heated at 60 °C for 2 h. The cooled solution was poured into a mixture of chloroform and aqueous sodium hydrogen carbonate. The standard procedure then gave the diester **5** as a syrup which was purified by chromatography (chloroform–methanol, 99:1): yield 1.12 g (86%); $[\alpha]^{20}_D$ +16.5° (*c* 0.5, CH_2Cl_2); ^1H NMR (90 MHz, $CDCl_3$) δ 2.38 (s, 6, 2 $ArCH_3$), 4.83 (s, 1, H-1), 5.80 (d, 1, H-1′, $J_{1',2'}$ = 3,5 Hz). Anal. Calcd. for $C_{32}H_{42}O_{13}S_2$: C, 55.01; H, 6.06; O, 29.77. Found: C, 55.17; H, 6.03; O, 29.54.

B. From *O*-(2,3-Anhydro-4-deoxy-α-D-*lyxo*-hexopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1). A mixture of epoxide **1** (1.476 g) and lithium aluminum hydride (0.5 g) in oxolane (50 mL) was stirred for 30 min at room temperature, treated with ethyl acetate, methanol, and water, and finally extracted with ether. The dried ether solution was concentrated to a syrup, which was directly treated with *p*-toluenesulfonyl chloride and pyridine as above to give the diester **5** (2.23 g, 84%).

***O*-(6-Azido-2,3,4,6-tetradeoxy-α-D-*erythro*-hex-2-enopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (6).** A solution of the diester **5** (0.78 g) and sodium azide (3.6 g) in *N*,*N*-dimethylformamide (50 mL) was heated for 16 h at 110 °C and then diluted with water. Chromatography (ether–petroleum ether, 1:1) of the ethereal extract gave the monoazide **6** as a syrup (0.52 g, 98%): $[\alpha]^{20}_D$ −97° (*c* 0.8, CH_2Cl_2); ^1H NMR (90 MHz, $CDCl_3$) δ 3.30 (d, 2, CH_2N_3, $J_{5,6}$ = 6 Hz), 5.20 (br s, 1, H-1), 5.70, 5.98 (2 d with broaden peaks, 2, H-2, H-3, $J_{2,3}$ = 11 Hz), 5.84 (d, 1, H-1′, $J_{1',2'}$ = 3.5 Hz). Anal. Calcd. for $C_{18}H_{27}O_7N_3$: C, 54.40; H, 6.85; O, 28.18; N, 10.57. Found: C, 53.78; H, 6.79; O, 28.62; N, 10.40.

Reaction at 60 °C during 12 h gave a mixture of compound **6** with *O*-(6-azido-2-(*O*-toluenesulfonyl)-3,4,6-trideoxy-α-D-*threo*-hexopyranosyl)-(1→3)-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose: ^1H NMR (90 MHz, $CDCl_3$) δ 2.39 (s, 3, CH_3SO_3), 4.93 (s, 1, H-1), 5.82 (d, 1, H-1′, $J_{1',2'}$ = 3.5 Hz), 7.30, 7.77 (2 d, 4, aromatic protons).

***O*-(3,4-Dideoxy-2,6-bis(*O*-methanesulfonyl)-α-D-*threo*-hex-3-enopyranosyl)(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3).** Methanesulfonyl chloride (2 mL) was added dropwise at 0 °C to a solution of the diol **2** (1.3 g) in pyridine (10 mL). The mixture was allowed to warm to room temperature, and the diester was isolated according to the standard procedure, except that a high vacuum was used for the last evaporation to remove pyridine. Crystallization (chloroform–ether) gave a first crop (1.486 g, 82%). More compound was obtained by evaporation to dryness of the mother liquor and chromatography (chloroform–methanol, 99:1) of the residue, making the total yield 95%: mp 149 °C, $[\alpha]^{20}_D$ +68° (*c* 1.5, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$) δ 3.04, 3.10 (2 s, 6, 2 CH_3SO_3), 5.36 (s, 1, H-1), 5.85 (d, 1, H-1′, $J_{1',2'}$ = 3.5 Hz), 6.06 (q, 1, H-3, $J_{3,4}$ = 10 Hz, $J_{2,3}$ = 4 Hz), 6.13 (q, 1, H-4, $J_{4,5}$ = 0.5 Hz). Anal. Calcd for $C_{20}H_{32}O_{13}S_2$: C, 44.11; H, 5.92; S, 11.77. Found: C, 43.94; H, 6.05; S, 11.75.

***O*-(2,6-Diazido-2,3,4,6-tetradeoxy-α-D-*erythro*-hex-3-enopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (7) and *O*-(4,6-Diazido-2,3,4,6-tetradeoxy-α-D-*erythro*-hex-2-enopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (8).** A solution of the dimesylate **3** (0.873 g) and sodium azide (0.8 g) in dimethyl sulfoxide (10 mL) was kept for 2 h at 100 °C under nitrogen, then diluted with water, and extracted with ether. Chromatography (ether–petroleum ether, 1:1) of the dried, ethereal extract first gave the diazide **8** as an oil (0.294 g, 42%): $[\alpha]^{20}_D$ +55° (*c* 1.8, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$) δ 3.46 (q, 1, H-6a, J_{gem} = 12 Hz, $J_{5,6a}$ = 5.5 Hz), 3.62 (q, 1, H-6b, $J_{5,6b}$ = 2 Hz), 5.28 (d, 1, H-1, $J_{1,2}$ = 2 Hz), 5.87 (d, 1, H-1′, $J_{1',2'}$ = 3.5 Hz), 5.92 (dt, H-2, $J_{2,3}$ = 11 Hz, $J_{1,2}$ = 2 Hz, $J_{2,4}$ = 2 Hz), 6.01 (d, H-3). Anal. Calcd for $C_{18}H_{26}N_6O_7$: C, 49.31; H, 5.98; N, 19.17. Found: C, 49.62; H, 6.04; N, 19.15.

The next fraction in the above chromatography was the diazide **7**: an oil (0.206 g; 30%); $[\alpha]^{20}_D$ −50° (*c* 1, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$) δ 3.34 (q, 1, H-6a, J_{gem} = 13 Hz, $J_{5,6a}$ = 6 Hz), 3.48 (q, 1, H-6b, $J_{5,6b}$ = 3.8 Hz), 3.84 (t, 1, H-2, $J_{1,2}$ = $J_{2,3}$ = 3.5 Hz), 5.45 (d, 1, H-1, $J_{1,2}$ = 3.5 Hz), 5.87 (d, 1, H-1′, $J_{1',2'}$ = 3.5 Hz), 5.89 (br, 2, H-2, H-3); ^1H NMR (250 MHz, C_6D_6) δ 5.29, 5.45 (2 d, 2, H-2, H-3, $J_{2,3}$ = 11 Hz). Anal. Calcd for $C_{18}H_{26}N_6O_7$: C, 49.31; H, 5.98; N, 19.17. Found: C, 49.64; H, 6.07; N, 19.08.

Continued elution finally gave an unresolved mixture of two threo diazides (0.131 g; 19%).

***O*-(2,6-Diacetamido-2,3,4,6-tetradeoxy-α-D-*erythro*-hexopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (10).** A solution of the diazide **7** (0.206 g) in methanol (10 mL) in the presence of Adams catalyst (0.150 g) was shaken for 16 h at room temperature under hydrogen. The mixture was filtered, and acetic anhydride (1 mL) was added to the solution which was kept for 2 h at room temperature. Coevaporation with toluene then gave a residue which was purified by chromatography (chloroform–toluene–acetone, 1:1:3). Thus was obtained the protected disaccharide **10** as a white powder (0.188 g, 85%): $[\alpha]^{20}_D$ +58° (*c* 1.2, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$) δ 1.94, 2.00 (2 s, 6, 2 $COCH_3$), 3.08 (m, 1, H-6a), 3.5 (octet, 1, H-6b), 4.85 (d, 1, H-1, $J_{1,2}$ = 3.2 Hz), 5.87 (d, 1, H-1′, $J_{1',2'}$ = 3.5 Hz), 6.09 (t, 1, NH-6), 6.23 (d, 1, NH-2 $J_{2,NH}$ = 8.5 Hz). Anal. Calcd for $C_{22}H_{36}N_2O_9$: C, 55.92; H, 7.68; N, 5.93. Found: C, 55.56; H, 7.81; N, 5.68.

***O*-(4,6-Diacetamido-2,3,4,6-tetradeoxy-α-D-*erythro*-hexopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (9).** Catalytic reduction of the diazide **8** (0.294 g) followed by the same workup as above gave the protected disaccharide **9** as a white powder (0.27 g, 86%): $[\alpha]^{20}_D$ +83° (*c* 1.3, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$) δ 2.00, 2.01 (2 s, 6, 2 $COCH_3$), 5.04 (br s, 1, H-1), 5.82 (d, 1, H-1′, $J_{1',2'}$ = 3.5 Hz), 6.40 (d, 1 NH-2, $J_{2,NH}$ = 8 Hz), 6.53 (q, 1, NH-6 $J_{6,NH}$ = 3.75 and 7.5 Hz). Anal. Calcd for $C_{22}H_{36}N_2O_9$: C, 55.92; H, 7.68; N, 5.93. Found: C, 55.48; H, 7.70; N, 5.60.

2,6-Diacetamido-2,3,4,6-tetradeoxy-α-D-*erythro*-hexose Diethyl Dithioacetal (11). Starting from compound **9** (0.2 g) the procedure of Cooper[18] was followed, except that silver carbonate was used after lead carbonate in the neutralization of hydrochloric acid. The dithioacetal **11** was obtained as crystals (55 mg, 39%): mp 130–131 °C (benzene); $[\alpha]^{20}_D$ +28° (*c* 0.7, methanol); ^1H NMR (250 MHz, pyridine-d_5) δ 2.06, 2.14 (2 s, 6, 2 $COCH_3$), 3.64 (m, 2 H-6, H-6′), 4.02 (br s, 1, H-5), 4.46 (d, 1, H-1, $J_{1,2}$ = 3.6 Hz), 4.71 (m, 1, H-2), 6.44 (d, 1 OH, $J_{5,OH}$ = 4.5 Hz), 8.64 (d, 1, NH-2, $J_{2,NH}$ = 8 Hz), 8.71 (d, NH-6). All these attributions were confirmed by double irradiation of H-1 to H-6, H-6′, NH-2, and HN-6.

Methyl 13,14-Dihydro-13,14-epoxyretinoate

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Of the various retinoid epoxides, only 5,6[1] and 7,8 isomers are known.[2] We have now prepared a third isomer, methyl 13,14-dihydro-13,14-epoxyretinoate (**2**). We first attempted to prepare **2** by application of the Darzen's reactions to the C-18 ketone **1**. However, under all conditions which we explored, the ring-opened isomer **3** was the only isolable product. The structure of **3** was demonstrated by its infrared spectrum (3500 cm^{-1}), ^1H NMR spectrum (δ 4.4, one-proton singlet for the C-14 proton; δ 5.66, one-proton triplet for the C-4 vinyl proton), and ultraviolet spectrum (identical with that of the authentic retroacid **4**[3]).

A successful synthesis of **2** was achieved by ozonization of the known epoxy ester **5**[4] to obtain aldehyde **6**. Con-

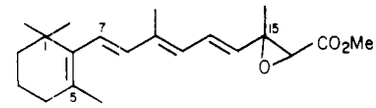
(1) (a) P. Karrer and E. Jucker, *Helv. Chim. Acta*, **28**, 717 (1945); **30**, 559 (1947); (b) F. B. Jungalwala and H. R. Cama, *Biochem. J.*, **95**, 17 (1965); (c) K. V. John, M. R. Lakshanan, and H. R. Cama, *ibid.*, **103**, 539 (1967).

(2) D. Davalian and C. H. Heathcock, *J. Org. Chem.*, in press.

(3) H. O. Huisman, A. Smit, P. H. van Leenwen, and J. H. van Rij, *Recl. Trav. Chim. Pays-Bas*, **75**, 977 (1956).

(4) I. M. Helibron, A. W. Johnson, E. P. H. Jones, and A. Spinks, *J. Chem. Soc.*, 727 (1942).

0022-3263/79/1944-4988$01.00/0



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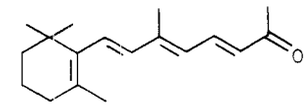

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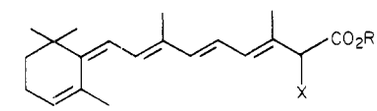
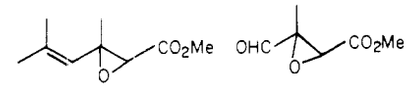


3, X = OH; R = Me
4, X = H; R = H



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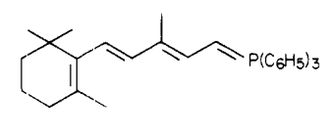

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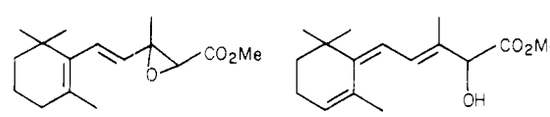
densation of **6** with phosphorane **7**[5] in THF at −30 °C affords epoxy ester **2** in 80% yield. Compound **2** is exceedingly labile. It rearranges to isomer **3** in *neutral methanol* with a half-life of 7 min at room temperature!

Epoxy ester **8**, obtained by application of the Darzen's reaction to β-ionone,[6] is much more stable; its half-life for rearrangement to the retroester **9** is 9 h in neutral methanol at room temperature.



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Experimental Section

Boiling points are uncorrected. IR spectra were determined with a Perkin-Elmer Model 297 infrared recording spectrophotometer. UV spectra were determined with a Cary Model 118 ultraviolet spectrophotometer; results are expressed as λ_{max} in nm (log ϵ). ^{1}H NMR spectra were determined on a Varian EM 390 spectrometer. ^{13}C NMR spectra were measured at 25.14 MHz with a Nicolet TT-23 spectrometer. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Significant ^{1}H NMR data are tabulated in the following order: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant(s) in hertz. Mass spectra were obtained with Atlas MS-12 and Consolidated 12-110B mass spectrometers. Mass spectral data are tabulated as *m/e* (intensity expressed as percent of total ion current). High-pressure liquid chromatography (LC) was done with a Waters Model ALC/GPC-244 liquid chromatograph (analytical) or a Waters PrepLC/System 500 (preparative). Microporasil columns were used for analytical high-pressure LC.

Methyl (2*SR*,3*RS*)-3,5-Dimethyl-2,3-epoxyhex-4-enoate (5). To a stirring solution of methyl chloroacetate (83.8 g, 0.77 mol) and mesityl oxide (37.7 g, 0.38 mol) in 80 mL of dry ether at −60 °C was added portionwise 41.6 g (0.77 mol) of sodium methoxide. After addition was complete, the reaction mixture was stirred for 18 h at room temperature and then at reflux for a further 6 h. The dark brown mixture was poured onto 200 g of ice and the resulting mixture neutralized by the addition of 15 mL of 6 N acetic acid. The layers were separated and the aqueous phase extracted with ether (2 × 200 mL). The combined ether layers were washed (150 mL of water, 100 mL of saturated $NaHCO_3$, 100 mL of brine), dried, and evaporated to furnish a brown oil. This material was distilled to provide 50 g (77%) of epoxy ester, bp 51–52 °C (0.5 torr) [lit.[4] bp 59–61 °C (1 torr)]. ^{1}H NMR and analytical high-pressure LC showed the product to be a 7:3 mixture of the *SR,RS* and *SS,RR* racemates. Pure *SR,RS* compound was obtained by preparative high pressure LC (93:7 hexane/ether). In a typical separation, 7.0 g of mixed diastereomers afforded 3.4 g of pure **8**: ^{1}H NMR (CCl_4) δ 5.16 (1 H, m), 3.63 (3 H, s), 3.26 (1 H, s), 1.70 (3 H, s), 1.66 (3 H, s), 1.43 (3 H, s); IR (neat) 1760 cm^{-1}.

Methyl (2*SR*,3*SR*)-2-Formyl-2,3-epoxybutanoate (6). A solution of epoxy ester **5** (3.3 g, 19 mmol) in a mixture of 45 mL of methylene chloride and 5 mL of methanol was ozonized at −78 °C. After ozonation was complete (as evidenced by appearance of the characteristic blue color of ozone), the solution was flushed well with nitrogen, and 3 mL of dimethyl sulfide was added. After the solution warmed to room temperature, the solvent was removed in vacuo and the residue distilled to obtain 2.13 g (77%) of aldehyde **6** [bp 38–41 °C (0.5 torr)]. This material was used without further purification: ^{1}H NMR ($CDCl_3$) δ 8.53 (1 H, s), 3.83 (3 H, s), 3.66 (1 H, s), 1.50 (3 H, s); ^{13}C NMR ($CDCl_3$) 40.0, 51.8, 58.2, 62.4, 166.0, 196.8; IR (neat) 1750, 1220 cm^{-1}; mass spectrum, 115 (0.96), 101 (2.05), 85 (5.66), 78 (3.47), 69 (4.74).

Methyl (13*RS*,14*SR*)-13,14-Dihydro-13,14-epoxyretinoate (2). To a stirring suspension of (β-ionylidineethyl)triphenylphosphonium bromide[5] (2.72 g, 5 mmol) in 15 mL of dry ether at −30 °C was added 3.3 mL of 1.58 N *n*-butyllithium in hexane (5 mmol). The reaction mixture was stirred for 15 min at −30 °C, and a solution of 0.77 g (5 mmol) of epoxy ester **6** in 5 mL of ether was added. After 45 min, the reaction mixture was allowed to warm to 0 °C and was then filtered through a 1-cm column of silica gel. The silica gel was rinsed with ether, and the combined ether solution was concentrated in vacuo to provide 680 mg (41%) of epoxy ester **2**. Because of its extreme lability, we were unable to distill or chromatograph compound **2**. However, its ^{13}C NMR and ^{1}H NMR spectra indicate that it is one stereoisomer, presumably having the 11*E* configuration: ^{1}H NMR (CCl_4) δ 7.20 (1 H, m), 5.90–6.53 (4 H, m), 3.53 (3 H, s), 3.33 (1 H, s), 1.86 (3 H, s), 1.70 (3 H, s), 1.53 (3 H, s), 1.02 (6 H, s); ^{13}C NMR ($CDCl_3$) 12.1, 19.2, 21.5, 23.5, 28.8, 33.0, 34.2, 39.6, 48.3, 51.7, 64.0, 124.7, 128.1, 128.2, 129.4, 137.7, 138.2, 138.6, 139.2, 168.0; IR (neat) 1760, 1740 cm^{-1}; UV (hexane) λ_{max} 293 (4.3); mass spectrum, 330 (0.36), 312 (1.61), 197 (1.12); High-resolution mass spectrum *m/e* required for $C_{21}H_{30}O_3$, 330.2205; observed, 330.2200.

Methyl (2*RS*)-2-Hydroxy-*retro*-retinoate (3). (A). To a solution of 200 mg (0.6 mmol) of epoxy ester **2** in 5 mL of methanol was added 2 drops of 10% aqueous HCl. After 30 min at room temperature 30 mL of ether was added, and the solution was washed with water. After being dried over Na_2SO_4, the solvent was removed in vacuo to furnish a yellow oil (198 mg) which was purified by chromatography on Wöelm neutral alumina (activity V; 4:1 hexane/ether) to obtain 160 mg (80%) of hydroxy ester **3** as a pale yellow oil: ^{1}H NMR (CCl_4) δ 5.96–6.73 (5 H, m), 5.66 (1 H, t), 4.4 (1 H, s), 3.73 (3 H, s), 1.90 (6 H, s), 1.76 (3 H, s), 1.30 (3 H, s); IR (neat) 3500, 1760, 1740 cm^{-1}; UV (ethanol) λ_{max} 369 (4.85), 350 (4.96), 334 (4.89). The literature values for acid **4** are as follows: UV λ_{max} 369 (4.84), 350 (4.91), 335 (4.74); mass spectrum, 330 (1.19), 256 (0.19). A 10^{-5} M solution of epoxy ester **2** in pure methanol was prepared and immediately inserted into the ultraviolet spectrophotometer. The ultraviolet spectrum was measured periodically until it no longer changed (about 1 h). At this point, the spectrum observed was that of pure hydroxy ester **3**. The half-life was found to be 7 min.

(B). To a solution of 0.8 mL of 1.5 M *n*-butyllithium in hexane at 0° C was added 210 mg (1.3 mmol) of hexamethyldisilazane.

(5) (a) W. Sarnecki and H. Pommer, German Patent 1 060 386 (1959), U.S. Patent 2 950 321 (1960); *Chem. Abstr.*, **55**, 4577 (1961); (b) H. Pommer and W. Sarnecki, German Patent 1 068 710 (1959); *Chem. Abstr.*, **55**, 12,446 (1961).

(6) H. Oediger and K. Eiter, *Chem. Ber.*, **97**, 549 (1964), and references cited therein.

The ice bath was removed, and the solution was allowed to warm to room temperature. After 15 min, the solvent was removed in vacuo to obtain crystalline lithium hexamethyldisilazide. This material was dissolved in 1 mL of THF and cooled to −78 °C. A solution of 258 mg (1 mmol) of ketone 1, 228 mg (1.5 mmol) of methyl bromoacetate, and 0.1 mL of hexamethylphosphoric triamide in 2 mL of THF was added over a 5-min period. After addition was complete, the mixture was stirred for 35 min and then allowed to warm to 0° C. At this point, 78 mg (1.3 mmol) of acetic acid was added, and the mixture was diluted with 30 mL of ether. The ether solution was washed with water, dried (Na_2SO_4), and immediately evaporated to provide 330 mg (100%) of orange oil, identical in all respects with a sample of hydroxy ester 3 prepared as described in part A.

Acknowledgment. Support for this research was provided by a contract from the National Cancer Institute (CP-75934).

Registry No. 1, 17974-57-1; 2, 71987-70-7; 3, 71987-71-8; 5, 72016-48-9; 5 (*SS,RR*), 71987-72-9; 6, 71987-73-0; 7, 71987-74-1; Mesityl oxide, 141-79-7; methyl chloroacetate, 96-34-4; (β-ionylidineethyl)triphenylphosphonium bromide, 1180-79-6.

Marked Influence of Minute Amounts of Water on the Selectivity of Alkylation Site of Sodium 2-Naphtholate (Ambident Anion) in Aprotic Solvent

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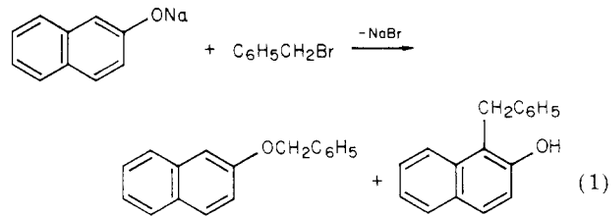
It has been established that solvation is an integral part of most bimolecular reactions in solution. In particular, Parker[1] has demonstrated that the reactivities of anionic species are dramatically affected by the solvation through hydrogen bonding with protic solvent species. The marked activation of anionic species observed in dipolar aprotic solvents has since been attributed to the desolvation effect, that is, exclusion of hydrogen bond forming molecules from the reaction center.[1] On the other hand, the reaction rate in dipolar aprotic solvents has been believed to be affected little by small amounts (several millimolar) of remaining water,[2-4] since dipolar aprotic solvent molecules (i.e., hygroscopic molecules) can compete with reacting anions as acceptors for water molecules.[3] It was found, however, that the rate constants for the nucleophilic reactions of oxyanions are affected by a water concentration of less than 1 M, and the plots of rate constants vs. $[H_2O]$ increased exponentially with decreasing water concentration.[5-7] The influence of small amounts of water on the reaction rate is an old but still controversial problem.

The reactivity of ambident anions is highly solvent dependent;[8-11] therefore, it is expected that it is influenced by small amounts of water remaining in solvents in the order of 10^{-3} M concentration. However, there is no precedent for this type of investigation. In this paper, we wish to report that the ratio of O- vs. C-alkylation products (P_o/P_c) in the reaction of sodium 2-naphtholate (1) with benzyl bromide (2) (eq 1), which is known to change from



(1)

97/0 in *N,N*-dimethylformamide to 10/84 in water,[8] is markedly affected by a several millimolar concentration of water remaining in tetrahydrofuran (THF) and that, without accurate determination of the water concentration, the quantitative estimation of the reactivity of the ambident anion becomes meaningless.

The results of the P_o/P_c determination as a function of the water concentration is summarized in Table I. THF was chosen as solvent because it provides the convenient

Table I. Effect of Water Concentration in THF on the Alkylation Site of Sodium 2-Naphthoate[a]

water concn, M			
initial	final	18-crown-6	P_o/P_c
0.006	0.033	0	2.08
0.08	0.22	0	1.12
0.51	0.69	0	0.99
0.94	1.19	0	0.79
2.00	2.66	0	0.41
0.02	0.05	1.43	51.7
0.08	0.09	1.43	46.5
0.16	0.16	1.43	40.6
0.69	0.70	1.43	40.1
1.09	1.11	1.43	37.6

[a] [Sodium 2-naphtholate] = [benzyl bromide] = 0.286 M.

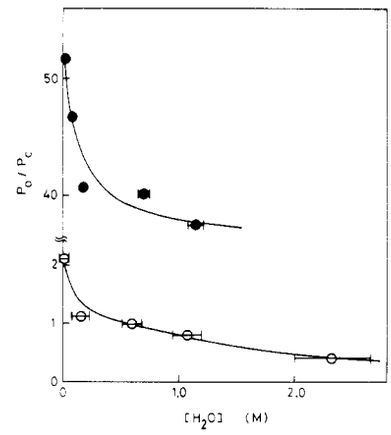


Figure 1. Plots of P_o/P_c as a function of water concentration in THF (○) and in THF/18-crown-6 (●).

(1) A. J. Parker, *Q. Rev., Chem. Soc.*, **16**, 163 (1962); *Chem. Rev.*, **69**, 1 (1969).
(2) E. A. S. Cavell, *J. Chem. Soc.*, 4217 (1958).
(3) A. J. Parker, *Aust. J. Chem.*, **16**, 585 (1963).
(4) J. A. Leary and M. Kahn, *J. Am. Chem. Soc.*, **81**, 4173 (1959).
(5) S. Shinkai and T. Kunitake, *Chem. Lett.*, 109 (1976); S. Shinkai, N. Nakashima, and T. Kunitake, *J. Am. Chem. Soc.*, **100**, 5887 (1978).
(6) S. Shinkai and T. Kunitake, *J. Chem. Soc., Perkin Trans. 2*, 980 (1976).
(7) S. Shinkai, N. Nakashima, and T. Kunitake, *Bull. Chem. Soc. Jpn.*, submitted for publication.
(8) N. Kornblum, R. Seltzer, and P. Haberfield, *J. Am. Chem. Soc.*, **85**, 1148 (1963).
(9) R. Gompper, *Angew. Chem.*, **76**, 412 (1964).
(10) N. Kornblum, R. A. Smiley, R. K. Blachwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955); N. Kornblum, P. J. Berrigan, and W. J. le Noble, *ibid.*, **85**, 1141 (1963); **82**, 1257 (1960); N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2707 (1959).
(11) For comprehensive reviews, see S. Asahara, M. Seno, and T. Arai, "Yohbai Kohka", Sangyo Tosho, Tokyo, 1970, p 195; Y. Yamashita, *Kagaku (Kyoto)*, **19**, 68 (1964); T. M. Harris and C. M. Harris, *Org. React.*, **17**, 155 (1969).

0022-3263/79/1944-4990$01.00/0