Unstable Compounds. Synthesis and Experimental and Computational Study of the Chemical Behavior of 9-[1-(2,4,6-Cycloheptatrienyl)]-9-xanthydrol

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Received May 24, 1989

The title alcohol (1) was synthesized in good yield by a novel umpolung method involving reaction of the lithium dianion of 9-xanthone with tropylium ion. It was prepared to see if its derived carbenium ion might undergo spontaneous α fragmentation to form tropylium ion and singlet-state xanthylidene. In contrast to expectation, treatment of 1 with Brønsted and Lewis acids under a variety of experimental conditions produced 9benzylidenexanthene (8) as the exclusive dehydration product. Stable ion and trapping studies established that the 9-benzyl-9-xanthyl cation was the immediate precursor of 8. When this cation was generated from 1 or 8 and trapped with triethylsilane- d_1 , 9-benzylxanthene- $9-d_1$ was produced with primary deuterium kinetic isotope effects of 1.27 ± 0.07 and 1.28 ± 0.07 , respectively. The energy surfaces leading to contraction of the cycloheptatrienyl ring to the phenyl ring were explored by molecular mechanics and MNDO calculations. The computational results indicated that the most probable mechanism involved the intervention of a phenonium ion intermediate but not a tropylium ion. It was estimated that the activation energy of the reaction pathway leading to the observed ring-contracted product was ca. 31.0 kcal/mol lower than that of the unobserved α -fragmentation route (40.1 vs 71.1 kcal/mol).

The formation of new carbon-carbon bonds is important in organic chemistry. On the other hand, there is much to be learned from the study of reactions where carboncarbon bonds in organic compounds undergo spontaneous cleavage to form new fragmentation products. For example, it has recently been shown that some remarkable spontaneous heterolytic fragmentations of covalent organic compounds into carbocation-carbanion pairs may occur in solution.¹⁻⁷ In addition, it is known that whether the carbon-carbon bond cleaves heterolytically to produce ion pairs or homolytically to produce radical pairs is influenced by the polarity of the solvent and that the equilibrium between ion pairs and radical pairs already formed is affected by changes in the solvent (eq 1).^{8,9} It is not surprising that internal steric, inductive, and resonance effects play expected roles in directing these fragmentations.



The fragmentation of carbon-carbon bonds in carbocations has been known for some time. The most common form of this fragmentation is seen in the cleavage of bonds β to a carbocation center to produce an alkene and a "daughter" carbocation (eq 2). Such β fragmentations are understood in classical terms; they are generally driven by

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thermodynamics, through formation of the C=C bond and a daughter carbocation no less stable than its precursor.¹⁰⁻¹⁵



Much less common than β fragmentations are α fragmentations of carbocations which lead to a new daughter carbocation and a carbene in the singlet electronic state (eq 3). Among the few reported examples of carbenes

believed to be formed by the carbenium ion fragmentation route shown in eq 3 are those derived from "hot" (vibrationally excited) carbenium ion-iodide ion pairs from photolysis of alkyl iodides,¹⁶ from the diazotization of some enamines which give "hot" vinyl cations prior to proton loss,¹⁷ and from the base-induced deprotonation of the dimethoxycarbenium ion and its thio analogue.¹⁸ There is also a report of the fragmentation of a simple alkyl cation by this route under mass spectrometric conditions¹⁹ and the suggestion of extrusion of dimethylcarbene from a sterically strained alkyl cation.²⁰

Our present work is the result of a search for unstable compounds that may form carbocations prone to undergo spontaneous α fragmentations to give daughter carbocations and singlet carbenes. It is clear that the design of

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such molecules must incorporate driving forces that make fragmentation competitive with more common reaction behavior. The fragmentation products, both daughter carbenium ion and singlet carbene, should be as stable as possible.

We felt that 9-[1-(2,4,6-cycloheptatrienyl)]-9-xanthydrol (1) would offer such possibilities by behaving as indicated in eq 4 upon treatment with acid. Ion 2, a rather stable



9-xanthyl cation, could fragment to yield xanthylidene (3), a carbene known from both experimental and theoretical studies to be relatively unreactive and to have a singlet electronic ground state,^{21,22} and the stable tropylium ion (4).²³ The tropylium ion is known to be formed from the heterolytic dissociation of C-C bonds in hydrocarbons⁵ and from the β fragmentation of carbocations.¹⁵

Results and Discussion

Synthesis of Alcohol 1. The target alcohol is simple in structure; however, it presents a formidable synthetic challenge. The classical approach through addition of an organometallic carbanion equivalent to the electrophilic carbonyl carbon of a ketone is not feasible in this case. This is because of the great difficulty in generating a synthetically well-behaved functional equivalent of the antiaromatic tropylium anion to add to 9-xanthone (5).24-26 In contrast to the anion, the tropylium cation is readily available.²³ We therefore explored the umpolung approach to the synthesis of 1.2^7 The strategy was one of finding a method to convert the carbonyl carbon of 9-xanthone from its normal electrophilic state to that of a nucleophile.

It has been known for some time that diaryl ketones such as benzophenone and 9-xanthone will not only accept a single electron from sodium metal to become a ketyl radical anion but may also receive a second electron to become a dianion that is capable of being alkylated at the Lithium or potassium metals can carbonyl carbon.²⁸ perform a similar electron-donor role.^{29,30}

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Previous work suggested that use of less than a stoichiometric amount of 4,4'-di-tert-butylbiphenyl (DBB) as an electron-transfer agent^{31,32} from a stoichiometric excess of lithium sand (alloyed with ca. 3% sodium³³) would promote the efficient formation of the desired dianion of xanthone (7) in THF. The reaction sequence that we used successfully is depicted in Scheme I.

The reaction sequence involved first the generation of lithium DBB radical anion through single electron transfer from the lithium metal onto DBB.^{34,35} This was accompanied by the formation of a deep-green solution. The DBB radical anion then successively transferred one electron onto the 9-xanthone to generate a monoanion (deep blue, 6), followed by subsequent electron transfer again from the DBB radical anion onto the monoanion 6 to form a dianion or dilithio-9-xanthone (deep-purple solution, 7). The dilithio-9-xanthone was then alkylated with tropylium bromide to give 1 in ca. 80% yield. The product was fully characterized. All spectroscopic and analytical features were in full accord with expectations for the structure of 1.

In the absence of DBB, no dianion formed even after 48 h. This indicates that DBB served as an electrontransfer reagent from the lithium metal onto the 9xanthone and substantiates the evidence that the generation of dilithio-9-xanthone involved two sequential single-electron-transfer reactions. The rate of formation of the DBB radical anion was found to be greatly dependent on whether the reaction mixture was sonicated or mechanically stirred.^{36,37} When the reaction vessel was immersed in a laboratory ultrasonic bath, the deep-green colored solution of the DBB radical anion formed almost immediately, whereas if mechanical stirring was employed. it took about 2 h for the THF solution to turn deep green.

We conclude that all elements of this synthetic technique are important; the use of THF as solvent, the use of DBB as an electron-transfer agent, the use of an excess of lithium metal, and the use of ultrasonics during the reaction. The technique is simple, yet appears to be rarely used in modern organic synthesis. It could be used for the preparation of many compounds by the creation of new carbon-carbon bonds through addition of electrophiles to carbonyl groups having functionally reversed polarities.

Formation of Carbocations from Alcohol 1. Alcohol 1 was subjected to a variety of acid conditions designed to lead to the formation of carbenium ions. In one experiment 1 was dissolved in dichloromethane, and the solution was saturated with dry hydrogen chloride. The system was then closed and maintained at 25 °C for 30 min. Following quenching with saturated aqueous sodium bicarbonate solution and workup, the product was subjected to GC/MS, ¹H NMR, and ¹³C NMR analyses. Surprisingly, the olefin 9-benzylidenexanthene (8), obtained in 96% yield, was the exclusive product. None of the known heterofulvene isomer 938 was obtained. Tri-

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Scheme II н -H2C -H2O 10 Scheme III Et3Si-H (D) 11

fluoroacetic acid, methanesulfonic acid, and boron trifluoride etherate all promoted the same behavior.



In an effort to understand the origin of this behavior, 9-benzyl-9-xanthydrol (10) was prepared by addition of benzylmagnesium chloride to xanthone and subjected to the same acid conditions as was 1. It, too, gave exclusively olefin 8 (Scheme II).

In separate experiments, excess trifluoroacetic acid was added at 0 °C to dichloromethane solutions containing a stoichiometric excess of the carbocation-trapping agent triethylsilane³⁹ and compounds 1, 8, and 10. In each case, the only product observed following workup was 9benzylxanthene (11).⁴⁰ Substitution of triethylsilane- d_1 for triethylsilane produced 9-benzylxanthene-9- d_1 product. This product was obtained with a primary deuterium kinetic isotope effect (KIE) of $k_{\rm H}/k_{\rm D} = 1.27 \pm 0.07$ from 1 and $k_{\rm H}/k_{\rm D} = 1.28 \pm 0.07$ from 8. These isotope effects are consistent with other primary KIEs observed for similar carbocations captured by deuteriated silicon hydrides.⁴¹ It was concluded from these experiments that the 9benzyl-9-xanthyl cation (12) was the common reaction intermediate derived from all of the cation sources (Scheme III). Solutions prepared from both alcohols 1 and 10 in an equal mixture of trifluoroacetic and meth-



anesulfonic acids at -10 °C displayed identical NMR spectra consistent only with the presence of ion 12 exclusively.

Computational Investigation of the Reaction Mechanism. To investigate possible mechanistic reasons for the experimentally discovered facile acid-catalyzed conversion of 1 to 8, the energies and structures of various molecular species that might reasonably be expected to intervene along reaction pathways leading from 1 to 8 were calculated by using both molecular mechanics and MNDO semiempirical methods.

The MNDO calculations were carried out by appropriate modifications of the MNDO program^{42,43} based on the restricted Hartree-Fock (RHF) method. MNDO has been shown to reproduce the ground-state properties of a wide variety of organic molecules in a satisfactory manner and to be generally superior to MINDO/3 in handling carbenes, cations, radicals, and anions.^{43,44} The properties of the neutral compounds 1, 8, and 9 were also calculated by the MMX molecular mechanics program.⁴⁵⁻⁴⁷

Total geometry optimizations in MNDO were done with estimations of second derivatives (Hessian matrix) for each of the 3n - 6 parameters in each species (2n - 3 for planar structures).⁴⁸ An energy minimum (a stable compound or a reactive intermediate) has no negative vibrational force constants. A transition state is a saddle point which has one and only one negative vibrational force constant.49 Since an optimized geometry may turn out to be a local minimum, the optimization started from at least two starting geometries to verify global minima. The activation energy of a certain pathway was checked by the "reaction coordinate" method. 50-52 The "in vacuo" calculations of the type performed in this study are partly justified by the relatively low polarity of the reaction solvent.

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Several possible routes were considered for the formation of 8 from 1. Scheme IV shows the mechanism that seems most reasonable based on the relatively low energy calculated for progress along it. The numbers in parentheses are the MNDO-calculated heats of formation and activation energies, in units of kcal/mol.

The reaction mechanism postulated in Scheme IV involves protonation of the hydroxyl group of 1 and elimination of water leading to intermediate 2, which can interconvert to 8 by the indicated three-step process $(2 \rightarrow 13 \rightarrow 14 \rightarrow 8)$ involving as stable intermediates the norcaradienylxanthylium cation 13 and a substituted benzenonium ion, 14.53

The first step of this pathway involves cyclization of the cycloheptatriene ring of 2 to a norcaradiene ring (13). The calculated activation energy of this step is 18.2 kcal/mol. Some years ago it was reported that interconversion of cycloheptatriene to norcaradiene can take place by ionic or radical mechanisms.^{54–56} A rough value of 11 ± 4 kcal/mol for the activation energy of this process was estimated from bond energies.⁵⁶ Moreover, the existence of an equilibrium for the interconversion of 1-cyano-1-(trifluoromethyl)cycloheptatriene to the corresponding norcaradiene has been demonstrated by Ciganek.⁵⁷ It is worth noting that the stabilities of ions 2 and 13 are estimated to be virtually the same (233.6 vs 233.3 kcal/mol). The stability of the norcaradienyl species 13 is expected to be enhanced because of the electron-withdrawing effect of the adjacent electron-deficient center at C-9 of the xanthyl system.58

The next step involves fission of the bond β to the positive carbon atom in the norcaradiene ring. Our calculated activation energy of this fission $(13 \rightarrow 14)$ is 20.4 kcal/mol. Arenium ions (e.g., 14) are generally highly reactive intermediates that continue on through further reactions: however, their isolation has been reported.⁵⁹ The arenium ion 14 is stabilized by deprotonation and aromatization, a process that leads to product 8. Isotope effect studies indicate that, in many instances, deprotonation of benzenium ions to benzene rings is a fast step, and the C-H bond is not broken in the rate-determining step.⁵⁹ However, in our case the calculated activation energy of this step is 27.2 kcal/mol. It is worthy of note that the activation energy of this step $(14 \rightarrow 8)$ was calculated by stretching the C-H bond in increments of 0.1 Å, without including the effect of the conjugate base (Cl⁻). We believe the base (Cl⁻) can decrease the activation energy by several kcal/mol.

The calculated overall activation energy along the minimum energy reaction path (MERP) for $2 \rightarrow 13 \rightarrow 14 \rightarrow 8$ is 40.1 kcal.⁵³ The reaction mechanism represented by this pathway is thus similar to one suggested for the contraction of the 7-cycloheptatrienyltropylium ion to the benzyltropylium ion.⁶⁰

There is a possibility that intermediate 9 could be involved in the reaction pathway, but this seems unlikely. Alkene 9 would be an improbable final product since 8 is

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so much more stable (heats of formation of 54.4 vs 77.5 kcal/mol from MNDO, 55.5 vs 87.1 kcal/mol from MMX calculations). Because cation 15 is calculated to be significantly more stable than 2, it might be expected that it would be formed from 2 either indirectly by way of protonation-deprotonation of alkene 9 or directly by reversible intramolecular 1,2-hydride shifts from 2. This is not the case. When 15 was formed by a different reaction route, it was found, as expected from its calculated properties, to be stable in the absence of strong nucleophiles and to give only alkene 9 upon treatment with weak bases.⁶¹ There appears to be a large kinetic barrier separating 2 from both 15 and 9. We are currently exploring this phenomenon.

The original goal of this work was to experimentally investigate the question of whether or not carbenium ion 2 from alcohol 1 might undergo direct spontaneous α fragmentation to a stable carbene (3) and a smaller "daughter" carbenium ion (4) as depicted in eq 4. As this was not observed, we have sought an explanation by probing the energy surfaces with MNDO calculations. Our calculations enable us to estimate that the enthalpy change for eq 4 is 63.4 kcal/mol and that the activation energy is on the order of 71.1 kcal/mol. Since the estimated activation barrier along the MERP of the experimentally observed ring contraction of 2 to 8 is only 40.1 kcal/mol, it is not difficult to understand why the α -fragmentation process was not competitive in this case and was therefore not experimentally observed.

Experimental Section

General nuclear magnetic resonance spectra were obtained on a Varian VXR-400 spectrometer. The solvent used was $CDCl_3$ (pretreated with basic alumina) unless otherwise indicated. Chemical shifts (ppm) were referenced to Me_4Si . Infrared spectra were determined on a Nicolet 60 SX FTIR instrument. The GC/MS experiments were performed on a Hewlett Packard 5988A instrument using a 12-m methyl silicone capillary column. Mass spectra were recorded as m/z (relative intensity). Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. The MNDO calculations were performed on a DEC VAX 6220 and the force constant calculations on a CRAY X-MP/24 computer. The molecular mechanics calculations were obtained on a Zenith Z-286 microcomputer.

Tropylium Bromide. The compound was synthesized with slight modification by using the method of Doering and Knox.²³ A solution of Br_2 (0.12 mol) in CCl_4 (63 mL) was added dropwise at 0 °C with vigorous stirring to a solution of cycloheptatriene (0.11 mol) in CCl₄ (80 mL) over 3.5 h. After all the Br₂ solution was added, the reaction mixture was stirred at 0 °C for an additional 15-30 min. The crude mixture was concentrated under vacuum (water aspirator) over a period of 1.5 days. After all the solvent was removed, the dark lump of tropylidene dibromide was dehydrobrominated by heating under vacuum (water aspirator) at 55-60 °C over a 3-day period. The dark-green cake was then washed several times with CCl4 and filtered under vacuum overnight. The greenish-yellow solid was then dissolved in hot absolute ethanol (70 mL). It precipitated almost immediately at -50 °C. The solid was filtered dry and kept in a CaCl₂-charged desiccator under vacuum for 2.5 days. Washing with hot absolute EtOH was repeated once more. The greenish-yellow solid (11.72 g, 63%, mp 200-202 °C) was then triturated with hot anhydrous CHCl₃ to remove any traces of hydrogen bromide or ethanol and then heated under vacuum at 80 °C for 15 min. The ¹H NMR (D₂O) spectrum showed one signal at δ 9.17 (s). The ^{13}C NMR (D_2O) spectrum showed only one signal at δ 157.75. The IR (KBr) spectrum had sharp absorptions at 2988, 1224, 1044, and 650 cm⁻¹.

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Behavior of 9-[1-(2,4,6-Cycloheptatrienyl)]-9-xanthydrol

9-[1-(2,4,6-Cycloheptatrienyl)]-9-xanthydrol (1). Into an oven-dried flask equipped with a condenser (under argon atmosphere) containing 0.100 g of lithium sand (14.41 mmol, alloyed with 3% Na³³) washed with dry pentane was added 0.77 g of DBB (2.88 mmol) dissolved in dry THF (15 mL). The reaction mixture was sonicated for 15 min. Into the dark-green solution of the radical anion, xanthone (4.80 mmol, Aldrich) in dry THF (20 mL) was added dropwise over 1.0-1.5 h at room temperature with vigorous stirring. After the formation of the dianion (3-4 h), the deep-purple solution was cooled to -50 °C, and solid tropylium bromide (4.80 mmol) was quickly added. The reaction mixture was then warmed to room temperature and stirred for an additional 19 h. The reaction mixture (dark blue-green solution) was diluted with CH_2Cl_2 :hexanes (1:1, 50 mL) and quenched with saturated aqueous ammonium chloride solution. The aqueous layer was extracted twice more with the mixed solvent. The combined organic layer was washed with aqueous saturated sodium bicarbonate and brine, respectively, and dried over anhydrous magnesium sulfate. It was then concentrated by rotary evaporation to give 2.70 g of crude product. Purification by elution from a silica gel column (230-400 mesh, 100 g) with hexanes:ether (12:1) followed by recrystallization from pentane:THF (2:1) gave pure alcohol as a white solid (82%, compared to unrecovered ketone), mp 142-143 °C. The ¹H NMR spectrum showed signals at δ 7.81 (2 H, dd, J = 1.59, 7.70 Hz), 7.35-7.21 (6 H, m), 6.55 (2 H, t, J = 3.10 Hz), 6.12 (2 H, br d, J = 9.09 Hz), 5.40 (2 H, dd, J = 5.90, 9.06 Hz), 2.49 (1 H, OH, s), and 1.97 (1 H, br t, J = 5.86Hz). The ¹³C NMR spectrum had signals at δ 151.1, 130.7, 129.1, 127.1, 126.4, 125.2, 123.5, 121.5, 116.3, 69.9, and 53.5. The IR spectrum (CDCl₃) had sharp absorptions at 3575, 3021, 2838, 1572, 1469, 1449, 1309, 1240, and 915 cm⁻¹; MS m/z 288 (1), 270 (79), 210 (13), 197 (100), 196 (97), 91 (82). Anal. Calcd for C₂₀H₁₆O₂: C, 83.33; H, 5.56. Found: C, 83.38, H, 5.55.

9-Benzyl-9-xanthydrol (10).62 A solution of benzyl chloride (2 g, 15.8 mmol) in ether (10 mL) was added to magnesium turnings (0.38 g, 15.6 mmol) in dry ether (6 mL). The mixture was refluxed for 30 min and then cooled to 0 °C. A solution of xanthone (1.57 g, 8.00 mmol) in ether (25 mL) was added dropwise. After all the xanthone solution was added (15 min), the reaction mixture was heated again to reflux for 15 min. The cooled reaction mixture was diluted with ether and washed with saturated aqueous ammonium chloride. The aqueous layer was extracted twice with ether. The combined ether layer was washed with saturated aqueous sodium bicarbonate and then brine, dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation to give crude product, 2.35 g. The crude reaction product was recrystallized by using pentane:THF (2:1) to give 1.8 g (78%) of pure product, mp 135-137 °C. The ¹H NMR showed signals at δ 7.75 (2 H, dd, J = 1.70, 7.73 Hz), 7.33–6.95 (9 H, m), 6.44 (2 H, dd, J = 1.35, 8.37 Hz), 3.18 (2 H, s) 2.53 (1 H, OH, s). The ¹³C NMR spectrum had signals at δ 150.5, 135.0, 130.4, 128.9, 127.4, 126.6, 126.5, 126.4, 123.1, 115.8, 70.3, and 53.1. The IR spectrum (CCl₄) had sharp absorptions at 3591, 3065, 3055, 3029, 2912, 1597, 1453, 1315, and 1249 cm⁻¹; MS m/z 288 (M⁺, 1), 270 (80), 197 (100), 196 (4), 91 (1).

Treatment of 1 with Acid. A 2-mL portion of dry CH₂Cl₂ was saturated with anhydrous hydrogen chloride gas at 25 °C. Alcohol 1 (100 mg) was added quickly into the saturated CH_2Cl_2 . The color of the reaction turned deep-green immediately. After 30 s at 25 °C, the reaction was quenched with saturated aqueous NaHCO₃ and diluted with CH₂Cl₂. The aqueous layer was extracted twice with CH₂Cl₂. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated on a rotary evaporator to give 90 mg (96%) of alkene 8. Extended reaction time and higher temperature did not affect the yield or composition of the product; mp 108–110 °C (lit. mp 63 110-111 °C). The ¹H NMR spectrum showed signals at δ 7.90 (1 H, dd, J = 1.50, 8.27 Hz), 7.38-7.19 (11 H, m), 7.09 (1 H, s),6.84 (1 H, tt, J = 1.38, 7.00 Hz). The ¹³C NMR spectrum showed signals at δ 153.7, 152.2, 138.7, 130.3, 129.7, 129.3, 129.26, 129.2, 127.8, 127.3, 125.5, 124.9, 124.3, 123.6, 123.2, 121.9, 117.9, and 117.5. The IR spectrum (CCl₄) showed strong absorptions at 3074, 3056, 3029, 1623, 1550, 1453, 1272, 1213, 1102, 979, and 878 cm⁻¹; MS m/z 271 (M⁺ + 1, 19), 270 (M⁺, 100), 269 (M⁺ - 1, 98), 268 (63), 255 (8), 240 (8), 239 (30), 237 (8), 213 (8), 134 (39), 51 (9), and 39 (12). These properties are consistent with the structure of alkene 8.⁶³

Treatment of 10 with CF_3CO_2H . A solution of 0.5 g of 9-benzyl-9-xanthydrol (10) in 10 mL of dry CH_2Cl_2 was treated with 17.73 mmol of CF_3CO_2H at 0 °C for 5 min and at 25 °C for 10 min. The reaction was quenched with solid, anhydrous K_2CO_3 . The reaction mixture was diluted with CH_2Cl_2 and washed with water. The aqueous layer was extracted once more. The combined organic layer was dried over anhydrous MgSO₄ and concentrated by rotary evaporation to give 0.46 g (96%) of solid, mp 108–110 °C. Spectral analysis was consistent with structure 8.

Silane Reduction of 1. Trifluoroacetic acid (0.88 mmol, 0.24 mL) was added to a solution containing 25.4 mg of 1 and triethylsilane (56.3 μ L, 0.353 mmol) in dry CH₂Cl₂ (2.5 mL) at 0 °C. The reaction mixture was warmed up to room temperature for 15 min.³⁹ The solution was then diluted with CH₂Cl₂ and neutralized with saturated aqueous sodium bicarbonate. The aqueous layer was extracted twice. The combined organic layer was washed with brine, dried over anhydrous magnesium sulfate, and then concentrated by rotary evaporation to give 26 mg of crude product. The crude product was separated by preparative TLC, to give 21.1 mg (88%) of pure product, mp 65-67 °C. The ¹H NMR spectrum showed signals at δ 7.30-6.70 (13 H, m), 4.25 (1 H, t, J = 6.59 Hz), and 2.95 (2 H, d, J = 6.59 Hz). The ¹³C NMR spectrum showed signals at δ 152.3, 138.2, 129.8, 128.9, 127.9, 127.6, 126.3, 124.7, 122.9, 116.3, 47.5, and 41.8. The IR spectrum (CDCl₃) showed strong absorptions at 3086, 3029, 2918, 2851, 1479, 1253, 1186, and 1031 cm⁻¹; MS m/z 272 (M⁺, 3) 182 (14), 181 (100), 152 (10), 91 (10), 83 (5). These data are consistent with the structure of 9-benzylxanthene, 11.40

Et₃SiD Reduction of 1. Trifluoroacetic acid (0.25 mL, 1.74 mmol) was added to a solution containing 50.0 mg of 1 and Et₃SiD (0.102 g, 0.87 mmol) in dry dichloromethane (1 mL) t 0 °C. The reaction mixture was stirred at 0 °C for 10 min and warmed to room temperature for 1.0 h. After 1.0 h at room temperature 0.37 g of anhydrous potassium carbonate was carefully added. The crude mixture was diluted with dichloromethane and washed with water. The aqueous layer was extracted once more with dichloromethane. The combined organic layer was washed with brine, dried $(MgSO_4)$, filtered, and concentrated by rotary evaporation. The crude product was purified by preparative TLC using hexane:EtOAc (9:1) to give 35.5 mg (75%) of 9-benzylxanthene-9- d_1 . The ¹H NMR spectrum showed signals at δ 7.30-6.70 (13 H, m) and 2.98 (2 H, s). The ²H NMR spectrum showed a signal at δ 4.3. The ¹³C NMR spectrum showed signals at § 152.3, 138.2, 129.8, 127.9, 127.6, 126.3, 124.6, 122.9, 116.3, 47.4, and 41.5 (t, J = 22 Hz). The IR spectrum (CCl₄) showed strong absorptions at 3056, 3020, 2912, 2840, 2137, 1930, 1894, 1579, and 1299 cm⁻¹; MS m/z 273 (M⁺, 1), 183 (13), 182 (100), 153 (10), 91 (5), and 86 (2). These data are consistent with the structure of 9-benzylxanthene-9- d_1 . Use of an excess of an equimolar mixture of triethylsilane and triethylsilane- d_1 and analysis of the ¹H NMR spectrum of the product showed that it was formed with a primary deuterium kinetic isotope effect equal to 1.27 ± 0.07 .

Silane Reduction of 8. Trifluoroacetic acid (3.7 mmol, 0.52 mL) was added to a solution containing 5 (100 mg, 0.37 mmol) and triethylsilane (0.30 mL, 1.85 mmol) in dry dichloromethane (2 mL) at 0 °C. The reaction mixture was warmed up to room temperature for 20 min and then neutralized with anhydrous potassium carbonate (0.75 g). The reaction mixture was diluted with dichloromethane and washed with water, and the aqueous layer was twice extracted with dichloromethane. The combined organic layer was washed with brine, dried (MgSO₄), filtered, and concentrated by rotary evaporation to give 94.4 mg (94%) of pure product whose spectral properties were consistent with those of compound 11. Use of an excess of an equimolar mixture of triethylsilane and triethylsilane- d_1 and analysis of the NMR spectrum of the product showed that it was formed with a primary deuterium kinetic isotope effect equal to 1.28 ± 0.07 .

Silane Reduction of 10. Trifluoroacetic acid (3.5 mmol, 0.50 mL) was added to a solution containing 9-benzyl-9-xanthydrol

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(10, 100 mg, 0.35 mmol) and triethylsilane (0.28 mL, 1.75 mmol) in dry dichloromethane (2 mL) at 0 °C. The reaction mixture was warmed up to room temperature for 20 min and then neutralized with anhydrous potassium carbonate. The reaction mixture was diluted with dichloromethane and washed with water, and the aqueous layer was extracted twice with dichloromethane. The combined organic layer was washed with brine, dried (Mg-SO₄), filtered, and concentrated by rotary evaporation to give 90.7 mg (96%) of product. The spectral analyses were consistent with the structure of compound 11.

Study of Stable Carbocations Derived from 1 and 10. Solutions were prepared by adding 40 mg of 1 or 10 into 1 mL of a rapidly stirred mixture of $CF_3CO_2H:CH_3SO_3H$ (1:1) at -10 °C. The yellow solutions were examined by ¹H NMR spectroscopy. The spectra were the same, regardless of starting material. The chemical shifts were determined from Me₄Si mixed with acetone- d_6 (1:1 v/v) and sealed in a capillary tube inserted into the sample tube; ¹H NMR δ 8.20 (2 H, d, J = 8.78 Hz), 7.94 (2 H, t, J = 7.84 Hz), 7.73 (2 H, d, J = 9.00 Hz), 7.44 (2 H, t, J = 7.55 Hz), 6.42 (5 H, m), and 4.80 (2 H, s). These spectra were consistent with formation of the 9-benzyl-9-xanthyl cation (12). Due to the high instability of the initially formed 9-cycloheptatrienyl-9-xanthyl cation (2), efforts to obtain its NMR spectrum at -78 °C failed.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work, the Ohio Supercomputer Center for time on the CRAY X-MP/24, the State of Ohio Academic Challenge Program for the funds for the high-field NMR spectrometer, and the U.S. Department of Education for a cost-sharing grant for the purchase of the GC/MS/DS instrument.

Supplementary Material Available: Geometries, heats of formation, and distributions of formal charge calculated by MNDO for the various species discussed in the text (4 pages). Ordering information is given on any current masthead page.

Formation of Acrylic Acid from Lactic Acid in Supercritical Water

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Received May 26, 1989

Supercritical (SC) water is an unusual medium in which fast and specific heterolytic reactions can be conducted at temperatures as high as 400 °C. In supercritical water, lactic acid decomposes into gaseous and liquid products via three primary reaction pathways. Products of the acid-catalyzed heterolytic decarbonylation pathway are carbon monoxide, water, and acetaldehyde. Products of the homolytic, decarboxylation pathway are carbon dioxide, hydrogen, and acetaldehyde. Products of the heterolytic, decarboxylation pathway are carbon dioxide, hydrogen, and acetaldehyde. Products of the heterolytic, decarboxylation pathway are cardon dioxide, hydrogen, and acetaldehyde. Products of the heterolytic, dehydration pathway are acrylic acid and water. The intramolecular nucleophilic displacement of the α -hydroxyl by the carbonyl group of lactic acid, producing α -propiolactone as an unstable intermediate which subsequently rearranges to become the unsaturated acid, is a likely mechanism for acrylic acid formation, although an intramolecular E2 elimination initiated by attack of the carbonyl oxygen on a methyl hydrogen cannot be ruled out. Support for the former mechanism comes in part from the observed 100% relative yield of acrylic acid from β -propiolactone in SC water.

Introduction

In the vicinity of its critical point ($P_c = 22$ MPa, $T_c = 374$ °C), water is a fascinating solvent with many unusual properties. For example, as the hydrostatic pressure P increases from P_c to 34.5 MPa, the dielectric constant of water¹ at 375 °C rises from 4 D to over 12 D, while its density increases from 0.2 to 0.6 g/mL and its ion product^{2,3} k_w exceeds 10^{-12} . Thus the properties of supercritical (SC) water more closely resemble the familiar properties of low-temperature aqueous water than those of steam,^{4,5} even at temperatures as high as 400 °C. Because of its high temperature, only trace concentrations (10^{-3} M) of acids or salts in SC water are required to effect changes in the pH and ion strength which can influence the rates and

mechanisms of many aqueous phase heterolytic chemical reactions.^{6,7} Similarly, the novel, gross variations in solvent dielectric constant and density near the critical point can also dramatically influence the reaction chemistry of dissolved species.⁸ This paper illustrates the magnitude of these influences on a reaction of particular interest to the biotechnology community: the selective formation of acrylic acid from lactic acid in supercritical water.

Lactic (2-hydroxypropanoic) acid is a commerical fine chemical used primarily by the food, medical, and cosmetic industries. A wide array of biomass, including corn, whey, and sugarcane bagasse can be used as fermentation feedstocks in the manufacture of lactic acid. Lactic acid also appears as a byproduct of many industrial carbohy-

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