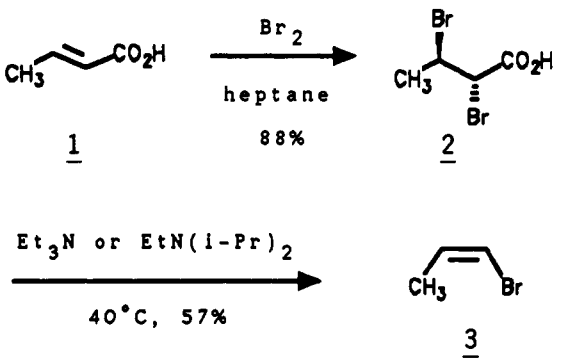
Scheme I



bromo(trialkylsilyl)propane derivative,[8,9] the most commonly employed synthesis of **3** involves bromination of *trans*-crotonic acid (**1**) followed by bromo decarboxylation of the resulting *erythro*-2,3-dibromobutanoic acid (**2**).[10-13] Unfortunately, the reported bromo decarboxylations of **2** to **3** with pyridine,[10] aqueous Na_2CO_3,[11,12] or $NaHCO_3$ in DMF[13] all proceed in poor yield.

In this paper we report a substantial improvement in the procedure (Scheme I) by carrying out the bromo decarboxylation of **2** in neat Et_3N or $EtN(i\text{-}Pr)_2$ at 40 °C. Use of either amine provided isomerically pure **3**[14] reproducibly in 57% yield (50% overall yield from **1**).

Storage of freshly distilled **3** in tightly sealed, light-excluding containers at −20 °C[15] showed no isomerization and/or decomposition of **3** over several months, as monitored by 360-MHz NMR spectroscopy. Thus, addition of either $NaHCO_3$[6] or K_2CO_3[7] as a stabilizing agent appears to be unnecessary for **3** prepared by this methodology.

We believe this improved synthesis provides a convenient and economical means for preparing isomerically pure *cis*-1-bromopropene. This bromoalkene is useful for synthetic applications requiring *cis*-propenyllithium[6,12,16] and *cis*-propenylmagnesium bromide.[5,16]

Experimental Section

Melting points are uncorrected. **Caution!** Heptane poses a dangerous fire and explosion hazard when exposed to heat or flame. Vapors are heavier than air and may travel a considerable distance to a source of ignition and flash back. Situtations which might cause electrostatic discharges should be avoided when handling this solvent.

***erythro*-2,3-Dibromobutanoic Acid (2).** A 500-mL flask equipped with an overhead stirrer, thermometer, and addition funnel was charged with *trans*-crotonic acid (**1**) (51.68 g, 0.60 mol, Aldrich) and 320 mL of heptane. The resulting mixture was stirred and brought to 30 °C (warm water bath) under dry N_2. Br_2 (34.4 mL, 0.63 mol, 1.05 equiv, Fisher) was added dropwise over ca. 45 min while maintaining a reaction temperature of 30 °C (cold water bath). Within 4–5 min after complete addition, crystallization of **2** commenced. A cold water bath was applied to maintain a reaction temperature of ca. 34 °C. The mixture was brought to ambient temperature, stirred an additional 16 h, and cooled in an ice water bath for 30 min. The colorless crystals were collected by suction filtration, washed with heptane (2 × 75 mL), and dried in vacuo at ambient temperature to constant weight to afford 130 g (88%) of **2**: mp 87–89 °C (lit.[11] mp 87–88 °C).

***(Z)*-1-Bromopropene (3).** A 2-L flask equipped with an overhead stirrer, thermometer, and reflux condenser with a mineral oil bubbler attached to the top of the condenser was charged with 517.5 mL (3.71 mol, 4.13 equiv) of 99% triethylamine (Aldrich). With vigorous stirring, a total of 221 g (0.90 mol) of acid **2** was added in ten portions at 5-min intervals. During this addition period, gas evolution (bubbler) and an exotherm to 40 °C were noted. The reaction was stirred at ambient temperature for 3.5 h followed by heating at 40 °C for an additional 3.5 h (gas evolution complete). The mixture was cooled to ambient temperature, and 321 mL of water was added. The solids were rinsed in and allowed to dissolve. Concentrated HCl solution (230 mL, Fisher) was added while maintaining a reaction temperature of 0 °C. Separation of the lower phase in a separatory funnel gave 82.2 g (75%) of crude **3**.[17] The aqueous phase was saved for recovery of triethylamine.

The crude **3** was washed twice with an equivalent volume of saturated $NaHCO_3$ solution and brine and dried (Na_2SO_4). Simple distillation at atmospheric pressure[18] afforded 62.4 g (57%)[19] of isomerically pure *cis*-1-bromopropene (**3**)[14,15] as a colorless liquid: bp 59–60 °C (lit.[10] bp 58–60 °C).

The acidic aqueous phase was cooled to 0–5 °C, and 750 mL of 25% aqueous NaOH solution was added dropwise with good stirring. Separation of the upper phase in a separatory funnel afforded a quantitative recovery of the triethylamine.

A similar result was obtained by substituting an equimolar amount of $EtN(i\text{-}Pr)_2$ for the Et_3N in the conversion of **2** to **3**.

(7) Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3422.
(8) Fleming, I.; Lawrence, N. J. *Tetrahedron Lett.* **1990**, *31*, 3645.
(9) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1979**, *44*, 4623 and references cited therein.
(10) Bachman, G. B. *J. Am. Chem. Soc.* **1983**, *55*, 4279; 28% yield.
(11) Farrell, J. K.; Bachman, G. B. *J. Am. Chem. Soc.* **1935**, *57*, 1281; 0% yield.
(12) Braude, E. A.; Coles, J. A. *J. Chem. Soc.* **1951**, 2078; 16% yield.
(13) Norris, W. P. *J. Org. Chem.* **1959**, *24*, 1579; 38% yield. A second 1-bromopropene fraction consisting of Z/E = 96/4 was also obtained in 38% yield, for a total of 76% **3** from this reaction.
(14) Analysis of the distillate by NMR spectroscopy (360 MHz, $CDCl_3$/TMS) showed no contamination by *trans*-1-bromopropene when compared with an NMR spectrum of commercial material (Aldrich, Z/E = 70/30).
(15) Immediately after distillation, the distillate was transferred to a narrow-mouth screw-top amber bottle, tightly sealed with parafilm, and refrigerated at −20 °C until needed. Prior to use in a reaction, the *cis*-1-bromopropene was allowed to warm to ambient temperature.
(16) Beak, P.; Yamamoto, J.; Upton, C. J. *J. Org. Chem.* **1975**, *40*, 3052 and references cited therein.
(17) The 360-MHz NMR spectrum showed *cis*-1-bromopropene and unidentified triethylammonium salt byproducts. No *trans*-1-bromopropene was detected.
(18) The product was distilled as one fraction; no forerun was collected.
(19) This yield represents a significant improvement over the best current literature yield[13] for preparation of *cis*-1-bromopropene (**3**) of high (>99%) isomeric purity.

6-Phenyl-2,4,6-trioxohexanoic Acid

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The title compound **1** is of current interest because of its relationship to the enolic acids **2** and **3**, which have been implicated in the bacterial oxidation of biphenyl[2] and certain polychlorobiphenyls,[3] respectively. In this paper,

(1) Inquires concerning the crystallographic study should be addressed to this author.
(2) Gibson, D. T.; Roberts, R. L.; Wells, M. C.; Kobal, V. M. *Biochem. Biophys. Res. Commun.* **1973**, *50*, 211. Catelani, D.; Colombi, A.; Sorlini, C.; Trecani, V. *Biochem. J.* **1973**, *134*, 1063. Omori, T.; Sugimura, K.; Ishigooka, H.; Minoda, Y. *Agric. Biol. Chem.* **1986**, *50*, 931.
(3) Furukawa, K.; Tomizuka, N.; Kamibayashi, A. *Appl. Environ. Microbiol.* **1979**, *38*, 301.

0022-3263/91/1956-4067$02.50/0

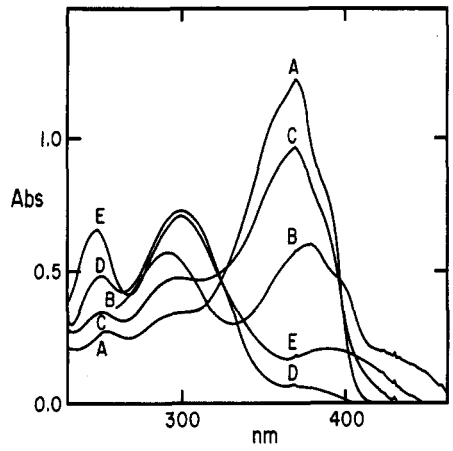
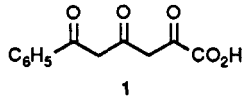
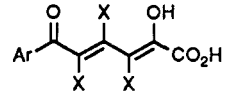


Figure 1. Ultraviolet spectra of 1 (5.0×10^{-5} M) in the following: ethyl ether (A); DMSO (B); methanol (C); 0.01 M aqueous HCl (D); and 0.01 M aqueous NaOH (E).

we report the preparation and characterization of **1**, including an X-ray crystal structure analysis.



1



2, X = H; Ar = C_6H_5
3, X = H or Cl; Ar = $C_6H_nCl_{5-n}$

Triketo acids with the general structure of **1** have not been described previously.[4] Dorman[5] called attention to some of the difficulties attending synthetic efforts in a related system. It was anticipated, moreover, that characterization of **1** could be complicated if the various possible tautomers were of comparable stability.

Treatment of benzoylacetone with dimethyl oxalate in the presence of magnesium methyl carbonate,[6] followed by acid hydrolysis, gave **1** in 52% yield. The substance was readily purified by extraction of the crude product into pH 7 buffer, followed by reacidification. Crystallization from organic solvents was slow and inefficient, but crystals suitable for X-ray analysis could be grown from ethyl ether solution.

Compound **1** behaves as a diprotic acid in aqueous solution. Potentiometric titration yielded a value of 7.50 for pK_2. A rough value of 3 for pK_1 could be approximated from the titration data, but low solubility in water prevented an accurate determination. The corresponding values for 2,4-dioxopentanoic acid are 7.70[7] and 2.58.[8] A small increase in intensity of the 387-nm absorption band at pH 12, compared to pH 9, may be associated with removal of a third proton from **1**, but the titration curve did not exhibit any inflection in the region.

Proton NMR spectra of **1** in acetone-d_6 revealed that the fully enolic tautomer **1a**[9] (singlets at δ 6.46 and 6.63)

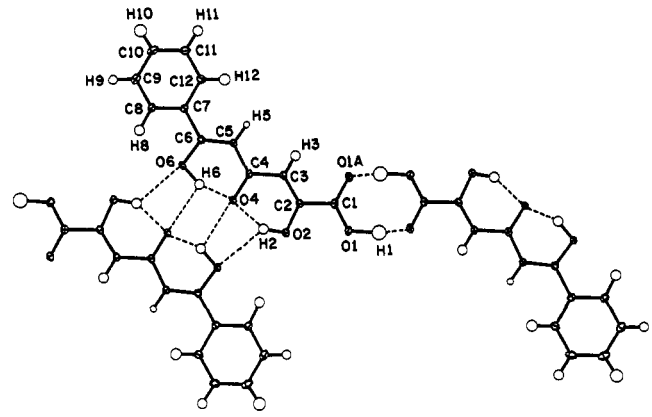
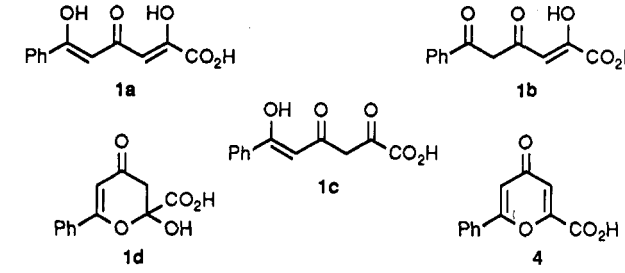


Figure 2. ORTEP[16] plot of the structure of **1** showing 50% probability ellipsoids. Intramolecular and intermolecular hydrogen bonding are indicated.

predominates (86%) in that solvent. The monoenol **1b** (ca. 7%) could also be identified by the singlet methylene signal at δ 4.44 and the corresponding ethylenic proton at δ 6.61. In addition, very small concentrations of two other species could be detected, one of which is clearly **1d**. By contrast, the cyclic isomer **1d** is the major component (52%) in DMSO-d_6, along with 42% of **1a** and 6% **1b**. The methylene protons of **1d** appear as a well-resolved AB quartet (δ 2.74 and 3.03, J = 15 Hz).

When a solution of **1** in DMSO was warmed to 90 °C for 1 h, quantitative conversion to **4**[10] was observed.[11] The reaction occurs slowly at room temperature, and the ratio (NMR) of **1a** to **1d** remains constant during the formation of **4**.

Ultraviolet spectra of **1** (Figure 1) illustrate dramatically the effect of solvent on the equilibrium distribution of tautomers. Absorption maxima fall into three distinct regions: a, 370–390 nm, which is assigned to the fully enolic tautomer **1a**; b, 290–300 nm, characteristic of the enolic



1a **1b** **1c** **1d** **4**

β-diketone chromophores in **1b** and **1c**, as well as the 6-phenyl-2,3-dihydropyran-4-one chromophore[12] of **1d**; and c, the 250-nm region for aromatic ketone absorption. In nonpolar solvents such as ethyl ether (curve A) and hexane (nearly identical with curve A) the fully enolic tautomer

(4) The diethyl ester of 2,4,6-trioxoheptanedioic acid, which contains the same array of functional groups as **1**, has been prepared as an intermediate in the synthesis of chelidonic acid: Riegel, E. R.; Zwilgmeyer, F. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, 126.

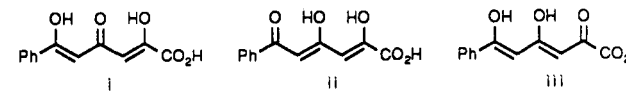
(5) Dorman, L. *J. Org. Chem.* **1967**, *32*, 4105.

(6) This reagent has been used principally as a carboxylating agent (Inoue, S.; Yamazaki, N. *Organic and Bioorganic Chemistry of Carbon Dioxide*; J. Wiley and Sons: New York, 1982) but its use to promote acylation and alkylation of enolizable substrates has been reported: Stiles, M. *J. Am. Chem. Soc.* **1959**, *81*, 2598. Finkbeiner, H. L. *J. Org. Chem.* **1965**, *30*, 3414.

(7) Guthrie, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 7020.

(8) Lehninger, A. L.; Witzemann, E. J. *J. Am. Chem. Soc.* **1942**, *64*, 874.

(9) In principle, the three rapidly interconverting species *i–iii* as well as possible geometric isomers, contribute to the averaged NMR spectrum. Chemical-shift variations between different solvents may reflect different equilibrium distribution of these subspecies.



i ii iii

(10) (a) Still, I. W. J.; Plavac, N.; McKinnon, D. M.; Chauhan, M. S. *Can. J. Chem.* **1976**, *54*, 280. (b) Borsche, W.; Peter, W. *Liebigs Ann. Chem.* **1927**, *453*, 148.

(11) The conditions for the conversion of **1** to **4** are far milder than described previously for cyclization of triketones to 4-pyrones, see: Light, R. J.; Hauser, C. R. *J. Org. Chem.* **1960**, *25*, 538.

(12) Gelin, S.; Gelin, R. *Bull. Soc. Chim. Fr.* **1968**, 288.

1a predominates, in general agreement with the NMR result found for acetone solutions. In DMSO (curve B), the maxima in regions a and b are of comparable intensity, in satisfactory agreement with the NMR result, which indicated nearly equal proportions of 1a and 1d. In solvents of intermediate polarity such as methanol (curve C) or ethanol (not shown), the fraction of 1a lies between the former two. Aqueous solutions of the free acid (curve D) exhibit the major peak at 299 nm, with only a very weak shoulder in region a, indicating that 1a is only a minor component. In aqueous solutions above pH 10, compound 1 is completely converted to the dianion, and under these conditions 1d (i.e., its anion) can be eliminated from consideration. Since the spectrum at pH 12 (curve E) is very nearly identical with that at pH 2 in region b, it appears that the monoenols, rather than 1d, are the major species in aqueous solution. We cannot rule out the existence of a hydrate of 1c (or a nonenolic hydrate) in the acidic solution; Guthrie[7] has shown that 2,4-dioxopentanoic acid forms a hydrate at acidic pH, and the hydrate of oxaloacetic acid is well characterized.[13]

Efforts to explore the chemistry and biochemistry of 1 are underway.

Crystal Structure Analysis of 1. An ORTEP plot of compound 1, as determined by X-ray diffraction, is shown in Figure 2. Bond angles and distances in the molecule are consistent with a localized structure, in which ketonic carbonyl C4–O4 (1.273 (4) Å) is flanked by two enols C2–O2 (1.343 (4) Å) and C6–O6 (1.333 (4) Å). Within the carbon backbone, there are double bonds between C2 and C3 (1.338 (5) Å) and C5 and C6 (1.345 (5) Å). Enolic hydrogens H2 and H6, which were located and refined, are intramolecularly hydrogen bonded to ketone oxygen O4. The entire molecule is nearly planar, with a maximum deviation of any non-hydrogen atom from the mean molecular plane being −0.141 (5) Å for C9. The plane of the phenyl group (C7 to C12) forms a dihedral angle of only 5.2° with the rest of the molecule. There is strong hydrogen bonding between adjacent molecules (Figure 2). The carboxylic acid group C1–O1–O1A forms a typical asymmetrically hydrogen-bonded dimer, with O1–H1, O1A–H1, and O1–O1A distances of 1.27 (6), 1.38 (6), and 2.624 (4) Å, respectively. There is weaker hydrogen bonding between the keto/enol portions of adjacent molecules, arranged in a head-to-tail fashion; H2 bonds to O6 (2.51 (4) Å) and H6 bonds to O4 (2.41 (4) Å). There is also a close approach (2.60 (4) Å) of O1 to H11. This leads to the formation of hydrogen-bonded sheets of molecules, separated by normal van der Waals distances between sheets.

The finding that 2,4,6-trioxo-6-phenylhexanoic acid exists as 1a in the solid state is in accord with previous structures of 1,3,5-triones. For example, the structure of 1,5-diphenyl-1,3,5-pentanetrione[14] shows a nearly identical hydrogen-bonded geometry. The structures of several tetracycline derivatives[15] also show very similar geometries, although one of the enol groups is actually a phenol in these cases.

Experimental Section

Starting materials were obtained from Aldrich Chemical Co. and used without purification.

6-Phenyl-2,4,6-trioxohexanoic Acid (1). 1-Phenylbutane-1,3-dione (0.324 g, 2 mmol) and dimethyl oxalate (0.471 g, 4 mmoles) were dissolved in 11 mL of 2 M solution of magnesium methyl carbonate in DMF (Aldrich). The pale yellow solution was heated at 145 °C in a distilling flask for 4 h, during which time a few drops of distillate (methanol + DMF) condensed. The viscous, deep amber reaction mixture was hydrolyzed by pouring into rapidly stirred ice (30 g) and concentrated HCl (4 mL). The yellow precipitate was taken up in ethyl ether, washed with water, and extracted (2 × 20 mL) into pH 7 phosphate buffer (0.2 M). Acidification of the buffer extract to pH 1–2 precipitated a light yellow solid that was taken up in ethyl ether, washed with water, and dried over sodium sulfate. Removal of solvent yielded 0.242 g (52%) of light yellow powder. The NMR spectrum of this material did not differ significantly from that of material obtained by recrystallization from ethyl ether, from acetone–hexane, or from acetone–water. Mass spectrum: 234.0527 (M^+), 189, 162, 160, 147, 105, 103, 91, 77, 69, 51, 50. Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.53; H, 4.30. Found: C, 61.51; H, 4.20.

Heating the compound in a capillary tube or on a hot stage caused melting to begin near 160 °C. Before melting was complete, colorless rods began to form in the melt. As the temperature was raised, the whole mass was converted to nearly colorless rods that melted with decomposition at 248–250 °C.

^{1}H NMR Spectra. In acetone-d_6, all the aromatic protons appeared as multiplets grouped between δ 7.5 and 8.1. The remainder of the spectrum was analyzed as follows: 86% **1a** δ 6.46 (s, H3), 6.63 (s, H5); 7% **1b** δ 4.44 (s, CH_2), 6.61 (s, H3); ca. 3% **1d** δ 2.8 and 3.2 (AB, J = 15 Hz), 6.15 (s); ca. 3% unknown component (1c ?) with singlet at 4.15. At −40 °C the OH protons were resolved into 3 signals at 12.7 (broad), 13.1 (sharp) and 15.2 δ (sharp); otherwise, the spectrum differed little from that observed at room temperature.

In DMSO-d_6, the aromatic protons appeared between δ 7.45 and 8.03. The remainder of the spectrum was analyzed as follows: 42% **1a** δ 6.22 (s, H3) 6.87 (s, H5); 6% **1b** δ 4.45 (s, CH_2), 6.33 (s, H3); 52% **1d** δ 2.74 and 3.03 (AB quartet, J = 15 Hz), 6.17 (s, H5).

^{13}C NMR Spectra. In acetone-d_6: (all signals attributed to **1a**) δ 195.2 (C4), 178.5 (C1), 163.4 and 160.4 (C2 and C6), 134.0, 133.7, 129.8, and 127.6 (aromatic), 105.1 and 98.4 (C3 and C5). In DMSO-d_6: **1a** δ 188.7 (s, C4), 169.3 (s, C1), 166.3 and 163.8 (C2 and C6), 103.9 (d, J = 167 Hz) and 101.8 (d, J = 168 Hz) (C3 and C5); **1d** δ 190.9 (t, J = 6 Hz, C4), 180.9 (s, COOH), 156.6 (s, C6), 100.2 (s, C2), 97.9 (d, J = 166 Hz, C5), 44.0 (t, J = 131 Hz, C3).

Ultraviolet Spectra. The curves illustrated in Figure 1 were obtained by dissolving 0.0117 g of 1 in 10 mL of methanol and diluting 0.50 mL of that solution to 50.0 mL with the indicated solvent.

4-Oxo-6-phenyl-4*H*-pyran-2-carboxylic Acid (4). The triketo acid 1 (0.021 g) was dissolved in 1.5 mL of acetic acid and heated at 110 °C for 2 h. Dilution with hexane precipitated an oil that crystallized from acetone to yield 0.016 g (80%) of colorless leaflets that melted with effervescence at 250–252 °C (lit.[10b] mp, 237 °C dec.). The ^{13}C NMR spectrum agreed with that published previously.[10a] ^{1}H NMR (DMSO-d_6): δ 6.90 (d, 1 H, J = 2.3 Hz), 7.15 (d, 1 H, J = 2.3 Hz), 7.6 (m, 3 H), and 8.0 (m, 2 H).

Crystal Structure Analysis. A yellow crystal of 1 approximately 0.6 × 0.3 × 0.2 mm^3 was obtained by slow cooling of an ethyl ether solution. It was mounted in air on the tip of a glass fiber by using epoxy cement. Data were collected at 23 °C with graphite-monochromatized Mo Kα radiation on an Enraf-Nonius CAD-4 diffractometer. Cell constants were determined from least-squares refinement of the setting angles of 25 reflections with 5.4° < Θ < 13.6°. The compound has a formula weight of 234.21, belonging to the monoclinic space group $P2_1/c$ (No. 14) with a = 6.610 (3) Å, b = 7.418 (3) Å, c = 21.880 (6) Å, β = 93.44 (2)°, V = 1071.11 Å^3, Z = 4, ρ_{calcd} = 1.452 g·cm^{-3}. Diffraction intensities were collected out to Θ = 27.5° using an ω–2Θ scan technique. Of 4804 unique reflections, 1909 with $I \geq 3\sigma(I)$ were used to solve and refine the structure. Lorentz and polarization corrections, but no absorption correction (μ = 1.070 cm^{-1}), were applied. The structure was solved and refined by using the direct methods program MULTAN77 and local versions of Ibers' NUCLS least-squares program and Zalkin's FORDAP Fourier program.

(13) Kokesh, F. C. *J. Org. Chem.* **1976**, *41*, 3593.
(14) Cea-Olivares, R.; Rodriguez, I.; Rosales, M. J.; Toscano, R. A. *Aust. J. Chem.* **1987**, *40*, 1127–1130.
(15) (a) Stezowski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 6012–6018. (b) Jogun, K. H.; Stezowski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 6018–6026.
(16) Johnson, C. K. *Report ORNL 5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Least-squares refinements minimized the function $\Sigma_{hkl} w(F_o - F_c)^2$ where the weighting factor was $w = 1/\sigma(F_o)^2$. All hydrogen atoms were located in a difference Fourier map. The largest peak in the final difference Fourier map showed 0.062 e·Å^{-3} near O1. Full-matrix least-squares refinement with anisotropic thermal parameters for 17 carbon and oxygen atoms, and isotropic thermal parameters for 10 hydrogen atoms, led to $R = 5.7\%$, $R_w = 6.9\%$, maximum $\Delta/\sigma = 0.35$ (x of H1), with 195 variables. Additional crystallographic details are presented in the supplementary material.

Acknowledgment. We thank Claude Dungan for the careful NMR measurements and the University of Kentucky Major Research Instrumentation Bond Program for equipment.

Supplementary Material Available: Listings of crystal structure data, positional and thermal parameters, bond distances and angles, least-squares planes, torsion angles, and experimental and calculated structure factors for the structure of 1 (21 pages). Ordering information is given on any current masthead page.

Perturbations of an Isotopically Substituted Nonhydroxylic Solvent upon the Chemistry of an Anion Radical

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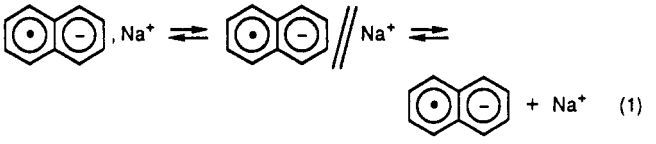
Received December 10, 1990

Introduction

There have been a number of studies on the effect of the replacement of hydrogen with deuterium upon acidity and basicity, and the results show that deuterium behaves as though it were electron donating relative to hydrogen.[1] This behavior is responsible for a number of observed solvent isotope effects.[2] Most reports of solvent isotope effects have involved kinetic studies where water/deuteriated water or other hydroxylic solvents served as the solvent systems.[3] We wish to report an equilibrium isotope effect from a nonhydroxylic solvent that is consistent with the electron-releasing nature of deuterium. EPR evidence indicates that the perdeuteriation of the most common anion radical solvent, tetrahydrofuran (THF), measurably increases its ability to separate ions involved in ion-pairing equilibria.

When naphthalene dissolved in THF is exposed to a freshly distilled sodium mirror under vacuum, the solvated anion radical ($C_{10}H_8^{\bullet -}$) is generated and exists in at least three different states of ion association. These include the free solvated ion ($C_{10}H_8^{\bullet -} + Na^+$)[4a] as well as the solvent-separated ($C_{10}H_8^{\bullet -}//Na^+$) and contact ion pairs ($C_{10}H_8^{\bullet -},Na^+$) first reported by Zandstra and Weissman.[4b] Upon EPR analysis, the resulting solution exhibits an averaged sodium hyperfine splitting ($A_{Na} = 1.03$ G) at 28 °C (see Figure 2 in ref 4b). This observed splitting is controlled by the overall degree of ion association between the anion radical and the sodium cation, reaction 1,[4] and



(1)

is a time or weighted average of those for the solvated tight or contact ion pair ($A_{Na''}$), the solvent-separated ion pair ($A_{Na'}$), and the free solvated ion (A_{Na^0}), eq 2.[4c,5] The

$$A_{Na} = (A_{Na''}[C_{10}H_8^{\bullet -},Na^+] + A_{Na'}[C_{10}H_8^{\bullet -}//Na^+] + A_{Na^0}[C_{10}H_8^{\bullet -} + Na^+])/([C_{10}H_8^{\bullet -} + Na^+] + [C_{10}H_8^{\bullet -},Na^+] + [C_{10}H_8^{\bullet -}//Na^+]) \quad (2)$$

coupling constant for the free ion is zero, and that for the solvent-separated ion pair also appears to be near zero, while that for the contact ion pair is reported to be larger than 1.5 G.[4c]

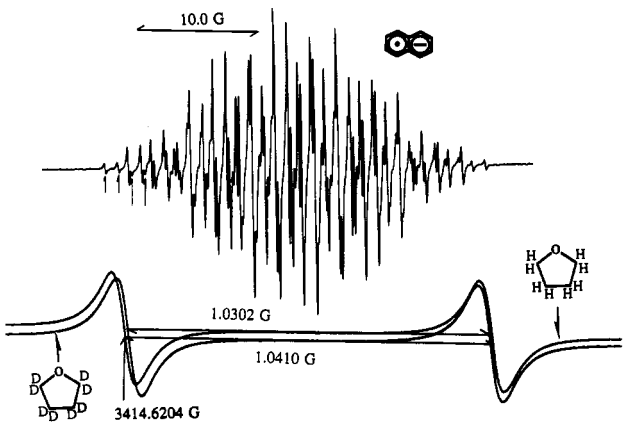


Figure 1. (Top) EPR spectrum of the sodium salt of the naphthalene anion radical in THF-d_8 at 298 K. The vertical arrows mark the low-field quartet due to the sodium splitting. (Bottom) computer simulations of the first two lines of the spectrum using the average of the field positions (marked for first line) for each line as measured with the Gaussmeter. Note that both lines recorded from the sample in THF lie outside of those for the sample in THF-d_8.

Results and Discussion

Exposure of naphthalene solutions in perdeuteriated THF (THF-d_8) to a freshly distilled sodium mirror under high vacuum leads to anion radical solutions that yield the typical 100-line EPR pattern at room temperature (splitting from 4 β and 4 α protons and 1 Na) or 25 line pattern at −100 °C (no sodium splitting). Careful recordings (sweep widths of 1.2 and 1.4 G) taken within a few minutes to a few days of sample preparation of the low-field portion of the EPR spectrum of sodium naphthalene anion radical at 298 K reveal that the sodium splitting (A_{Na}) is smaller for samples dissolved in THF-d_8 than it is for those samples generated in normal THF (Figure 1). Samples of the naphthalene anion radical were generated using identical techniques in THF and in THF-d_8. A sample in THF was placed in the front cavity

(1) (a) A single deuterium will split the degeneracy of the antibonding MO's of benzene as does an electron-releasing group; see: Alper, J. S.; Silby, R. *J. Chem. Phys.* **1970**, *52*, 569. Stevenson, G. R.; Reidy, K. A.; Peters, S. J.; Reiter, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 6578. (b) The electrochemical reduction potential of deuteriated polyaromatics is more negative than those of their light isotopic analogues; see: Goodnow, T. T.; Kaifer, A. E. *J. Phys. Chem.* **1990**, *94*, 7682. See also: (c) Bary, Y.; Gilboa, H.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 938. (d) Srinivasan, R.; Stewart, R. *J. Am. Chem. Soc.* **1976**, *98*, 7648.

(2) For example, see: (a) Schowen, R. L. *Prog. Phys. Org. Chem.* **1972**, *9*, 275. (b) Albery, W. J. In *Proton-Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Chapman Hall: London, 1975; 263. (d) Schowen, R. L. In *Isotope Effects in Enzyme Catalyzed Reactions*; Cleland, W. W., O'Leary, M. H., Northrup, D. B., Eds.; University Park Press: Baltimore, 1977; 64.

(3) Schowen, R. L. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1987; Vol. 7, p 2.

(4) (a) Chang, R.; Johnson, C. S. *J. Am. Chem. Soc.* **1966**, *88*, 2338. (b) Zandstra, P. J.; Weissmann, S. I. *J. Am. Chem. Soc.* **1962**, *84*, 4408. (c) Hirota, N. *J. Phys. Chem.* **1967**, *71*, 127.

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