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Semipinacol Rearrangements Involving Trifluoromethylphenyl Groups[1]

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Received August 23, 1976

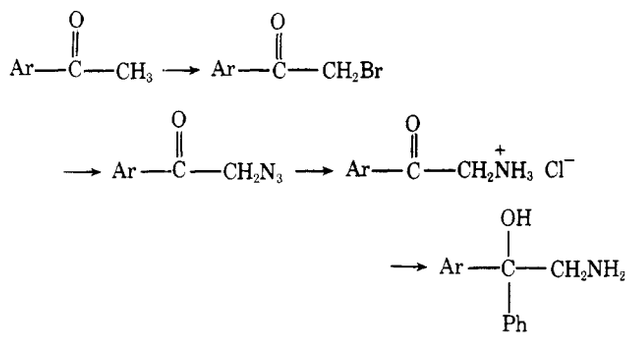
Semipinacolic deamination of 2-amino-1-(3-trifluoromethylphenyl)-1-phenylethanol (1) with sodium nitrite in aqueous acetic acid yields 3′-trifluoromethyldeoxybenzoin (3) and 3-trifluoromethyldeoxybenzoin (4). The migratory aptitude of the *m*-trifluoromethylphenyl group (phenyl = 1.0) is 0.47 at 0 °C and 0.39 at 25 °C. Similarly, deamination of 2-amino-1-(4-trifluoromethylphenyl)-1-phenylethanol (2) yields 4′-trifluoromethyldeoxybenzoin (5) and 4-trifluoromethyldeoxybenzoin (6). The migratory aptitude of the *p*-trifluoromethylphenyl group is 0.30 at 0 °C.

Little information is available regarding the behavior of trifluoromethylphenyl groups in pinacol-type reactions.[2] Our interest in deaminative rearrangements has led us to investigate semipinacol rearrangements of 2-amino-1-(3-trifluoromethylphenyl)-1-phenylethanol (1) and 2-amino-1-(4-trifluoromethylphenyl)-1-phenylethanol (2).

Results

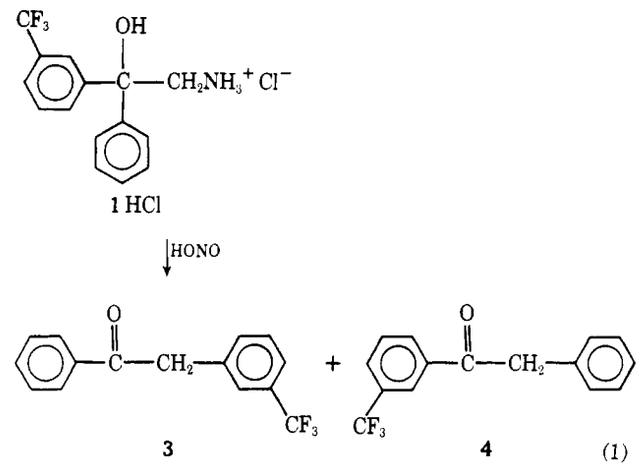
The amino alcohols were synthesized according to the general outline of Scheme I (see Experimental Section).

Scheme I



Ar = *m*- or *p*-$CF_3C_6H_4$; Ph = C_6H_5

Deamination of the meta-substituted amino alcohol hydrochloride, 1 HCl, was carried out with sodium nitrite in aqueous acetic acid at 0 °C[3] and at 25 °C (eq 1). The ketones 3 and 4 (combined yield 77% of theoretical at 0 °C) were separated from nonketonic products by column chromatography on alumina, and the ratios of 3 to 4 were determined by ^1H NMR and also by ^{19}F NMR spectroscopy using comparisons with authentic samples of 3 and 4 independently prepared (see Experimental Section). Results are summarized in Table I. The ketones were shown to be stable to the deamination conditions.

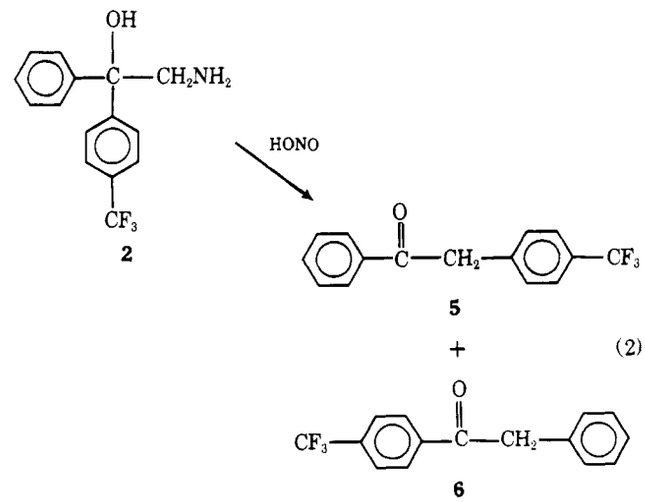


1 HCl

HONO

3 + 4 (1)

Deamination of the para-substituted amino alcohol 2 was carried out with sodium nitrite at 0 °C in aqueous acetic acid (eq 2). The ketonic fraction (67% of theoretical) was isolated



2 → HONO → 5 + 6 (2)

Table I. Ketone Composition from Amino Alcohol Deaminations

Amino alcohol	Temp, °C	Ketone	Percentage (migratory group)	Migration ratio aryl/phenyl
1	0	3	32 (m-$CF_3C_6H_4$)	3/4 = 0.47
		4	68 (C_6H_5)	
1	25	3	28 (m-$CF_3C_6H_4$)	3/4 = 0.39
		4	72 (C_6H_5)	
2	0	5	23 (p-$CF_3C_6H_4$)	5/6 = 0.30
		6	77 (C_6H_5)	

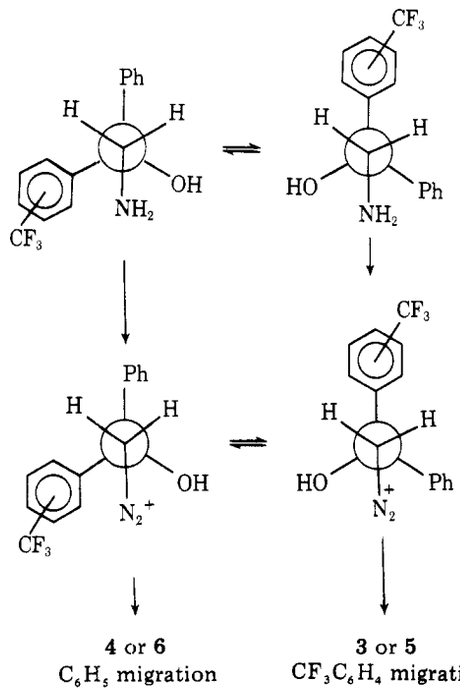
and analyzed as above using comparisons with authentic samples of 5 and 6 independently prepared (see Experimental Section). Results are summarized in Table I. The ketones were shown to be stable to the deamination conditions.

Discussion

The migration ratios (phenyl = 1.0) observed for the trifluoromethylphenyl groups (see Table I) are less than 1. In general, for cases in which the migration terminus is primary, the relative migratory aptitudes of aryl groups during deamination of amino alcohols follow the order expected from consideration of relative rates of electrophilic aromatic substitution.[4] Some representative examples[4] are p-methoxyphenyl, 1.5; p-tolyl, 1.3; p-chlorophenyl, 0.9.

Scheme II presents our analysis of the observed results of

Scheme II



the deamination reactions. A gauche relationship between hydroxy and amino groups has been shown to be preferred.[5] We represent the reactive intermediates as diazonium ions in which aryl migration takes place in an anti relationship with the leaving group; the rationale for such a scheme has been presented previously.[6] Migration is presumably competitive with central C–C bond rotation.[7]

The fact that the m-trifluoromethylphenyl group has a higher migratory aptitude than its para analogue under the same conditions is reasonable, since Hammett substituent constants indicate more electron withdrawal by CF_3 in the meta position.[8] However, any detailed analysis of the significance of the migration ratios would be highly speculative since we have no data concerning rates of loss of N_2 and aryl migration relative to C–C bond rotation or about the conformational equilibria involved.

We are currently attempting to learn more about the conformational preferences of systems such as the amino alcohols involved here.

Experimental Section

All melting points were determined in open capillary tubes in a Thomas-Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on Beckman IR-8 and Perkin-Elmer 700 spectrophotometers. Nuclear magnetic resonance (NMR) spectra were taken on a Hitachi Perkin-Elmer R-20 60-MHz spectrometer. Combustion analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside. N.Y.

***m*-Trifluoromethylbenzyl Alcohol (7).** m-Trifluoromethylbenzoic acid (Sigma Chemicals) (5 g, 26 mmol) was reduced with $LiAlH_4$ in the usual way. Distillation provided 3.8 g (83%) of a clear liquid, bp 82–83 °C (3.3 Torr): IR (neat) 3350 cm^{-1} (OH, broad); NMR (CCl_4) δ 7.4 (4 H, m, ArH), 4.5 (2 H, s, $-CH_2-$), 4.3 (1 H, s, OH).

***m*-Trifluoromethylbenzyl Chloride (8).** Compound 7 (7.5 g, 42.5 mmol) and thionyl chloride (16.8 g, 142 mmol) were heated at reflux for 10 h. Distillation gave 7.5 g (90%) of a clear liquid, bp 71–74 °C (10 Torr).

3′-Trifluoromethyldeoxybenzoin (3). 3-Trifluoromethylbenzylmagnesium chloride was prepared from dry compound 8 (7.5 g, 38.5 mmol) and magnesium turnings (0.9 g, 34 mmol) in absolute ether (70 ml). To the stirred solution was added dropwise freshly distilled benzaldehyde (3.7 g, 34.9 mmol) in absolute ether (10 ml). The solution was stirred at reflux for 15 min. The cooled solution was poured into an ice-cold solution of 3 N sulfuric acid (150 ml). When the hydrolysis was complete, the ether layer was separated, and the aqueous phase was extracted with several small portions of ether. The combined ether extracts were concentrated to half volume in a rotary evaporator. To the cold, stirred ether solution was added, dropwise, a solution of sodium dichromate (7.4 g, 28.3 mmol) and concentrated sulfuric acid (6.3 ml) in water (25 ml). The mixture was stirred at 5 °C until it turned blue-green (3 h). The ether layer was separated and the aqueous phase was extracted with two small portions of ether. The combined ether extracts were washed with water, saturated sodium carbonate, and water. After drying (Na_2SO_4), the ether was removed in a rotary evaporator, and the residue was distilled to give a clear liquid that solidified to white crystals in the receiver. Yield of 3, 5.4 g (60%), bp 146–148 °C (2 Torr); mp (petroleum ether) 35–37 °C; IR ($CHCl_3$) 1670 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.6 (9 H, m, ArH), 4.35 (2 H, s, CH_2CO); 2,4-dinitrophenylhydrazone (2,4-DNP) mp 185–187 °C (from methanol). Anal. Calcd for $C_{15}H_{11}F_3O$: C, 68.18; H, 4.20. Found: C, 68.15; H, 4.22.

***m*-Trifluoromethylbenzoyl Chloride (9).** Thionyl chloride (13.3 g, 110 mmol) was added to m-trifluoromethylbenzoic acid (Sigma Chemicals) (10 g, 52 mmol). After the initial reaction subsided, the mixture was heated at reflux for 26 h. The excess thionyl chloride was distilled at atmospheric pressure. The acid chloride 9 was distilled to yield 9.8 g (90%) of a clear liquid, bp 84.3–85 °C (10 Torr).

3-Trifluoromethyldeoxybenzoin (4). Benzylmagnesium bromide was prepared from dry benzyl bromide (15.4 g, 90 mmol) and magnesium turnings (2.4 g, 90 mmol) in absolute ether (100 ml). The solution was heated at reflux (30 min) with stirring, and then cooled to 0 °C. To the cold, stirred solution dry cadmium chloride (8.6 g, 47 mmol) was added in small portions. After the addition was complete, the mixture was heated at reflux (50 min) with vigorous stirring. The ether was distilled from the stirred solution until a very viscous, dark residue remained. At this point 100 ml of dry, thiophene-free benzene

was added. The mixture was stirred and an additional 30 ml was distilled. The mixture was cooled in an ice bath, and *m*-trifluoromethylbenzoyl chloride (**9**, 10.4 g, 49.9 mmol) in benzene (20 ml, dried over sodium) was added dropwise to the stirred mixture. Stirring was continued for 24 h at room temperature. The mixture was poured into a solution of concentrated sulfuric acid (15 ml) and ice (130 g). After hydrolysis was complete, the organic layer was separated, and the aqueous phase was extracted with three small portions of ether. The combined organic layers were washed with water, saturated sodium carbonate, and water. After drying ($MgSO_4$) the solvent was removed in a rotary evaporator. The residue was distilled to yield 1.4 g (11%) of **4** as a yellow oil: bp 150–153 °C (2 Torr); IR (neat) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.6 (9 H, m, ArH), 4.3 (2 H, s, ArCH_2); 2,4-DNP (from methanol) mp 164–166 °C (lit.[9] 166 °C).

2-Amino-3′-trifluoromethylacetophenone Hydrochloride (10). Anhydrous $AlCl_3$ (50 mg) was added to a stirred, ice-cold solution of 3-trifluoromethylacetophenone (Chemical Procurement) (10 g, 53.2 mmol) in 20 ml of dry ether. Then bromine (8.4 g, 52.6 mmol) was added dropwise to the stirred solution. After the bromine color disappeared (25–35 min) the ether and dissolved hydrogen bromide were removed at once under reduced pressure. The residue, a yellow oil (a lachrymator), was washed with water (10 ml).

To the yellow oil from above (2-bromo-3′-trifluoromethylacetophenone) dissolved in 20 ml of absolute ethanol was added at once a slurry of sodium azide (14 g, 215 mmol) in 4 ml of water. The mixture was stirred at room temperature for 3 h. At the end of that time, the mixture was diluted with water to twice its volume, and extracted with several portions of ether. The combined ether extracts were dried and the ether was removed in a rotary evaporator. A yellow oil, 2-azido-3′-trifluoromethylacetophenone, remained: IR (neat) 2100 (N_3), 1685 cm^{-1} (C=O).

To the azido ketone from above, dissolved in 40 ml of absolute ethanol, were added 4 ml of concentrated hydrochloric acid and 2 g of 5% palladium on charcoal. The mixture was hydrogenated at atmospheric pressure for 36 h. The mixture was filtered and the catalyst was washed with several small portions of absolute ethanol. The solution was concentrated in a rotary evaporator until a precipitate began to form. At this point the solution was removed from the rotary evaporator, and absolute ether (400 ml) was added. After 3 days of refrigeration the solid was collected, washed with absolute ether, and dried to yield 7.6 g (60%) of the white, crystalline salt (**10**): mp (methanol–ether) 225–227 °C dec; IR (KBr) 3000 (NH_3^+ broad), 1680 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.8 (3 H, s, broad, NH_3^+), 8.1 (4 H, m, ArH), 4.75 (2 H, s, $CH_2NH_3^+$).

2-Amino-1-(3-trifluoromethylphenyl)-1-phenylethanol Hydrochloride (1 HCl). Phenylmagnesium bromide was prepared by reaction of dry bromobenzene (7.8 g, 50 mmol) with magnesium turnings (1.4 g, 50 mmol) in absolute ether (50 ml). The finely powdered keto amine salt **10** (2 g, 8.13 mmol) was added in small portions with stirring over a period of 15 min to the cold (5 °C) Grignard reagent. The mixture was stirred for an additional 50 min at room temperature. The reaction mixture was then poured into a solution of ammonium chloride (2 g) in water (100 ml plus 3 drops of concentrated ammonium hydroxide). After hydrolysis was complete, the layers were separated and the aqueous layer was extracted with two small portions of ether. The combined ether layers were washed with two small portions of water. After drying (Na_2SO_4), the solution was diluted with absolute ether (100 ml) and then saturated with gaseous hydrogen chloride. The solution was further diluted with absolute ether (150 ml) and refrigerated for 3 days. A white solid was formed during the refrigeration period. The product was filtered, washed with absolute ether (50 ml), and allowed to dry. Yield of **1** HCl, 1.9 g (73%); mp (ethanol) 195–198 °C dec; IR (KBr) 3360 (OH), 2980 cm^{-1} (NH_3^+, broad); NMR (Me_2SO-d_6) δ 8.15 (3 H, s, broad, NH_3^+), 7.6 (9 H, m, ArH), 6.85 (1 H, s, OH), 3.8 (2 H, s, $CH_2NH_3^+$).

Anal. Calcd for $C_{15}H_{15}ClF_3NO$: C, 56.70; H, 4.76; N, 4.41. Found: C, 56.71; H, 4.75; N, 4.55.

The free amine (**1**) was obtained by dissolving the hydrochloride (1.1 g) in water (5 ml) and adding 1 M sodium hydroxide dropwise until pH 8 was obtained. The solution was extracted with several small portions of ether. After drying (Na_2SO_4), the ether was removed in a rotary evaporator. The residue, a clear oil, 0.7 g (72%), decomposed very slowly on standing: IR (neat) 3400 (OH), 3100 cm^{-1} (NH_2); NMR ($CDCl_3$) δ 7.5 (9 H, m, ArH), 4.2 (2 H, s, CH_2NH_2), 3.35 (1 H, s, broad, OH), 2.6 (2 H, s, broad, NH_2).

2-Amino-4′-trifluoromethylacetophenone Hydrochloride (11). The procedure followed was that for compound **10**. The yield obtained was 44%; mp (methanol) 245–247 °C dec; IR (KBr) 3000 (NH_3^+, very broad), 1680 cm^{-1} (C=O); NMR (Me_2SO-d_6) δ 8.7 (3 H, s, broad, NH_3^+), 8.2 (4 H, m, ArH), 4.7 (2 H, s, $CH_2NH_3^+$).

2-Amino-1-(4-trifluoromethylphenyl)-1-phenylethanol (2). This compound was prepared in the same way as compound **1** HCl except that gaseous hydrogen chloride was not passed through the ether solution, which rather was evaporated in a rotary evaporator. The residue was dissolved in hot pentane. Upon cooling a light yellow solid (**2**) was isolated by filtration in 57% yield: mp (pentane) 99–101 °C; IR (KBr) 3100 (OH, broad), 2800 cm^{-1} (NH_2); NMR (Me_2SO-d_6) δ 7.4 (9 H, m, ArH), 3.3 (2 H, s, CH_2NH_2), 2.7 (3 H, very broad, OH and NH_2).

Anal. Calcd for $C_{15}H_{14}F_3NO$: C, 64.05; H, 5.02; N, 4.98. Found: C, 64.14; H, 4.98; N, 4.71.

***p*-Trifluoromethylbenzaldehyde (12).** Compound **12** was synthesized by the procedure of Trahanovsky[10] et al., using 50% acetic acid–water as the solvent. The yield thus obtained was 81% of a clear liquid: bp 40–43 °C (2 Torr); IR (neat) 1700 cm^{-1} (C=O).

4-Trifluoromethyldeoxybenzoin (6). This compound was synthesized using compound **12** (4.8 g, 27.6 mmol) in a procedure similar to that with the deoxybenzoin **3**: yield 4%; mp (petroleum ether) 127–129 °C; IR ($CHCl_3$) 1680 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.5 (9 H, m, ArH), 4.29 (2 H, s, ArCH_2); 2,4-DNP (from ethanol) mp 186–187 °C.

Anal. Calcd for $C_{15}H_{11}F_3O$: C, 68.18; H, 4.20. Found: C, 67.88; H, 4.54.

4′-Trifluoromethyldeoxybenzoin (5). This compound was prepared by the same procedure as compound **4**. 4′-Trifluoromethylphenylacetic acid (Chemical Procurement) was converted to the acid chloride and used as in the above procedure. The yield of **5** was 10% as a white solid: 2,4-DNP (from ethanol) mp 205–207 °C; IR ($CHCl_3$) 1680 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.5 (9 H, m, ArH), 4.31 (2 H, s, CH_2C=O).

Anal. Calcd for $C_{15}H_{11}F_3O$: C, 68.18; H, 4.20. Found: C, 68.05; H, 4.38.

Deaminations. The aminoethanol hydrochloride **1** HCl (217 mg, 0.683 mmol) was dissolved in 50% aqueous acetic acid (ca. 10 ml) at 0 °C. A solution of sodium nitrite (238 mg, 3.45 mmol) in water (10 ml) was added dropwise over about 30 min, and the resulting mixture was stirred at 0 °C for 14 h. The reaction was quenched by adding a 10% aqueous sulfamic acid solution dropwise until the solution no longer gave a positive test with starch–iodide paper. The solution was extracted with ether. After drying (Na_2SO_4), the ether was removed at reduced pressure to leave 198 mg of crude product which was subjected to column chromatography on neutral alumina. Elution with pentane removed a nonpolar substance which was not fully characterized; it did not contain nitrogen or fluorine and had no aromatic protons in its ^1H NMR spectrum. Elution with chloroform provided a mixture of ketones **3** and **4** (138 mg, 77%) which was subjected to the analysis described below. An apparently polymeric material remained on the column. Duplicate runs gave similar results; similar runs were conducted at 25 °C. Results are recorded in Table I. A mixture of ketones **3** and **4** was subjected to the deamination conditions and shown to be unchanged.

The aminoethanol **2** (45 mg, 0.160 mmol) in 50% aqueous acetic acid (10 ml) was treated as above with sodium nitrite (4 equiv) in water (ca. 3 ml) for 24 h at 0 °C. Similar workup gave 43 mg of crude material which upon chromatography as described provided 28 mg (67%) of a mixture of ketones **5** and **6**, along with contaminants similar to those mentioned above. The ketone mixture was analyzed as described below. Duplicate runs gave similar results. Results are recorded in Table I. Ketones **5** and **6** were shown to be stable to the deamination conditions.

Analysis of Ketone Mixtures. The ketone product mixtures were analyzed by two separate methods which agreed within ±1%. Standard mixtures of the ketone were prepared and the ^1H NMR signals for the methylene protons (δ 4.35 for **3** and 4.30 for **4**; 4.31 for **5** and 4.29 for **6**) were scanned at an expanded sweep width (60 Hz) and integrated. Since baseline was not reached between signals, corrections were applied to make integrated values agree with known composition. The product mixtures were then analyzed in the same manner, with appropriate corrections as determined from the standard samples.

Similarly, ^{19}F NMR spectra of the standard mixtures were recorded, and the well-separated peaks were integrated. Product mixtures were then analyzed and compared with the standard samples.

NMR analysis of the deamination product mixtures before and after column chromatography demonstrated that no fractionation of ketones occurred during such treatment.

Acknowledgment. We wish to thank Mr. Kent Campbell for his assistance in computer simulation of NMR spectra of

the product mixtures. Dr. Edward Rosenberg supplied helpful comments regarding preparation of the manuscript.

Registry No.—**1**, 61062-52-0; 1, HCl, 61062-53-1; **2**, 61062-54-2; **3**, 30934-66-8; **3** 2,4-DNPH, 30934-67-9; **4**, 1533-04-6; **5**, 30934-68-0; **5** 2,4-DNPH, 30934-69-1; **6**, 61062-55-3; **6** 2,4-DNPH, 61062-58-6; **7**, 349-75-7; **8**, 705-29-3; **9**, 2251-65-2; **10**, 61062-56-4; **11**, 339-58-2; **12**, 455-19-6; *m*-trifluoromethylbenzoic acid, 454-92-2; 3-trifluoromethylacetophenone, 349-76-8; 2-bromo-3′-trifluoromethylacetophenone, 2003-10-3; 2-azido-3′-trifluoromethylacetophenone, 61062-57-5; 4′-trifluoromethylphenylacetic acid, 32857-62-8; 2-amino-4′-trifluoromethylacetophenone HCl, 339-58-2; benzaldehyde, 100-52-7; benzyl bromide, 100-39-0.

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A Comparison of the Addition of Bromine and 4-Chlorobenzenesulfenyl Chloride to β-Substituted Styrenes and Ethylenes[1]

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Received August 30, 1976

A comparison has been made of the rates and products of addition of bromine and 4-chlorobenzenesulfenyl chloride to a series of β-substituted styrenes ($C_6H_5CH{=}CHR$) and ethylenes ($CH_2{=}CHR$), where R = $CH(OCOCH_3)_2$, CH_2Cl, CH_2OCOCH_3, CH_2OCH_3, CH_2OH, H, CH_3, C_2H_5. On the basis of structure–reactivity correlations and product compositions, it is concluded that the rate- and product-determining transition states in the mechanism of bromination of styrene derivatives have different structures. The rate-determining transition state is bridged while the product-determining transition state resembles an open α-bromocarbonium ion.

The structure of the rate-determining transition state in the mechanism of electrophilic additions to alkenes is principally a function of the electrophile, the alkene structure, and the solvent.[2] For some electrophiles the effect of alkene structure on the mechanism seems to be negligible. For example, the mechanism of hydration involves an open carbonium-ion-like rate-determining transition state[3] while a bridged one is involved in the mechanism of the reaction of arenesulfenyl chlorides.[4]

The effect of alkene structure on the mechanism of bromination of alkenes is not clear. It is generally agreed that a bridged rate-determining transition state is involved in the addition to simple alkenes.[5,6] However, the involvement of such a structure in the addition to styrene derivatives has been the subject of debate.

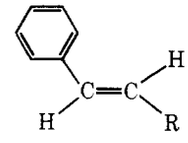
Yates and McDonald have used a thermochemical–kinetic method to probe the structure of the rate-determining transition state.[7] They found that the initial enthalpy difference between pairs of cis–trans isomeric alkenes was increased at the bromination transition state. The results were interpreted as evidence for a bridged rate-determining transition state.

Dubois[6] has compared the bromination of β-substituted styrenes ($C_6H_5C_\alpha H{=}C_\beta HR$) with the corresponding alkenes ($C_\alpha H_2{=}C_\beta HR$) and found that the reactivity of the former series is related to that of the later by a linear equation with slope 0.75. From the value of the slope together with the log k vs. σ^* correlations it was concluded that for the styrene series the rate-determining transition state corresponds to an open carbonium ion with the charge on C_α.

To resolve this problem, we have made a structure–reactivity comparison between bromination and an electrophilic addition whose mechanism is well established. We have chosen the addition of 4-chlorobenzenesulfenyl chloride as our model of a reaction whose mechanism involves a bridged rate-determining transition state independent of olefin structure.[8] Such a comparison should make it possible to arrive at a decision on the structure for the rate-determining transition state of the bromination of styrene derivatives.

Results

We have measured the rates of addition of 4-chlorobenzenesulfenyl chloride to a series of β-substituted trans styrenes, **1a–h**, and to the corresponding alkenes **2a–h** in acetic



1

$CH_2{=}CHR$

2

a, R = $CH(OCOCH_3)_2$
b, R = CH_2Cl
c, R = CH_2OCOCH_3
d, R = CH_2OCH_3
e, R = CH_2OH
f, R = H
g, R = CH_3
h, R = C_2H_5

acid at 25.0 °C. The addition was found to obey a second-order rate law, first order in alkene and first order in sulfenyl chloride to at least 80% completion of the reaction. The rate data are presented in Table I.

The product compositions were determined by NMR spectroscopy. The basis of this method is that protons α or β to chlorine are considerably deshielded relative to those α or β to sulfur.[9,10] The NMR parameters of the adducts obtained in this study are reported in Table II with the exception of data reported previously.[11,12] In every case it was possible to find at least one nonoverlapping signal from which the isomer distribution could be calculated.

The kinetically controlled product composition was determined by immediate NMR analysis of the reaction mixture.