solution is slowly acidified by the addition of concentrated sulfuric acid until 5 parts per volume of aqueous solution have been added. This mixture is distilled to remove TFA, which will distil along with some water. The fraction between 71 and 105° is collected, treated again with sulfuric acid, and redistilled. Anhydrous TFA results; bp 71.2°.

All compounds used were of reagent grade. The arenes were purified by distillation or recrystallization; the TFA was distilled prior to use.

**Registry No.**—TFA, 76-05-1; $NaNO_3$, 7631-99-4; $NaNO_2$, 7632-00-0; toluene, 108-88-3; phenol, 108-95-2; benzene, 71-43-2.

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# Study of the Trifluoroethanolysis of Cyclobutylcarbinyl and Related *p*-Bromobenzenesulfonates


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Our previous investigation[2] of the solvolytic behavior of cyclobutylcarbinyl brosylate (4-OBs) and related compounds revealed the kinetic and product distribution data were accommodated by Scheme I where solvent capture of a carbon-bridged species accounts for at least 99% of the acetolysis product. Justification for the intermediacy of a carbon-bridged species was based upon (1) the presence of 99% ring-expanded product, (2) the absence of a significant 1-ring substituent effect upon solvolytic reactivity, (3) the absence of cyclopentene product, and (4) the establishment of a good correlation between log $k_t$ for 4-OBs and log $k_t$ for neophyl tosylate.

Prompted by these findings, we extended our investigation to include a product distribution study in 2,2,2-trifluoroethanol (TFE) of the following cycloalkylcarbinyl brosylates. This paper reports the analysis of the product distribution data according to Scheme I in an effort to gain insight into the role of the solvent in the product partitioning process.

$(CH_2)_nCHCH_2OBs$

$n + 1 = 4$, 4-OBs
$n + 1 = 5$, 5-OBs
$n + 1 = 6$, 6-OBs

The product data are summarized in Table I. The vapor-phase chromatographic separations and characterizations of products were carried out on a Carbowax 20M–silver nitrate column. Urea was used as a buffer and product studies were conducted at the same temperature as the kinetic investigations.[2] Previously reported[3] stability studies have established that the reported products are indeed the initially formed products and not those of subsequent reactions.

On the basis[2] that solvolysis occurs by one or more of the discrete pathways outlined in Scheme I, the data in Table II are readily obtained. It is interesting to note that the solvent change from acetic acid to TFE is characteried by a decrease in the per cent $k_s$ reaction product for all three substrates, most dramatically for 6-OBs, which confirms the unique ability of TFE to accentuate neighboring group participation under nonacidic conditions.[3d,4-6] This result is readily accommodated by the interesting solvent properties of TFE,[7-10] particularly its enhanced ionizing ability relative to acetic acid without any significant change in solvent nucleophilicity,[10,11] for a substantial body of information[12-14] has accumulated in support of increasing anchimeric assistance (relative to solvent assistance) with increasing ionizing strength of the solvent in solvolysis reactions.

Focusing our attention on the product data summarized in Table I, we observe that the change from acetic acid to TFE results in a considerable increase in the amount of ring-expanded olefin obtained from the solvolysis of 4-OBs and 5-OBs. Thus the trifluoroethanolysis of 4-OBs yields

Scheme I

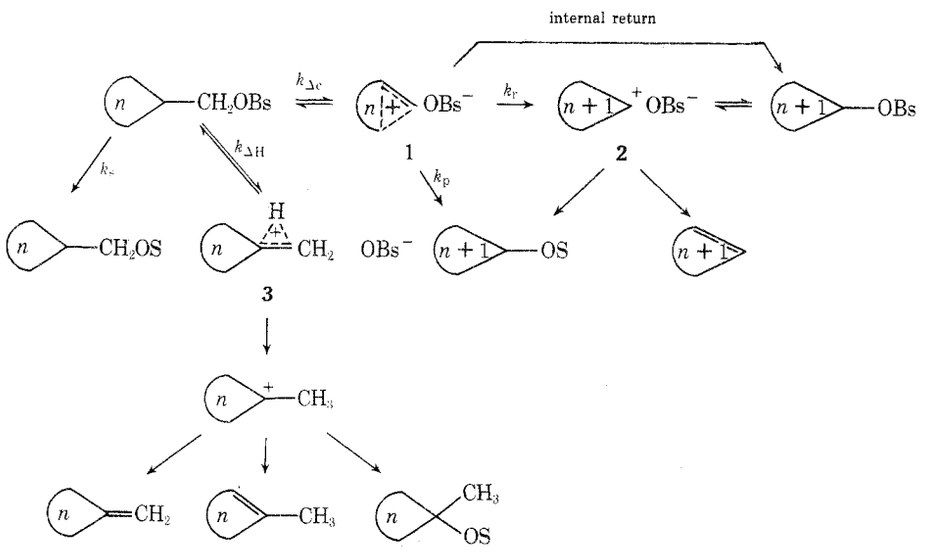
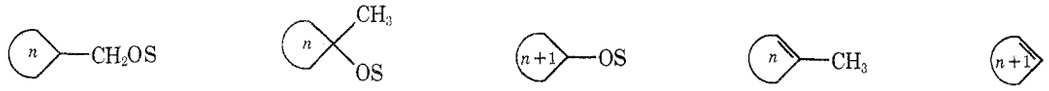


**Table I**
**Per Cent Product Data for Investigated Substrates[a,b]**



| Substrate | Solvent | A | B | C | D | E |
|---|---|---|---|---|---|---|
| 4-OBs | AcOH[c] | 1 | | 99 | | |
| | $CF_3CH_2OH$ | | | 50 | | 50 |
| c-$C_5H_9$OBs | AcOH[c] | | | 80 | | 20 |
| | $CF_3CH_2OH$[d] | | | 24 | | 76 |
| 5-OBs | AcOH[c] | 4 | 3 | 91 | 1 | 1 |
| | $CF_3CH_2OH$ | | | 34 | | 66 |
| c-$C_6H_{11}$OTs | AcOH[e] | | | 15 | | 85 |
| | $CF_3CH_2OH$ | | | 20 | | 80 |
| 6-OBs | AcOH[c] | 47 | 13[f] | | 40[f] | |
| | $CF_3CH_2OH$ | 8 | 56 | | 12[g] | |

[a] Acetolysis at 75°; 2,2,2-trifluoroethanolysis at 55°. [b] In acetolysis, OS = OAc, and in trifluoroethanolysis, OS = $OCH_2CF_3$. [c] Taken from ref 2. [d] Taken from ref 3f; 97% trifluoroethanol–3% water. [e] Taken from data of J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951). [f] Under reaction conditions, there is some conversion of 1-methylcyclohexyl acetate to 1-methylcyclohexene. [g] Also 24% methylenecyclohexane.

**Table II**
**Partitioning of Solvolysis Reactions According to Scheme I**

| Substrate | Solvent | % $k_s$ | % $k_{\Delta H}$ | % $k_{\Delta c}$ |
|---|---|---|---|---|
| 4-OBs | AcOH[a] | 1 | 0 | 99 |
| | $CF_3CH_2OH$[b] | 0 | 0 | 100 |
| 5-OBs | AcOH[a] | 4 | 5 | 91 |
| | $CF_3CH_2OH$[b] | 0 | 66 | 34 |
| 6-OBs | AcOH[a] | 47 | 53 | 0 |
| | $CF_3CH_2OH$[b] | 8 | 92 | 0 |

[a] Data taken from ref 2 at 75°. [b] Data taken from ref 2 at 55°.

50% cyclopentene while no detectable olefin was found in the acetolysis run. Similarly, the trifluoroethanolysis of 5-OBs yields 66% cyclohexene while only 2% olefin (1% *via* $k_{\Delta H}$ pathway) was found in the acetolysis run.

In view of Bartlett's suggestion[3b] that the folded geometry of bridged intermediate **1** is unfavorable for olefin production and our corroborating observation[2] of the absence of olefin among the ring-expanded acetolysis products of 4-OBs and 5-OBs, the detection of appreciable quantities of cycloalkenes in the trifluoroethanolysis products of 4-OBs and 5-OBs is mechanistically significant. We propose that in contrast to the nearly exclusive $k_{\Delta c}^1$ pathway ($k_{\Delta c}$ followed by $k_p$) postulated for acetolysis,[2] the $k_{\Delta c}^2$ pathway ($k_{\Delta c}$ followed by $k_r$) competes with the $k_{\Delta c}^1$ pathway in the trifluoroethanolysis reactions. That is, part of the product results from solvent interaction with the carbon-bridged species **1** and part results from solvent interaction with the classical cation **2**.[15]

It can be estimated, on the basis that all cyclopentene product is from **2** and the *E*/*S* ratio observed for the trifluoroethanolysis of cyclopentyl brosylate[3e] accurately represents the product partitioning from **2**, that 34% of 4-OBs suffers trifluoroethanolysis by $k_{\Delta c}^1$ and 66% by $k_{\Delta c}^2$ pathways. Likewise it can be estimated that 17% of 5-OBs suffers trifluoroethanolysis by $k_{\Delta c}^1$ and 83% by $k_{\Delta c}^2$ pathways.

This solvent-induced change in reaction pathway is understandable in terms of the following considerations. First, Winstein, *et al.*,[17] have supplied considerable evidence for the involvement of at least three different types of carbonium ion intermediates (the intimate (or tight) ion pair, the solvent-separated ion pair, and the dissociated ion) in solvolysis reactions and they have also supplied evidence that the solvent may enter the picture as a nucleophile (or base) at any of the several stages of reaction intermediates as depicted in Scheme II. Second, there is some

**Scheme II**

$$RX \rightleftharpoons R^+X^- \rightleftharpoons R^+\|X^- \rightleftharpoons R^+ + X^-$$

product set 1 product set 2 product set 3

evidence for the involvement of a later stage carbonium ion intermediate in the trifluoroethanolysis product step than that involved in the acetolysis product step. For instance, Shiner[18] has argued from $\alpha$-secondary deuterium isotope effects on reactivity of benzyl halides in solvolysis reactions that the products are mostly derived from the solvent-separated ion pair in TFE instead of the intimate ion pair as in acetic acid. And third, in accord with generally accepted theory, the high ionizing strength[19] and low nucleophilicity[10] of TFE should lead to greater structural reorganization of the carbonium ion than in acetic acid before the product step. In summary, then, we propose solvolysis of 4-OBs or 5-OBs in TFE generates a looser ion pair than in acetic acid and that with such a looser ion pair $k_r$ is competitive with $k_p$.

## Experimental Section

Nuclear magnetic resonance spectra were obtained on a Hitachi Perkin-Elmer R-24 instrument with tetramethylsilane as internal standard. A Beckman GC-4 chromatographic instrument equipped with a thermal conductivity detector, a Disc automatic integrator-printer, and a 24 ft × 0.25 in. column of 20% Carbowax 20M 2% $AgNO_3$ on Chromosorb W, AW-DMCS (45–60 mesh), was used for analytical gc work.

**Cyclobutylcarbinyl (4-OBs), cyclopentylcarbinyl (5-OBs),** and **cyclohexylcarbinyl (6-OBs) brosylate** were the same materials as previously described.[2]

**Cyclopentyl brosylate** was prepared, by published procedure,[2] in 35% yield: mp (after two recrystallizations from 12:1 petroleum ether (bp 30–60°)–ethyl acetate) 45–46° (lit.[20] mp 45.8–46.6°).

**Cyclohexyl *p*-toluenesulfonate** was prepared, by published procedure,[21] in 75% yield: mp (after two recrystallizations from petroleum ether (bp 30–60°), 44.3–44.9° (lit.[22] mp 44.4–44.8°).

**Preparation of Reference Olefins.** Cyclopentene, cyclohexene, cycloheptene, 1-methylcyclohexene, and methylenecyclohexane were purchased from Aldrich Chemical Co. and used as received. 1-Methylcyclopentene was the same material as previously described.[2]

**Solvent.** 2,2,2-Trifluoroethanol (Aldrich Chemical Co.) was redistilled prior to use and analytical purity checked by gc and nmr.

**Product Studies. A. Cyclobutylcarbinyl Brosylate (4-OBs).** Cyclobutylcarbinyl brosylate (5 mmol) was dissolved in sufficient solvent (containing 7.5 mmol of urea) to give 25 ml of solution. Five-milliliter aliquots were transferred to 10 ml ampoules, sealed under $N_2$ and immersed in a constant temperature bath at 55°. After 10 half-lives, the ampoule contents were poured into 50 ml of water and the resultant mixture was extracted once with a 5-ml portion of methylene chloride. The extract was washed four times with 10-ml portions of cold water and dried over magnesium sulfate. The crrude extract on analysis by gas chromatography (50°, 50 ml/min He flow rate) gave rise to two peaks, A (2.2 min retention time) and B (6.3 min retention time), with 1:1 relative peak areas, in addition to the air and solvent peaks. Peak A was identified as cyclopentene by comparison of retention time with that of an authentic sample. Peak B was identified as cyclopentyl 2,2,2-trifluoroethyl ether by nmr analysis: $\delta$ 3.70 (q, 2 H, $OCH_2CF_3$)[3d,10,16] and 1.5–2.0 (broad 8 H, ring protons).

**B. Cyclopentylcarbinyl Brosylate (5-OBs).** Cyclopentylcarbinyl brosylate was solvolyzed as in section A. After 10 half-lives, the ampoule contents were poured into 50 ml of water and the resultant mixture was extracted three times with 25-ml portions of methylene chloride. The combined extracts were washed three times with 30-ml portions of cold water and dried over anhydrous sodium sulfate, and most of the solvent was removed by distillation with a Nester-Faust NFA-200 autoannular still. The residue on analysis by gas chromatography (60°, 40 ml/min He flow rate) gave rise to two peaks, A (2.5 min retention time) and B (7.8 min retention time), with 1.9:1.0 relative peak areas, in addition to the air and solvent peaks. Peak A was identified as cyclohexene by comparison of retention time with that of an authentic sample. Peak B was identified by nmr analysis as cyclohexyl 2,2,2-trifluoroethyl ether: $\delta$ 3.73 (q, 2 H, $OCH_2CF_3$)[3d,10,16] and 3.2–3.5 (broad, 1 H, $C_2CHOCH_2CF_3$).[3d]

**C. Cyclohexylcarbinyl Brosylate (6-OBs).** Cyclohexylcarbinyl brosylate was solvolyzed and worked up as in section B. The residue on analysis by gas chromatography (60°, 40 ml/min He flow rate) gave rise to four peaks, A (3.0 min retention time), B (3.3 min retention time), C (9.3 min retention time), and D (12.4 min retention time), with 2.8:1.4:6.6:1.0 relative peak areas, in addition to the air and solvent peaks. Peaks A and B were identified as methylenecyclohexane and 1-methylcyclohexene respectively by comparison of retention times with those of authentic samples. Peak C was isolated by preparative gas chromatography and identified by nmr analysis as 1-methylcyclohexyl 2,2,2-trifluoroethyl ether: $\delta$ 3.70 (q, 2 H, $OCH_2CF_3$)[3d,10,16] and 1.1 (s, 3 H, $CCH_3$). Peak D was identified as cyclohexylmethyl 2,2,2-trifluoroethyl ether on the basis of retention time and nmr analysis of peak C fraction.

**D. Cyclohexyl Tosylate.** Cyclohexyl tosylate was solvolyzed as in section B. The solvolysis solution was then injected into the gas chromatograph, giving two peaks, A and B, with 4.0:1.0 relative peak areas, in addition to a very large solvent peak. By comparison with the chromatograms obtained in section B, A and B were identified as cyclohexene and cyclohexyl 2,2,2-trifluoroethyl ether, respectively.

**Registry No.**—4-OBs, 51108-24-8; 5-OBs, 38806-24-5; 6-OBs, 51108-25-9; c-$C_6H_{11}OTs$, 953-91-3.

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# Mobile Keto Allyl Systems. XVI.[1] The Thermal Decomposition of 2-(α-*N*-Methyl-*tert*-butylaminobenzyl)-1-indenone A Deamination–Rearrangement


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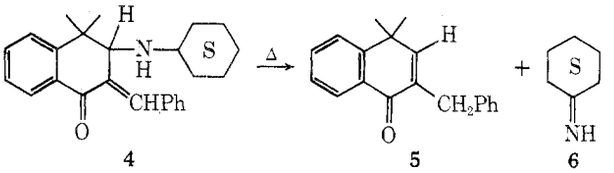
The first reported thermal decomposition of a β-keto allyl amine resulting in a deamination–rearrangement was that by Maury and Cromwell[2] in which 2-(α-diisopropylaminobenzyl)-1-indenone (**2a**) was found to form 2-benzal-1-indanone (**3**) upon heating and what was tentatively identified by vpc as diisopropylamine. Since that initial report Glaros and Cromwell[3,4] have studied extensively the thermal decomposition of the related β-keto allyl amine **4** and have shown that the decomposition proceeds *via* a retroene mechanism producing α,β-unsaturated ketone **5** and presumably imine **6.** In view of these previous results a rein-

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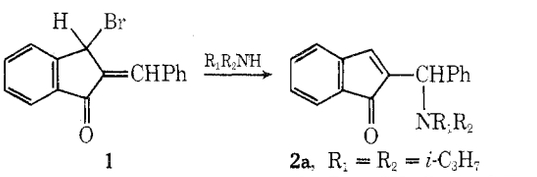
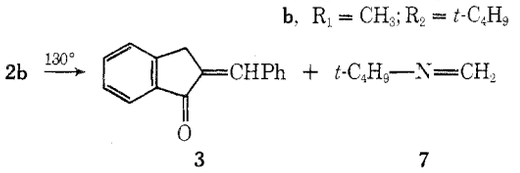
vestigation of the thermal rearrangment of compounds related to **2a** was undertaken. The results of this study for 2-(α-*N*-methyl-*tert*-butylaminobenzyl)-1-indenone (**2b**) are the subject of the present paper.

When **2b,** prepared by the reaction of *N*-methyl-*tert*-butylamine with 3-bromo-2-benzal-1-indanone[5] (**1**), was heated in a sealed tube at 130° for 3 hr 2-benzal-1-indanone (**3**) was isolated in 85% yield. In addition evidence was obtained for the existence of *N*-methylene-*tert*-butylamine (**7**) as a coproduct. Treatment of the decomposition




1 2a, $R_1 = R_2 = i\text{-}C_3H_7$
b, $R_1 = CH_3$; $R_2 = t\text{-}C_4H_9$

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