 shift. Apparently, ion-pair return on sulfur in this system is fast relative to equilibration of the 6,2 hydrogens. In mixed SbF_5–SO_2–SO_2F_2 at −120° a rate constant of greater than 3×10^5 sec.$^{-1}$ has been reported[20] for 6,2 hydrogen shift.

Experimental

***p*-Trifluoromethylthiobenzoyl Chloride.**—*p*-Trifluoromethylthiobenzoyl chloride was prepared by an adaptation of the method of Staudinger.[21] To a solution of *p*-bromobenzotrifluoride (100 g., 0.45 mole) in 200 ml. of ether was added 290 ml. of a 15% *n*-butyllithium solution in hexane (Foote Mineral Co.) by means of a syringe. The solution was stirred for 15 min., then added to 250 ml. of carbon disulfide at −40° in a nitrogen

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[18] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

[19] E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963).

[20] M. Saunders, P. v. R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5681 (1964).

[21] H. Staudinger and J. Siegmant, *Helv. Chim. Acta*, **3**, 824 (1920).

atmosphere by means of an L-shaped tube connecting two round-bottom flasks. The lithium *p*-trifluoromethyldithiobenzoate was extracted with 1 l. of water, the aqueous solution was washed with two 500-ml. portions of methylene chloride and neutralized with hydrochloric acid (50 ml., 12 *N*), and the liberated violet *p*-trifluoromethyldithiobenzoic acid was extracted with 500 ml. of ether. The ether solution was dried over magnesium sulfate, filtered, and concentrated to *ca.* 300 ml. Thionyl chloride (100 g., 1.3 mole) was added and the solution was refluxed overnight. Distillation at reduced pressure gave 19.8 g. (20% yield) of the purple *p*-trifluoromethylthiobenzoyl chloride, b.p. 39–40° (0.3 mm.), m.p. 10°.

Anal. Calcd. for $C_8H_4ClF_3S$: C, 42.77; H, 1.79. Found: C, 42.56; H, 1.88.

exo-**Norbornyl** *p*-**Trifluoromethylthionbenzoate.**—To a solution of *exo*-norborneol (5.0 g., 0.045 mole, Aldrich Chemical Co.) in 50 ml. of tetrahydrofuran, freshly distilled from lithium aluminum hydride at 0° was added 28.5 ml. of a 15% *n*-butyllithium in hexane solution (Foote Mineral Co.). The solution was stirred for 30 min. at 0°. *p*-Trifluoromethylthiobenzoyl chloride (7.8 g., 0.035 mole) was added and the solution was stirred for 1 hr. at room temperature. To this solution was added 100 ml. of ether and the resulting mixture was washed with two portions of water, dried over magnesium sulfate, and filtered; the ether was removed by distillation, leaving 11.2 g. of a red oil. The red oil was dissolved in 2 vol. of pentane and chromatographed on *neutral* alumina. The column was eluted with pentane until all the yellow *exo*-norbornyl *p*-trifluoromethylthionbenzoate was removed. The pentane was removed by distillation and the yellow oil was dried on a rotary evaporator at 1 mm. overnight leaving 5.8 g. (56% yield), λ_{max}^{HOAc} 420 mμ (ε 110).

Anal. Calcd. for $C_{15}H_{15}F_3OS$: C, 59.98; H, 5.03; S, 10.68; mol. wt., 300. Found: C, 59.98; H, 5.14; S, 10.43; mol. wt., 284.

exo-**Norbornyl Acetate.**—*exo*-Norbornyl acetate was prepared as described by Winstein.[22] Distillation at reduced pressure gave 5.8 g. (83% yield) of *exo*-norbornyl acetate, b.p. 34–35° (0.65 mm.), $n^{25}\mathrm{D}$ 1.4568 [lit.[21] b.p. 34–35° (0.65 mm.), $n^{25}\mathrm{D}$ 1.4565]. The substance was homogeneous by vapor phase chromatography on a 20% XF-1150 on a Chromosorb P column at 90°.

exo-**Norbornyl** *p*-**Trifluoromethylthiolbenzoate.**—Potassium hydroxide (5.4 g., 0.096 mole) was dissolved in 90% aqueous ethanol and hydrogen sulfide was bubbled through the solution until it was neutral to phenolphthalein. The solution was cooled to 0° and *p*-trifluoromethylbenzoyl chloride (10.0 g., 0.048 mole) was added slowly as described by Noble and Tarbell.[23] The solvent was removed by distillation and a solution of *endo*-norbornyl *p*-bromobenzenesulfonate, prepared as described by Winstein (10.0 g., 0.03 mole), in 150 ml. of acetonitrile was added and the resulting solution was refluxed for 22 hr. To this solution was added 100 ml. of ether and the resulting solution was washed with two portions of aqueous sodium bicarbonate and two portions of water and dried over magnesium sulfate; the solvent was removed by distillation. Distillation at reduced pressure gave 4.2 g. (46% yield) of *exo*-norbornyl *p*-trifluoromethylthiolbenzoate, b.p. 125–130° (0.25 mm.), m.p. 46–47° (from aqueous ethanol). The product was homogeneous by vapor phase chromatography on a 20% XF-1150 on Chromosorb P column.

Anal. Calcd. for $C_{15}H_{15}F_3OS$: C, 59.98; H, 5.03; S, 10.68. Found: C, 60.18; H, 5.25; S, 10.68.

Optically Active *exo*-**Norbornyl** *p*-**Trifluoromethylthionbenzoate.**—*exo*-Norborneol was resolved as described by Winstein and Trifan[24] yielding optically active *exo*-norborneol, m.p. 125–126° (lit.[22] m.p. 127–128°), $[\alpha]^{25}\mathrm{D}$ −1.72 (*c* 9.92, chloroform) (lit.[22] $[\alpha]^{24}\mathrm{D}$ −2.44°, chloroform). Optically active *exo*-norbornyl *p*-trifluoromethylthionbenzoate was prepared as described for the racemic ester, $[\alpha]^{29}\mathrm{D}$ +8.18° (*c* 10.26, chloroform), λ_{max}^{HOAc} 420 (ε 110).

Anal. Calcd. for $C_{15}H_{15}F_3OS$: C, 59.98; H, 5.03. Found: C, 59.79; H, 5.05.

Optically Active *exo*-**Norbornyl** *p*-**Trifluoromethylthiolbenzoate.**—*endo*-Norborneol (116.5 g., 1.04 moles), prepared from norcamphor and lithium aluminum hydride, was resolved as described by Winstein and Trifan,[22,24] yielding optically active *endo*-norborneol, $[\alpha]^{25}\mathrm{D}$ +1.59° (*c* 9.44, chloroform) (lit.[24] $[\alpha]^{24}\mathrm{D}$ 1.89°). Optically active *endo*-norbornyl *p*-bromobenzenesulfonate was prepared from optically active *endo*-norborneol and *p*-bromobenzenesulfonyl chloride as described by Winstein,[24] $[\alpha]^{25}\mathrm{D}$ −9.90° (*c* 9.96, chloroform) (lit.[24] $[\alpha]^{25}\mathrm{D}$ −11.78°). Treatment of the arenesulfonate ester with potassium *p*-trifluoromethylthiobenzoate gave optically active *exo*-norbornyl *p*-trifluoromethylthiolbenzote isolated as described previously for the racemic compound (in 43% yield), b.p. 126–130° (0.25 mm.), m.p. 46–47°, $[\alpha]^{25}\mathrm{D}$ +9.83°. The infrared and n.m.r. spectra of this compound were identical with those of the racemic material.

exo-**Norbornyl-1,2-*d*** *p*-**Trifluoromethylthionbenzoate.**—To a slurry of lithium aluminum deuteride (1.7 g., 0.044 mole) in 50 ml. of ether was added a solution of norcamphor (15 g., 0.138 mole) in 50 ml. of ether. The slurry was stirred for 15 min. and 3.4 ml. of water was added followed by 2.7 ml. of 10% aqueous sodium hydroxide. The mixture was stirred for 1 hr. and filtered and the precipitate was washed with 100 ml. of ether. The ether solution was concentrated and added to a solution of *p*-bromobenzenesulfonyl chloride (41 g., 0.160 mole) in 100 ml. of pyridine at 0°, and the resulting solution was refrigerated overnight. The pyridine solution was poured into 100 ml. of dilute hydrochloric acid and the mixture was extracted with ether. The ether solution was washed with dilute hydrochloric acid, aqueous sodium bicarbonate, and water and dried over magnesium sulfate, and the ether was removed by distillation, leaving 36.0 g. (79% yield) of the crude *endo*-norbornyl-2-*d* *p*-bromobenzenesulfonate. *endo*-Norbornyl-2-*d* *p*-bromobenzenesulfonate (36.0 g., 0.109 mole) was dissolved in 75% aqueous acetone containing 10 g. of powdered calcium carbonate and the solution was refluxed for 48 hr., at which time 400 ml. of water was added and the resulting mixture was extracted with three 50-ml. portions of ether. The ether solution was dried over magnesium sulfate, concentrated, and added to a solution of *o*-phthalic anhydride (14.8 g., 0.100 mole) in 50 ml. of pyridine, and the resulting solution was heated on a steam bath for 4 hr. The pyridine solution was poured into iced dilute hydrochloric acid and the mixture was extracted with benzene. The benzene solution was dried over magnesium sulfate and the benzene was removed by distillation leaving an oil. The oil was crystallized from ethyl acetate–pentane, yielding 14.1 g. (58% yield) of *exo*-norbornyl-1,2-*d* acid phthalate, m.p. 80–81° (lit.[24] 80.5–83.5°). The *exo*-norbornyl-1,2-*d* acid phthalate (14.1 g., 0.057 mole) was dissolved in 100 ml. of 10% aqueous sodium hydroxide and steam distilled. To this steam distillate was added sodium chloride and the resulting solution was extracted with two 100-ml. portions of pentane. The pentane solutions were combined and dried over magnesium sulfate, and the pentane was removed by distillation, leaving 6.8 g. (44% yield based on norcamphor) of *exo*-norborneol-1,2-*d*, m.p. 126–127°. The *p*-trifluoromethylthionbenzoate of this alcohol was prepared in the usual manner. Deuterium analysis by combustion showed 0.94 atoms of deuterium/molecule. The n.m.r. spectra showed relative integrated areas for the 2-*endo*, aromatic, and the remaining norbornyl hydrogens to be 1:11.7:28.7 which corresponds to 0.66 atoms of deuterium in the 2-*endo* position and, by difference, 0.28 atoms of deuterium in the remainder of the molecule.

Solvents.—Acetic acid was purified in the usual manner[16] and ethanol was purified as described by Fieser.[25]

Kinetic Procedure.—All reactions were run in sealed deoxygenated ampoules thermostated in a Carbowax-400 bath controlled to ±0.03°. At appropriate times, samples were removed from the bath, cooled, and analyzed for absorption at the appropriate wave length with a Beckman DU spectrophotometer equipped with a photomultiplier. A slit width of 0.3 mm. was used throughout. For the rate of racemization, a Carl Zeiss polarimeter was used to obtain the optical rotation at the sodium D line. A 2-dm. polarimeter tube was used.

Product Analysis.—The quantitative product analysis was done by vapor phase chromatography. In a typical experiment, 0.7553 g. of *exo*-norbornyl *p*-trifluoromethylthionbenzoate was dissolved in 25 ml. of acetic acid and the solution was degassed. The solution was heated in a Carbowax bath at 140.0° for 130 hr. and cooled, and 0.2300 g. of 4,4′-dimethylbenzophenone and

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[22] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 (1952).

[23] D. Noble and D. S. Tarbell, *Org. Syn.*, **32**, 101 (1952).

[24] S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952).

[25] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, pp. 286.

125 ml. of water were added. The resulting solution was extracted with three 50-ml. portions of pentane. The pentane solution was washed with a dilute sodium bicarbonate solution, dried over magnesium sulfate, and decanted into a one-necked round-bottom flask. The pentane solution was concentrated at 45–50° through a 1-ft. Vigreux column. A 0.02–0.05-ml. sample was injected into a XF-1150 (silicon nitrile) on Chromosorb P column at 90°. After the *exo*-norbornyl acetate came off the column, the temperature was raised to 170°. The areas for the various peaks were measured by means of a disk chart integrator. All of the product analyses as well as the controls on the extraction procedure were done in this manner. The extraction procedure was found to be accurate to ±2% for three determinations. For the runs in aqueous ethanol, the 0.02–0.05-ml. sample of the pentane extract was injected into the column at 170°.

Stability Determinations.—In a typical experiment, 0.3124 g. of *exo*-norbornyl *p*-trifluoromethylthionbenzoate and 0.1823 g. of *exo*-norbornyl *p*-trifluoromethylthiolbenzoate were dissolved in 10 ml. of acetic acid. The solution was degassed and heated at 140.0° for 130 hr. This solution was analyzed by v.p.c. as described previously. The analysis showed 0.235 g. of thiol ester which corresponds to all of the added thiol ester as well as an additional 17% formed in the solvolysis reaction. All of the stability runs in acetic acid and with added lithium perchlorate were done in this manner.

To check the stability of *exo*-norbornyl *p*-trifluoromethylthiolbenzoate in aqueous ethanol, 0.7509 g. of the thiol ester was dissolved in 85% aqueous ethanol and the solution was heated at 125° for 13.5 days. The solution was analyzed by vapor phase chromatography as described previously. Only 75% of the original thiol ester was detected in this experiment.

Optical Stability of *exo*-Norbornyl *p*-Trifluoromethylthiolbenzoate.—A solution of 0.06 g. of optically active *exo*-norbornyl *p*-trifluoromethylthiolbenzoate and 0.272 g. of *exo*-norbornyl *p*-trifluoromethylthionbenzoate in 5 ml. of acetic acid, α +0.26 ±0.02°, was heated at 140° for 70 hr. at which time the optical rotation was 0.25 ± 0.02°. A 1-dm. polarimeter tube was used to determine the optical rotation.

Exchange.—A solution of 0.357 g. of *exo*-norbornyl *p*-trifluoromethylthionbenzoate and 0.615 g. of potassium thiobenzoate in 10 ml. of acetic acid was heated at 140° for 130 hr. By vapor phase chromatography, no *exo*-norbornyl thionbenzoate was detected under conditions such that 1% was easily observed.

Isolation of Thiol Ester.—A solution of 3.004 g. of optically active *exo*-norbornyl *p*-trifluoromethylthionbenzoate in 50 ml. of acetic acid, α +2.80°, was heated at 140° for 130 hr. The solution was cooled, 250 ml. of water was added, and the resulting solution was extracted with two 100-ml. portions of pentane. The pentane extract was washed with a dilute sodium bicarbonate solution, dried over magnesium sulfate, and decanted into a one-necked round-bottom flask. The pentane solution was concentrated to *ca.* 10 ml. at 45–50° through a 1-ft. Vigreux column. A 0.3–0.5-ml. sample was injected into an XF-1150 on Chromosorb P column at 170°. The *exo*-norbornyl *p*-trifluoromethylthiolbenzoate (0.314 g.) was collected and dissolved in 5 ml. of acetic acid. The resulting solution had an optical rotation of 0.00 ± 0.02° in a 1-dm. tube. The thiol ester was found to be optically stable under the v.p.c. conditions.

An Electron Impact Study of Norbornenyl and Nortricyclyl Chlorides

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An electron impact study of norbornene, *endo*- and *exo*-5-chloro-2-norbornene, and 3-chloronortricyclene is presented. The fragmentation pattern of each of these compounds is discussed. Appearance potentials of the major ions have been measured and are compared for each compound.

For the last 15 years bicyclo[2.2.1] systems have been the subject of extensive investigations; particular interest has centered around bicyclic cations as reactive intermediates.[2] There remain many questions about the nature of these species, one of the most fundamental of which concerns the ease of ionization or dissociation of the parent compound as a function of molecular structure and reaction environment. Electron impact studies at low pressures can furnish fundamental information about primary ionization and dissociation processes of these compounds in the absence of solvent and also provide useful thermochemical data.[3] Although gaseous ions can be expected to behave differently from ions in solution, many results from such investigations may be pertinent to reactions in condensed phases.

We have carried out an electron impact study of *exo*- and *endo*-5-chloro-2-norbornene and 3-chloronortricyclene, all of which have previously been investigated in solution. It has been observed, for instance, that the *exo*-chloronorbornene solvolyzes much more rapidly than its *endo* epimer, the products from both isomers being predominantly nortricyclic compounds.[4,5] In our work we have been concerned primarily with the fragmentation patterns of these chloro compounds and the relative appearance potentials of several ions, the most significant of which are $C_7H_9Cl^+$, $C_7H_9^+$, $C_6H_7^+$, and $C_5H_6^+$. Using our observed appearance potentials for the C_5H_6 cation, we have also estimated the heats of formation of the compounds.

Experimental

The mass spectra and appearance potentials were measured on a Consolidated Electrodynamics Model 21-103C mass spectrometer with the ion source at 225° and the inlet system at ambient temperature. A rhenium filament was used in the ion source. Mass spectra were obtained using 70-v. electrons and voltage scanning. The method of measuring appearance potentials has been previously described.[6]

An Aerograph Model A-90-P (Wilkens Instrument and Research, Inc.) was used for all gas chromatography. Infrared spectra were taken on a Perkin-Elmer Model 137B Infracord; samples were neat except for norbornene which was dissolved in carbon tetrachloride. N.m.r. spectra were obtained on a

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