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Synthesis by SO_2 Extrusion: Photochemical and Thermal Reactions of Cinnamyl Benzyl Sulfone

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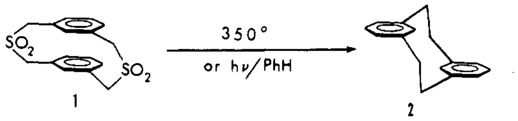
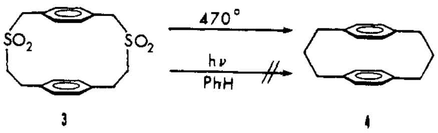
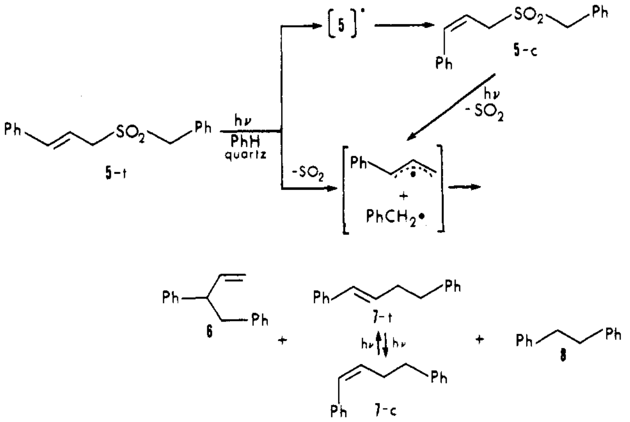
The photochemistry and pyrolytic behavior of *trans*-cinnamyl benzyl sulfone have been investigated. Direct photolysis in benzene gives high yields of the SO_2 extrusion products 3,4-diphenyl-1-butene and *cis*- and *trans*-1,4-diphenyl-1-butene. Addition of *trans*-piperylene to the photolysis substantially reduces the amount of *cis*-1,4-diphenyl-1-butene formed. Photolysis in acetone gives primarily trans–cis isomerization, though minor amounts of the SO_2 extrusion products and bibenzyl were also formed. Flash vacuum pyrolysis of cinnamyl benzyl sulfone gave only minor amounts of the SO_2 extrusion products; these were shown to be unstable under the conditions of pyrolysis. Instead, indene, styrene, bibenzyl, and toluene were formed. Pyrolysis of 1,4-diphenyl-1-butene gave these same products.

The extrusion of a small molecule from a larger molecular framework often provides a useful means of forming a new C–C bond.[3] Recently it has been shown that certain sulfones can extrude SO_2 by means of thermal[4] or photochemical[3,5] excitation. These methods have been applied most fruitfully to the synthesis of [2.2]cyclophanes,[4a-f,5] molecules whose inherent strain provides a rigorous test for the viability of this extrusion method. To date most photochemical and thermal SO_2 extrusion reactions have involved the use of dibenzylic sulfones; for example, irradiation[5] of sulfone 1 gives [2.2]metacyclophane (2) in quantitative yield while pyrolysis[6] of 1 provides 2 in ca. 20% yield. In contrast, sulfone 3 undergoes smooth pyrolytic extrusion of SO_2 to give a 94% yield of [3.3]paracyclophane (4)[7] while irradiation of 3 produces no cyclophane 4 at all.[5] It has been suggested[5a] that initial homolytic benzyl carbon–sulfur bond cleavage occurs but that loss of SO_2 from the resultant biradical intermediate requires a greater activation energy than is required for dibenzylic sulfones such as 1. It would appear, therefore, that for photochemical SO_2 extrusion some stabilization is required for each radical fragment.





Scheme I



Our objective was to expand the scope of the SO_2 extrusion method by incorporating other conjugated moieties in the sulfone, thereby expanding the usefulness of this synthetic technique. Since no single report has compared the relative effectiveness of both extrusion methods (thermal and photochemical), we wanted to make such a comparison.

Results and Discussion

trans-Cinnamyl benzyl sulfone (**5-t**) was chosen for our initial study; its synthesis was easily accomplished in 62% overall yield by the base-induced coupling of benzyl mercaptan and *trans*-cinnamyl bromide followed by *m*-chloroperoxybenzoic acid oxidation of the resultant cinnamyl benzyl sulfide.

Direct photolysis of **5-t** in benzene (Hanovia 450-W mercury arc lamp in a quartz immersion well apparatus) for 8 h resulted in the formation of 3,4-diphenyl-1-butene (**6**, 50%), *trans*-1,4-diphenyl-1-butene (**7-t**, 23%), and *cis*-**7** (**7-c**, 13%). Bibenzyl (**8**, 2%) was also detected, and a small amount of trans–cis photoisomerization was apparent, giving **5-c** as 8% of the product mixture (Scheme I). The SO_2 extrusion products **6** and **7** thus account for 86% of the product mixture as determined by gas chromatography (GC).[8] Table I provides a summary of the product yields for each of the reactions discussed in this paper.

When **5-t** was irradiated in the presence of 0.500 M *trans*-piperylene as a triplet quencher the amount of **7-c** produced was diminished to 2%, and no bibenzyl was

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[8] All yields determined by gas chromatography were corrected for detector response and are reported as a percentage of the volatile fraction.

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Table I. Product Yields from the Photolysis and Pyrolysis of 5-t and 7

		% yield of products[a]								
substr	reaction conditions	5-c	5-t	6	7-c	7-t	8	9	10	11
5-t	$h\nu^b$/PhH	8		50	13	23	2			
5-t	$h\nu^c$/PhH, piperylene	35		24	2	37				
5-t	$h\nu$,[d] acetone	60	21	5	4	2	3			
5-t	640 °C[e]				1	10	17	25	26	8
7-c	$h\nu^f$/PhH				34	59				
7[g]	640 °C[e]						9	43	15	6

[a] See ref 8. [b] Irradiation for 8 h with a quartz filter. [c] Irradiation for 36 h with a Corex filter; piperylene was added to make a 0.5 M solution. [d] Irradiation for 1 h with a Pyrex filter. [e] Flash vacuum pyrolysis; see the Experimental Section for details of the apparatus. [f] Irradiation for 5.5 h with a quartz filter. [g] Pyrolyzed as a mixture of cis and trans isomers.

detected by GC. The only significant products formed after 36 h of irradiation (23% conversion) were **6** (24%), **7-t** (37%), and **5-c** (35%). A Corex filter (transparent at $\lambda >$ ca. 260 nm) was used, allowing absorption by the $\pi \rightarrow \pi^*$ transition of **5-t** which tails out to >300 nm while preventing absorption by the piperylene quencher (λ_{max} = 223.5 nm).

A compariosn of the benzene photolyses with and without added piperylene quencher would suggest that **7-c** is produced directly in small quantity from radical recombination but more rapidly by triplet-state photoisomerization of the initially formed **7-t**. The interconvertability of **7-t** and **7-c** was confirmed by the irradiation of **7-c** in benzene under the same conditions used for the unquenched photolysis of **5-t**; irradiation led to rapid cis–trans isomerization of the alkene so that after 5.5 h a photostationary state was reached with a trans–cis ratio of 1.7.[9]

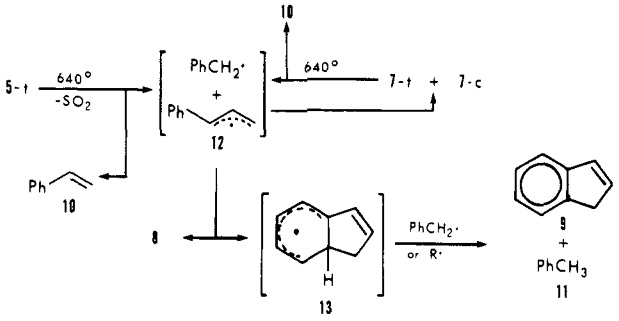
That isomerization of **5-t** to **5-c** still occurs in the presence of piperylene would suggest that either the triplet state of **5-t** lies lower than that of piperylene or that at least some of the isomerization originates from the singlet state.

Irradiation of **5-t** in acetone led to efficient isomerization to **5-c** so that after 1 h (Pyrex-filtered Hanovia 450-W medium-pressure lamp) a photostationary state was reached that had a **5-c**/**5-t** ratio of 2.9. Bibenzyl and the SO_2 extrusion products were also formed slowly so that after 2 h of irradiation the following were present: **5-t** (21%), **5-c** (60%), **6** (5%), **7-t** (2%), **7-c** (4%), and **8** (3%).

Flash vacuum pyrolysis of **5-t** at 640 °C gave only minor amounts of the extrusion products **7-t** (10%) and **7-c** (1%); GC analysis could detect no **6**. Instead, indene (**9**, 25%), styrene (**10**, 26%), **8** (17%), and toluene (**11**, 8%) were obtained as the major products in a typical pyrolysis. Repetition of this pyrolysis experiment consistently gave products **8–11**, but **7** was not always present.

Because the quantity of **7** produced in the pyrolysis of **5-t** varied, it seemed likely that **7** and possibly **6** were being produced initially by SO_2 extrusion and were undergoing further decomposition before leaving the pyrolysis tube. To test this hypothesis, we prepared **7** as a mixture of cis and trans isomers which was pyrolyzed by using the same conditions as those for the pyrolysis of **5-t**. Though the product ratio was somewhat different, the products were the same as those obtained from the thermolysis of **5-t**, and none of the starting alkene (**7**) survived intact. Thus, GC analysis of the pyrolysate gave **8** (9%), **9** (43%), **10** (15%), and **11** (6%) as the major products. Scheme II summarizes the results of these pyrolyses.

Scheme II



As shown in Scheme II indene could arise from internal attack of the cinnamyl radical **12**, giving intermediate **13**; H atom abstraction by the benzyl radical or other radical species could produce indene and account for the formation of toluene. Bibenzyl could arise from the coupling of the benzyl radicals initially produced by the extrusion of SO_2, and of course, **7** would result from the coupling of the benzyl and cinnamyl radicals. While mechanisms can be written to account for the formation of styrene, we are withholding speculation pending further investigation.

La Combe and Stewart[4h] reported that the pyrolysis of certain allylic sulfones gave SO_2 extrusion products in yields ranging from 24% to 79%. For cinnamyl benzyl sulfone, however, photolysis is clearly the method of choice for SO_2 extrusion. Further investigation will establish if this result is more general.

Experimental Section

Melting points were determined with a Laboratory Devices Mel-Temp apparatus and are uncorrected. The following instruments were used: NMR, Hitachi Perkin-Elmer R24A; IR, Perkin-Elmer 283B; UV, Perkin-Elmer 124; GC/MS, Hewlett-Packard 985 at 70 eV; GC (analytical), Hewlett-Packard 5840A with a flame-ionization detector and a 6 ft × $^1/_8$ in. 15% SE-30 on 80/100 Chrom W AW DMCS column (column A); GC (preparative), Varian Aerograph A-90-P with a thermal-conductivity detector and an 8 ft × $^1/_4$ in. 15% SE-30 on 60/80 Chrom W AW DMCS column (column B); HPLC, Beckman instrument with a 4.6 mm × 15.0 cm C-18 reverse-phase column. Baker analytical reagent benzene was used as received and was found to be greater than 99.9% pure by GC analysis. Baker Photrex grade acetone was used as received. All other chemicals were reagent grade and were used as received unless otherwise specified.

All photolyses were run by using a 450-W medium-pressure Hanovia mercury arc lamp placed in a quartz immersion well. Except as noted, sample tubes were placed parallel to the immersion well at the specified distances.

Cinnamyl Benzyl Sulfide. A 3-L three-necked flask was equipped with a condenser, addition funnel, and mechanical stirrer. The flask was charged with 1.0 L of 95% ethanol and 3.17 g (79.2 mmol) of NaOH. A mixture of freshly distilled cinnamyl bromide (6.25 g, 31.7 mmol) and benzyl mercaptan (3.94 g, 31.7 mmol) dissolved in 500 mL of CH_2Cl_2 was added dropwise to the refluxing ethanol solution. When the addition was complete, the reaction mixture was refluxed for an additional $^1/_2$ h, cooled, concentrated in vacuo to 100 mL, diluted with 300 mL of water, and extracted with ether (2 × 200 mL). The combined ether extracts were washed with 100 mL of brine and were dried over

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(9) The photochemical cis–trans isomerization of alkenes is well-known: Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum: New York, 1976, p 367–88.

anhydrous Na_2SO_4. Concentration in vacuo gave 6.62 g (87%) of clear yellow cinnamyl benzyl sulfide: IR (neat) 1600, 1494, 1453, 962, 746, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27 (s, 10 H, PhH), 6.36–5.77 (m, 2 H, vinylic), 3.66 (s, 2 H, $PhCH_2$), 3.16 (d, 2 H, allylic).

***trans*-Cinnamyl Benzyl Sulfone (5-t).** To a 750-mL round-bottomed flask were added 500 mL of CH_2Cl_2, cinnamyl benzyl sulfide (5.00 g, 20.8 mmol), and 80% pure *m*-chloroperoxybenzoic acid (10.0 g, 57.9 mmol). The solution was stirred magnetically for 1 h, at which time TLC analysis (silica gel, 50% ether/hexane) indicated complete loss of cinnamyl benzyl sulfide. The reaction mixture was extracted with 10% NaOH (2 × 300 mL), dried over anhydrous Na_2SO_4, and concentrated by rotary evaporation to give a white solid. Recrystallization (EtOH) gave 4.01 g (71%) of **5-t**: mp 124–125 °C; IR (KBr) 1322, 1300, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (s, 5 H, PhH), 7.30 (s, 5 H, PhH), 6.55–5.83 (m, 2 H, vinylic), 4.23 (s, 2 H, $PhCH_2$), 3.74 (d, 2 H, allylic); UV (EtOH) λ_{max} 206 nm (log ϵ 4.51), 217 (sh), 255 (4.31), 283 (sh), 293 (3.15). Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S, 11.77. Found: C, 70.46; H, 6.12; S, 11.98.

Triphenyl(3-phenylprop-1-yl)phosphonium Bromide. To a three-necked round-bottomed flask equipped with a condenser and magnetic stirrer were added triphenylphosphine (13.1 g, 50.1 mmol), 1-bromo-3-phenylpropane (10.0 g, 50.3 mmol), and 30 mL of toluene. After being refluxed for 4.5 h, the solution was filtered to give 12.1 g (53%) of white crystalline triphenyl(3-phenylprop-1-yl)phosphonium bromide which was used in the following reaction without further characterization.

***cis*- and *trans*-1,4-Diphenyl-1-butene (7).** A 250-mL round-bottomed flask was equipped with a condenser, addition funnel, N_2 inlet, and magnetic stirrer. To this flame-dried apparatus were added sodium hydride (1.41 g of a 50% oil dispersion, 26.3 mmol) and 80 mL of dry dimethyl sulfoxide (Me_2SO). The mixture was first warmed to 75 °C until the evolution of H_2 ceased (ca. $^1/_2$ h) and then cooled in an ice bath. Triphenyl(3-phenylprop-1-yl)phosphonium bromide (12.1 g, 26.3 mmol) in 40 mL of dry Me_2SO was added dropwise to the stirred solution. The reaction mixture became dark red after $^1/_2$ h of stirring at which time benzaldehyde (2.80 g, 26.4 mmol) in 20 mL of dry Me_2SO was added dropwise. After being stirred at room temperature for 16 h, the reaction mixture was diluted with 500 mL of water, producing a white precipitate. The entire mixture was extracted with ether (3 × 100 mL). The combined ether fractions were washed with 10% NaOH (3 × 100 mL), water (3 × 100 mL), and brine (100 mL), dried over Na_2SO_4, and concentrated in vacuo to give a clear light brown oil which crystallized on standing. Simple distillation afforded two fractions [0.55 g, bp 113–124 °C (0.42 torr); 2.72 g, bp 124–135 °C (0.35 torr)], each of which was a mixture of **7-c** and **7-t** (60% yield). Separation of the isomers for analytical purposes was accomplished by using a medium-pressure liquid chromatograph having a 2.8 × 100 cm silica gel column with petroleum ether as the eluent. **7-c**: IR (neat) 3086, 3067, 3029, 2930, 2855, 1602, 1495, 1450, 1077, 1028, 762, 745, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23 (s, 5 H, ArH), 7.21 (s, 5 H, ArH), 6.45 (d, J = 12 Hz, 1 H, PhC*H*=CH), 5.95–5.20 (m, 1 H, PhCH=C*H*), 2.90–2.50 (m, 4 H, CH_2CH_2); MS, *m/e* (relative intensity) 208 (13), 118 (17), 117 (100), 116 (14), 115 (54), 104 (25), 91 (58), 78 (11), 77 (13), 65 (15). **7-t**: IR (neat) 3087, 3066, 3028, 2930, 1601, 1495, 1454, 960, 734, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (s, 5 H, Ar H), 7.15 (s, 5 H, Ar H), 6.45–5.85 (m, 2 H, vinylic), 3.02–2.22 (m, 4 H, CH_2CH_2) (lit.[10]); MS, *m/e* (relative intensity) 208 (19), 118 (16), 117 (100), 116 (17), 115 (66), 91 (70), 77 (10), 65 (18).

Preparative Irradiation of 5-t in Benzene. To an 8 × 23 cm flask having a Ŧ 60/50 joint and two side arms were added 1.52 g (5.58 mmol) of **5-t** and 560 mL of benzene. The solution was degassed (20 min of N_2 bubbling), and the quartz cooling jacket surrounding a 450-W medium-pressure Hanovia mercury arc lamp was inserted into the reaction flask. The side arms were sealed with septa, and the magnetically stirred solution was irradiated (unfiltered) for 15 h. Concentration in vacuo gave a dark brown oil from which four major products were isolated by preparative GC on column B. In order of elution they are as follows.

Bibenzyl (**8**, 1.2 min) was characterized by comparison of the IR, NMR, and mass spectra to those of authentic material.

3,4-Diphenyl-1-butene (**6**, 1.6 min) was characterized by comparison of its IR and NMR spectra to published values (lit.[11] ^1H NMR and IR) and by its mass spectrum: MS, *m/e* (relative intensity) 208 (11), 118 (19), 117 (100), 116 (16), 115 (72), 91 (59), 65 (12).

***cis*-1,4-Diphenyl-1-butene** (**7-c**, 2.3 min) was characterized by comparison of its IR, NMR, and mass spectra to those of material prepared as described above.

***trans*-1,4-Diphenyl-1-butene** (**7-t**, 3.1 min) was characterized by comparison of its IR, NMR, and mass spectra to those of material prepared as described above.

Irradiation of 5-t in Benzene: Quantitative Procedure. To a 1.5 × 12 cm quartz tube were added **5-t** (72.5 mg, 0.266 mmol) and 10 mL of benzene. The sample was degassed (N_2 bubbling, 30 min), placed 20 cm from the water jacket of an unfiltered Hanovia 450-W medium-pressure mercury arc lamp, and irradiated. Progress of the photolysis was followed by GC (column A). After 8 h of irradiation 87% of **5-t** had been converted, giving **5-c** (8%), **6** (50%), **7-c** (13%), **7-t** (23%), and **8** (2%).[8]

Irradiation of 5-t with Piperylene Quencher. This procedure was identical to the quantitative irradiation of **5-t** in benzene except that after degassing, 341 mg (5.00 mmol) of piperylene was added to the solution to make a 0.500 M solution of the quencher, and the sample tube was placed 5 cm from the lamp's immersion well. After 36 h of Corex-filtered irradiation, 23% of **5-t** had been converted to the following products as determined by GC analysis (column A): **6** (24%), **7-t** (37%), **7-c** (2%), and **5-c** (35%).

Irradiation of 7-c in Benzene. The procedure was identical to the quantitative irradiation of **5-t** except that 5.0 mg (0.024 mmol) of **7-c** was dissolved in 0.5 mL of benzene, and the solution was irradiated in a quartz NMR tube placed 10 cm from the quartz immersion well. After 5.5 h GC analysis (column A) showed the presence of **7-t** (59%), **7-c** (34%), and one other minor product which was not identified. Longer irradiation resulted in slight additional loss of **7** but the **7-t**/**7-c** ratio remained constant at 1.7:1.

Acetone-Sensitized Irradiation of 5-t. To a Pyrex tube were added 2.0 mg (3.67 μmol) of **5-t** and 4.0 mL of acetone so that at 290 nm acetone would absorb more than 98% of the light. The solution was irradiated for 1 h at a distance of 10 cm at which time GC analysis (column A) showed that the following were present: **5-t** (21%), **5-c** (60%), **6** (5%), **7-t** (2%), **7-c** (4%), and **8** (3%).

Flash Vacuum Pyrolysis of 5-t. The pyrolysis apparatus is a modified version of that previously described;[12] modifications include the use of a quartz pyrolysis tube sealed at the sample end and the use of a two-stage tube furnace having a pyrolytic stage heated to 640 °C and an oven which could be warmed gradually to vaporize the sample. In a typical run 400 mg of **5-t** was pyrolyzed at 0.35 torr, and the products were isolated by preparative GC (column B). Since some of the products were volatile, no solvent was used to remove the pyrolysate from the cold trap, and recovery of the pyrolysate was not quantitative. Identification of the products was made by comparison of NMR and IR spectra with those of authentic material. While relative yields (as determined by GC using column A) varied somewhat, the following results were typical: **7-c** (1%), **7-t** (10%), **8** (17%), **9** (25%), **10** (26%), and **11** (8%).

Flash Vacuum Pyrolysis of 7. The pyrolysis of **7** was run as described above by using 500 mg of an isomer mixture with a **7-c**/**7-t** ratio of 71:29. GC analysis (column A) showed that the 370 mg of pyrolysate recovered from the trap contained the following: **8** (9%), **9** (43%), **10** (15%), and **11** (6%). No unreacted **7** was detected.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American

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(10) Blum, J.; Becker, Y. *J. Chem. Soc., Perkin Trans. 2* **1972**, 982.

(11) James, B. G.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1204.

(12) See ref 4c, pp 28–9.

Chemical Society, and to the National Science Foundation for support of this work. We thank Dr. David B. Ledlie for helpful suggestions.

Registry No. **5-c**, 87156-75-0; **5-t**, 87156-76-1; **6**, 33326-56-6; **7-c**, 70388-65-7; **7-t**, 27066-35-9; **8**, 103-29-7; **9**, 95-13-6; **10**, 100-42-5; **11**, 108-88-3; *trans*-cinnamyl benzyl sulfide, 87156-77-2; *trans*-cinnamyl bromide, 26146-77-0; benzyl mercaptan, 100-53-8; triphenyl(3-phenylprop-1-yl)phosphonium bromide, 7484-37-9; triphenylphosphine, 603-35-0; 1-bromo-3-phenylpropane, 637-59-2.

Heat Capacities of Activation for the Neutral Hydrolysis of Two Acyl-Activated Esters in Water-Rich 2-*n*-Butoxyethanol–Water Mixtures. Analysis in Terms of the Pseudo-Phase-Separation Model[1]

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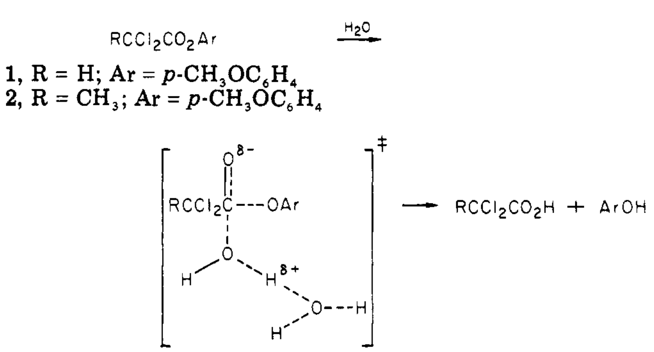
The water-catalyzed hydrolysis of *p*-methoxyphenyl dichloroacetate (1) and 2,2-dichloropropionate (2) in water-rich 2-*n*-butoxyethanol (2-BE)–H_2O exhibits large, *positive* heat capacities of activation (1, $\Delta C_p^{\ddagger} = 224 \pm 51$ cal mol^{-1} deg^{-1}; 2, $\Delta C_p^{\ddagger} = 342 \pm 51$ cal mol^{-1} deg^{-1}; temperature 20–48 °C) at 2 mol % of 2-BE ($n_{H_2O} = 0.98$). These positive $\Delta C_p^{\ddagger}$ values contrast sharply with the negative $\Delta C_p^{\ddagger}$'s found for S_N solvolysis reactions in highly aqueous mixed solvents. By use of a pseudothermodynamic approach, the $\Delta C_p^{\ddagger}$ values as well as positive heat capacities for transfer (ΔC_p^{θ},tr) of two model substrates from water to 2-BE–H_2O are rationalized within the framework of a *pseudo-phase-separation model*. Based on previous thermodynamic and other evidence, this model assumes the onset of microphase separation in 2-BE–H_2O at about $n_{H_2O} = 0.98$ at 25 °C. It is shown that temperature-dependent partitioning of the acyl-activated esters between a water-rich and a cosolvent-rich microphase provides an adequate explanation for the observed heat capacity data. The observed $\Delta C_p^{\ddagger}$ for solvolysis of *tert*-butyl chloride in 2-BE–H_2O at $n_{H_2O} = 0.98$ is also reconcilable with the proposed theory.

Water-catalyzed reactions in highly aqueous mixed solvents often show peculiar kinetic features which presumably reflect the unique solvent structural properties of these reaction media.[2] For example, the pH-independent hydrolysis of *p*-methoxyphenyl dichloroacetate (1) and 2,2-dichloropropionate (2) in 2-*n*-butoxyethanol (2-BE)–H_2O exhibited large and *positive* heat capacities of activation ($\Delta C_p^{\ddagger}$) at a mole fraction of water (n_{H_2O}) of 0.98 (1, $\Delta C_p^{\ddagger} = 224 \pm 51$ cal deg^{-1} mol^{-1}; 2, $\Delta C_p^{\ddagger} = 342 \pm 51$ cal deg^{-1} mol^{-1}).[3] By contrast, S_N solvolyses of a variety of neutral substrates in mixtures of water with a hydrophobic cosolvent invariably show *negative* extremes in $\Delta C_p^{\ddagger}$ in the highly aqueous region.[4,5] In a preliminary report we have argued that the positive $\Delta C_p^{\ddagger}$'s for 1 and 2 did not arise from mixed kinetics or a change in mechanism but probably resulted from hydrophobic interactions between the substrates and 2-BE. In this paper the $\Delta C_p^{\ddagger}$ values for 1 and 2 are analyzed in detail, taking into account recent thermodynamic and other data for the 2-BE–H_2O system which point to the occurrence of a microphase separation at n_{H_2O} ca. 0.98 (25 °C). Within the framework of this *pseudo-phase-separation model* and on employment of a pseudothermodynamic approach, the solvent dependence of $\Delta C_p^{\ddagger}$ can be rationalized. The analysis implies a temperature-dependent partitioning of the ester between the water-rich and cosolvent-rich microphases, leading to positive $\Delta C_p^{\ddagger}$ values, the magnitude depending on the hydrophobicity of the substrate.

Scheme I



1, R = H; Ar = p-$CH_3OC_6H_4$
2, R = CH_3; Ar = p-$CH_3OC_6H_4$

Results and Discussion

The hydrolysis of aryl dichloroacetates has been the subject of several mechanistic studies.[6] The pseudo-first-order rate constants (k_{obsd}) are independent of the pH between at least pH 1 and 5.5, and the rate constants for the water reaction of some esters fall on the same Brønsted plot as the rate constants for other general-base catalysts.[7] The mechanism, formulated in Scheme I, is further sup-

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