Although 1 was observed in the conversion of 2 to 3,[1] an analogous route to 12 would require the bridgehead diene 14. We propose that initial dehydrobromination of 7 to 15[5] is followed by S_N2' attack by hydroxide to yield the unstable difluoro alcohol 16. Spontaneous loss of HF produces 17, which further reacts to yield 12 (Scheme I).

Experimental Section

General Methods. All NMR spectra were obtained in $CDCl_3$ solutions at ambient temperature on a Varian Gemini 200 spectrometer. Chemical shifts (δ) are reported in parts per million downfield of internal tetramethylsilane. Infrared spectra were obtained from neat liquids or solutions as capillary films between KBr plates on a Perkin-Elmer 1420 ratio recording infrared spectrophotometer. All reagents and solvents were commercial samples used without purification. Elemental analyses were performed by Robertson Laboratory, Inc., Madison, NJ.

Addition of CF_2Br_2 to Alkenes. General Procedure. The procedure was patterned after that reported by Burton and Kehoe.[4] A mixture of 300 mmol of CF_2Br_2, 150 mmol of olefin, 75 mmol of ethanolamine, 2 mmol of CuCl, and 150 mL of *tert*-butyl alcohol was refluxed for at least 24 h. Adducts were worked up as described previously for the isolation of 2.[1]

1,3-Dibromo-1,1-difluoroheptane (4): yield 23%; ^1H NMR δ 4.20 (quint, J = 6.4 Hz, 1 H, CHBr), 2.8–3.25 (mult, 2 H), 1.7–2.0 (mult, 2 H), 1.2–1.6 (mult, 4 H), 0.9 (t, 3 H); ^{13}C NMR δ 121.1 (t, J_{FC} = 308 Hz, CF_2Br), 52.9 (t, J_{FC} = 21.4 Hz), 47.1, 38.4, 29.4, 22.1, 14.0; IR 2960, 2940, 2870, 1460, 1430, 1380, 1337, 1218, 1197, 1170, 1130, 1085, 1070, 1025, 995, 937, 915, 789, 766 cm^{-1}. Anal. Calcd for $C_7H_{12}Br_2F_2$: C, 28.60; H, 4.11. Found: C, 29.31; H, 4.25.

***trans*-1-(Bromodifluoromethyl)-2-bromocyclopentane (5):** yield 20%; ^1H NMR δ 4.4 (ddd, J = 6.6 Hz, J' = 5.2 Hz, J'' = 4.7 Hz, 1 H, CHBr), 3.25 (mult, 2 H, $CHCF_2Br$), 1.7–2.4 (unresolved mults, 6 H); ^{13}C NMR δ 124.8 (t, J_{FC} = 309 Hz, CF_2Br), 62.3 (t, J_{FC} = 20.2 Hz, C(1)), 48.0, 38.8, 28.0 (d, J = 2.6 Hz), 24.1; IR 2959, 2866, 1775, 1445, 1347, 1302, 1212, 1095, 1061, 1028, 985, 958, 908, 865, 769, 703 cm^{-1}. Anal. Calcd for $C_6H_8Br_2F_2$: C, 25.93; H, 2.90. Found: C, 26.52; H, 2.92.

1-Bromo-1-methyl-2-(bromodifluoromethyl)cyclohexane (6): yield 25%; ^1H NMR δ 2.99 (ddt, J = 22.6 Hz, J' = 9.1 Hz, J'' = 3.7 Hz, 1 H, $CHCF_2Br$), 2.20 (t, J = 10.1 Hz, 2 H), 19.3 (t, J = 2 Hz, 3 H, CH_3) 1.88–1.39 (complex mults, 6 H); ^{13}C NMR δ 125.4 (t, J_{FC} = 316 Hz, CF_2Br), 65.6, 60.4 (dd, J_{FC} = 18.3 Hz, $J_{FC'}$ = 15.3 Hz), 46.3, 28.6, 27.1 (d, J_{FC} = 2.6 Hz), 24.0, 23.5; IR 3006 (w), 2932, 2852, 1742, 1705, 1442, 1358, 1215, 1142, 1098, 908, 758 cm^{-1}.

***trans*-2-(Bromodifluoromethyl)-3-bromobicyclo[2.2.1]heptanes (7).** Two isomers were produced in 47% total yield. The ratio of **7a** (exo CF_2Br) to **7b** (endo CF_2Br) was 4.4 to 1: IR 2960, 2875, 1470 (w), 1450, 1350, 1265, 1250, 1235, 1220, 1205, 1190, 1175, 1150, 1115, 1090 (s), 1020, 980, 965, 940, 900, 835, 815, 800, 765, 745, 675 cm^{-1}; ^1H NMR δ 4.16 (t, J = 5 Hz, **7a**, CHBr, 0.815 H), 4.03 (dd, J = 7.7 Hz, J' = 2.6 Hz, **7b**, CHBr, 0.185 H), 2.9–2.3 (mult, 3 H), 2.1–1.9 (mult, 1 H), 1.8–1.5 (mult, 3 H), 1.4–1.2 (mult, 2 H); ^{13}C NMR **7a** δ 123.5 (t, J_{FC} = 309 Hz), 65.2 (t, J_{FC} = 20.5 Hz), 52.0, 44.5, 40.0, 36.0, 29.8, 23.8; **7b** δ 122.6 (t, J_{FC} = 312 Hz), 60.6 (t, J_{FC} = 19.8 Hz), 51.2, 48.5, 41.0, 35.4, 30.3, 27.1. Anal. Calcd for $C_8H_{10}Br_2F_2$: C, 31.61; H, 3.32. Found: C, 31.88; H, 3.32.

1,1-Difluoro-1,3-dibromo-4-phenylbutane (8). The standard procedure described above produced a mixture of 8 and unreacted allylbenzene. Pure 8 was isolated in 33% yield by flash chromatography on silica gel with hexane elution: ^1H NMR δ 2.9–3.4 (mult, 4 H), 4.35 (quintet, 1 H, CHBr), 7.2–7.5 (mult, 5 H); ^{13}C NMR δ 137.7, 129.9, 129.3, 128.0, 121.3 (t, J_{FC} = 308 Hz, CF_2Br), 51.9 (t, J_{FC} = 21.5 Hz), 46.5, 45.3; IR 3075 (w), 3055 (w), 3020, 2915, 1600, 1493, 1450, 1370, 1340, 1307, 1260, 1200 (s), 1165, 1104 (s), 1077, 1028, 980, 940, 917, 860, 1165, 1104 (s), 1077, 1028, 980, 940, 917, 860, 770, 745, 700 (s), 647 cm^{-1}.

Reaction of CF_2Br_2–Alkene Adducts with Potassium Hydroxide. General Procedure. Into a 10-mL screw-topped test tube were placed 5 mmol of KOH, 2 mL of deionized water, 1 mmol of the dibromodifluoro compound, and a small stirring magnet. The vessel was closed, and the lower half was suspended in an oil bath while the mixture was stirred and heated until it appeared homogeneous. Afterward the cooled reaction mixture was extracted with three 2-mL portions of chloroform to remove any unreacted alkyl halide. The reaction mixture was then acidified wth 3 M HCl and extracted with three 2-mL portions of chloroform. These second chloroform extracts were dried over anhydrous calcium sulfate and rotary evaporated to give the carboxylic acid.

2-Heptenoic Acid (9). A reaction of 4 with KOH was carried out as described above for 7 h at 130–140 °C to yield 96% **9**: ^1H NMR δ 10.62 (br s, 1 H, CO_2H), 7.10 (dt, J = 15.6 Hz, J' = 7.1 Hz, 1 H), 5.82 (d, J = 15.6 Hz, 1 H), 2.24 (quart., J = 7.1 Hz, 2 H), 1.65–1.25 (mult, 4 H), 0.92 (t, J = 7 Hz); the ^{13}C NMR agreed with the liteature;[6] IR 3300–2500 (br, OH), 2946, 2912, 2855, 2665, 1095, (s, C=O), 1642 (C=C), 1419, 1285, 1225, 981, 925 cm^{-1}.

1-Cyclopentene-1-carboxylic Acid (10). A reaction of 5 with KOH was carried out as described above for 6.5 h at 140 °C to yield 69% **10**: mp 117–119 °C (lit.[7] mp 119–120 °C); the ^1H NMR and IR spectra agreed with the literature;[7] ^{13}C NMR δ 171.5, 147.4, 136.5, 33.7, 31.1, 23.2.

2-Methyl-1-cyclohexene-1-carboxylic Acid (11). Reaction of 6 with KOH was carried out as described above for 41 h at 160 °C to yield 65% **11**. The crude material was recrystallized from methanol and water to give white needles, mp 84–85 °C. The ^1H NMR, ^{13}C NMR, and IR spectra agreed with those previously reported.[8]

Bicyclo[2.2.1]hept-2-ene-2-carboxylic Acid (12). Reaction of 7 with KOH was carried out as described above for 17 h at 130 °C to yield 73% **12**. The ^1H NMR and IR spectra were identical to those previously reported:[9] ^{13}C NMR δ 171.1 (CO_2H), 150.5, 140.9, 48.4, 44.0, 41.8, 24.7, 24.6.

4-Phenyl-3-butenoic Acid (13). Reaction of 8 with KOH was carried out as described above for 5 h at 130 °C to yield 72% **13**. The ^1H NMR spectrum agreed with that previously reported[10] and indicated an *E*:*Z* ratio of 5:1: IR 3400–2400 (br OH), 2890, 1695 (C=O), 1647 (C=C), 1457, 1375, 1290, 1220, 973, 912, 736, 680 cm^{-1}.

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Kinetic Medium Effects in *N*-Cyclohexyl-2-pyrrolidone–Water Mixtures. Evidence for a Low Critical Hydrophobic Interaction Concentration

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Binary mixtures of water with a relatively hydrophobic cosolvent have been defined as typically aqueous (TA) solutions.[1] Sufficiently hydrophobic solutes, dissolved in

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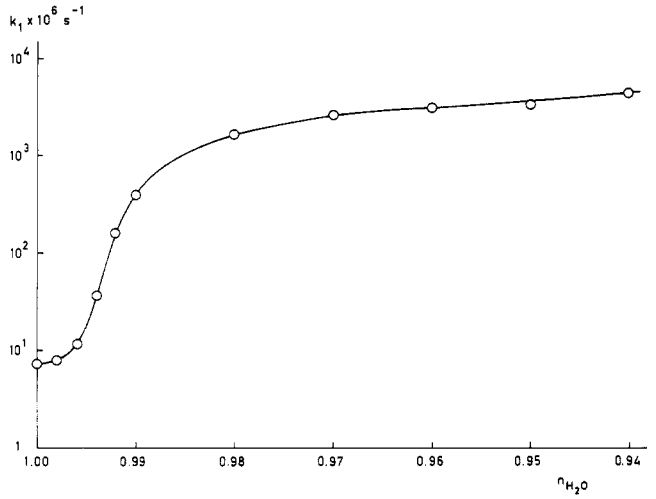


Figure 1. Plot of k_1 vs n_{H_2O} for the decarboxylation of 1 in CHP–H_2O at 30 °C.

Table I. First-Order Rate Constants and Isobaric Activation Parameters of the Decarboxylation of 1 in CHP–H_2O at 30 °C

n_{H_2O}	$k_1 \times 10^6$, s^{-1}	$\Delta^{\ddagger}H^{\ominus}$, kJ mol^{-1}	$\Delta^{\ddagger}S^{\ominus}$, J mol^{-1} K^{-1}	$E_T(30)^e$, kJ mol^{-1}
1.000	7.35[a]	134 ± 4[a]	80 ± 16[a]	262.5[f]
0.998	7.83			
0.996	11.6			253.3
0.994	36.1			243.3
0.992	159	142 ± 4[b]	148 ± 14[b]	237.5
0.990	396			230.8
0.980	1640			224.1
0.970	2440			
0.960	3150	105 ± 1[c]	52 ± 2[c]	
0.950	3520			219.8
0.940	4540	99 ± 1[d]	37 ± 2[d]	217.9

[a] Reference 10a, 303–323 K, μ = 1.0 (KCl). [b] 293–313 K. $\Delta^{\ddagger}C_p^{\ominus}$ = 3200 J mol^{-1} K^{-1}. [c] 288–308 K. [d] 283–303 K. [e] At 293 K. [f] Reference 6, 25 °C.

water-rich mixtures of this type, generally exhibit peculiar solvation effects which reflect hydrophobic hydration and hydrophobic interactions.[2] *N*-Cyclohexyl-2-pyrrolidone (CHP)–water is a remarkable example. Below 50 °C, CHP is miscible with water in all proportions. Apparently, hydration of the dipolar amide function more than compensates for the hydrophobicity of one CH group and eight CH_2 groups in the molecule. However, two-phase systems can be easily created either by increasing the temperature or by addition of electrolytes like NaCl.[3]

As discussed previously, TA solutions often exhibit pseudophase separation.[4] This is caused by destructive overlap of hydrophobic hydration shells of the cosolvent, leading to formation of small clusters. We have shown that cosolvent clustering starts at the critical hydrophobic interaction concentration (*chic*) as evidenced by kinetic[5] and spectroscopic data[6] and supported by theoretical analysis[7]

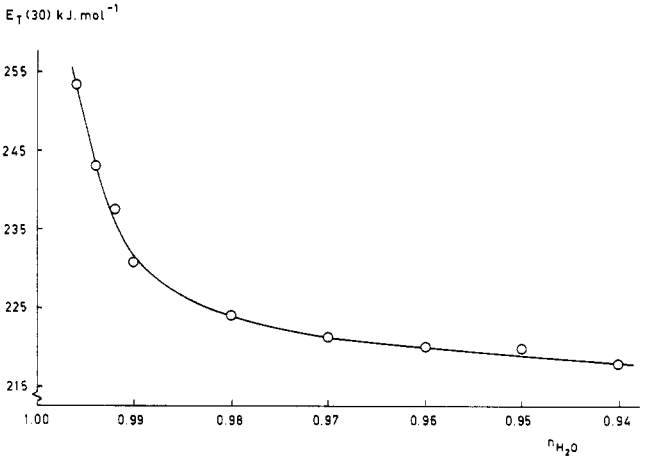
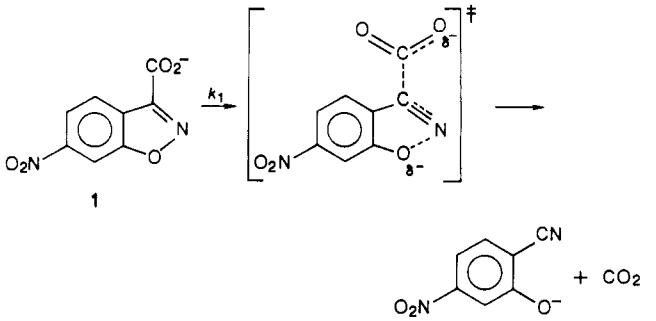


Figure 2. Plot of $E_T(30)$ vs n_{H_2O} for water-rich CHP–H_2O mixtures at 20 °C.

and computer simulations.[8] Herein we report an exceptionally low *chic* for CHP–H_2O based upon the use of 6-nitrobenzisoxazole-3-carboxylate (1) as a kinetic probe. In the activation process for the unimolecular decarboxylation of 1, the initial state with the negative charge localized on the carboxylate moiety is transferred into a highly charge dissipated transition state.[9] As a result, the



first-order rate constant (k_1) for decarboxylation is highly medium dependent[10] as illustrated[11] by k_1(THF)/k_1(H_2O) = 6 × 10^7 at 20 °C. First-order rate constants and isobaric activation parameters for the decarboxylation of 1 in highly aqueous CHP–H_2O mixtures are listed in Table I. The dependence of k_1 on solvent composition is shown graphically in Figure 1. After an initial small medium effect between 0 and 0.4 mol % of CHP, there is an enormous increase of k_1 between 0.4 and 1 mol % of CHP. Upon further addition of CHP, the rate increase levels off rapidly. In fact, the plot shown in Figure 1 is akin to similar plots for micellar catalysis of the decarboxylation of 1.[12] The kinetic medium effects are clearly indicative for pronounced pseudophase separation in CHP–H_2O with a *chic* at n_{H_2O} = 0.995 ± 0.001 (0.28 ± 0.05 M of CHP). Apparently, decarboxylation is greatly accelerated by binding of the substrate to clusters of CHP which provide a local reaction medium of decreased polarity relative to bulk solvent. As anticipated,[5] we find that just above the *chic*, $\Delta^{\ddagger}H^{\ominus}$ is highly temperature dependent (at n_{H_2O} =

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0.992, $\Delta^{\ddagger}C_p^{\ominus} = 3200$ J mol^{-1} K^{-1}), in accord with the onset of temperature-sensitive cluster formation. The occurrence of pseudophase separation is further supported by measurements of the Dimroth–Reichardt $E_T(30)$ solvent parameter[13] (Figure 2). There is a steep decrease of $E_T(30)$ going from $n_{H_2O} = 0.996$ to $n_{H_2O} = 0.98$, indicative for a large change in micropolarity experienced by the probe molecule and fully consistent with clustering of CHP. At still higher concentration of CHP only a modest further decrease of $E_T(30)$ is observed. Comparison of the *chic* at 0.28 ± 0.05 M for CHP–H_2O (30 °C) with that for the *t*-BuOH–H_2O system at 1.4 ± 0.3 M (25 °C)[5] illustrates the strongly hydrophobic character of CHP. Thus the present results characterize water-rich CHP–H_2O as an extreme case of a TA solution with significant overlap of hydrophobic hydration shells occurring already at concentrations well below 1 mol % of CHP.

Experimental Section

Materials. Sodium 6-nitrobenzisoxazole-3-carboxylate was prepared according to a literature procedure.[14] *N*-Cyclohexyl-2-pyrrolidone (obtained both from GAF Corp. and Janssen Chimica) was distilled twice (bp 96 °C (0.04 mm); $n^{20}_D = 1.4980$, lit.[15] $n^{20}_D = 1.4975$). Demineralized water was distilled twice in an all-quartz unit. 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenoxide (the $E_T(30)$ probe) was kindly supplied by Prof. Ch. Reichardt, Marburg, West Germany. All solutions were made up by mass and contained 10^{-3} M of NaOH to prevent protonation of the kinetic and spectroscopic probe.

Kinetic Measurements. These were performed by monitoring the increase of absorption as a function of time at 490 nm. All first-order rate constants (determined at least in duplicate) were reproducible to within 3%. A Perkin-Elmer λ5 spectrophotometer, equipped with a Perkin-Elmer 3600 data station, was employed. Isobaric activation parameters were obtained for the temperature ranges given in Table I. Linear Eyring plots were found, except just above the *chic*, where $\Delta^{\ddagger}C_p^{\ominus}$ was calculated by using the Valentiner equation.[16]

Spectroscopic Measurements. $E_T(30)$ values were calculated from $E_T(30) = Nhc\lambda_{max}^{-1}$ in which N = Avogadro's number, h = Planck's constant, and c = velocity of light. The λ_{max} values (±0.5 nm) were measured with the Perkin-Elmer λ5 spectrophotometer.

Acknowledgment. We thank A. van Warners for preliminary measurements on the CHP–H_2O system.

Supplementary Material Available: First-order rate constants at different temperatures for decarboxylation of **1** in CHP–H_2O at n_{H_2O} = 0.992, 0.960, and 0.940 (1 page). Ordering information is given on any current masthead page.

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Polar Effects in the Decomposition of Diaroyl Peroxides. Benzoyl Peroxide on Silica Gel

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Introduction

Many diacyl peroxides are known to give both ion pairs and radical pairs on thermal decomposition. In the Walling model,[1] the bifurcation of the reaction path occurs at a common intermediate rather than at the peroxide itself. The transition state leading to this intermediate is sufficiently polar for the disappearance of the peroxide to be accelerated both by polar solvents and by electron-releasing substituents. Since the rate- and product-determining steps are decoupled, the polar substituent or solvent can increase the rate of formation not only of the ion pairs but also of the radical pairs.

Since the rate-determining transition state and the common intermediate are represented as resonance hybrids of singlet radical pair and ion-pair structures, a continuum rather than a duality of mechanisms is possible. At one extreme the rate is insensitive to small polar perturbations and the products are almost entirely radical. At the other extreme the rate is very sensitive to polar effects, and the products are derived almost entirely from ion pairs. In general, polarizing substituents and polar solvents will increase both the overall rate and the proportion of products derived from ion pairs.

The best evidence for a Walling mechanism is the isolation of a mixture of ionic and radical products, but products have been thoroughly characterized only for a few peroxides. Increased rates in polar media are also indicative, although they may be due in part to induced decomposition. For alkanoyl peroxides with branches at the α-position, the formation of ion pairs is well established by product studies; these peroxides are also very sensitive to the polarity of the solvent. For unbranched alkanoyl peroxides, the product data are insufficient, but a moderate sensitivity to the polarity of common solvents supports a Walling mechanism. For the acetyl peroxide, a similar but not identical series of solvents shows almost no sensitivity to solvent polarity.[2] This extremely dangerous peroxide is therefore either an exception[3] or a representative of the radical extreme of the Walling continuum, although its behavior on silica has not been studied.

Aroyl peroxides are a special case in which an important ionic contributing structure should be like **1** of eq 1. The Walling mechanism is well established for benzoyl peroxides with *p*-methoxy substituents, for example *p*-methoxy-*p'*-nitrobenzoyl peroxide decomposing in thionyl chloride[4] and anisoyl peroxide decomposing on silica gel.[5] These reactions gave the carboxyinversion compound **2**, formed by the collapse of the intimate ion pair **1**, as a major product accompanied by minor amounts of radical products.

For benzoyl peroxide itself, however, no products analogous to **2** have ever been observed, and the use of more polar solvents has produced only moderate increases in rate. For example, the rates of the styrene-inhibited reaction in acetic anhydride,[6] and the 3,4-dichlorostyrene-inhibited reaction in acetonitrile,[7] were less than 1.7 times the rates in carbon tetrachloride. Although induced decomposition was suppressed as much as possible in obtaining those rates, it is not certain that the entire effect of the change in solvent was due to an increase in the unimolecular rate constant. The rate is also insensitive to the presence of strong carboxylic acids and even sulfuric acid.[8]

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