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Photochemical Reactions of Saccharin-α-Silylamine Systems. Desilylmethylation of α-Silylamine *via* Single Electron Transfer Pathway

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Photochemical reactions of saccharin with tertiary amines were explored. Saccharin was found to undergo an acid-base reaction with N-trimethylsilylmethyl-N,N-diethyl amine to form N-trimethylsilylmethyl-N,N-diethyl ammonium saccharin salt which is in equilibrium with free saccharin and N-trimethylsilylmethyl-N,N-diethyl amine in solution. Photoreaction of N-trimethylsilylmethyl-N,N-diethyl ammonium saccharin in CH_3OH or CH_3CN results in the generation of desilylmethylated product, N,N-diethyl ammonium saccharin mainly along with benzamide. Photoreaction of N-methylsaccharin with N-trimethylsilylmethyl-N,N-diethyl amine in CH_3OH leads to the production of *o*-(N-methylcarbamoyl)-N-ethylbenzenesulfonamide as the major product along with N-methylbenzamide as the minor product. On the other hand, photoreaction of N,N,N-triethyl ammonium saccharin, generated from saccharin and triethylamine, produces N-methylbenzamide as the exclusive product. These photoreactions are quenched by oxygen indicating that triplets of saccharin and N-methylsaccharin are the reactive excited states. Based on the consideration of the redox potentials of saccharin and N-trimethylsilylmethyl-N,N-diethyl amine, and the nature of photoproducts, pathways involving initial triplet state single electron transfer are proposed for photoreactions of the saccharins with the α-silylamine.

Introduction

The photochemistry of imides has been intensively investigated in the past two decades.[1] One subclass in this family, phthalimides, exhibit a variety of photoreactivities including photoreduction, photoaddition, photocyclization, photocycloaddition, and Norrish type I and type II reactions. Studies in the area of single electron transfer (SET) photochemistry using α-silyl electron donors led to the observation that photoinduced sequential SET-desilylation pathways serve as efficient and highly regioselective methods for carbon centered radical generation.[2] Phthalimides are known to undergo smooth photoaddition reactions in methanol or acetonitrile with α-silyl-*n*-electron donors to generate 3-substituted products *via* mechanistic routes which involve sequential SET-desilylation.[3] Similarly phthalimides tethered with α-silyl-n-

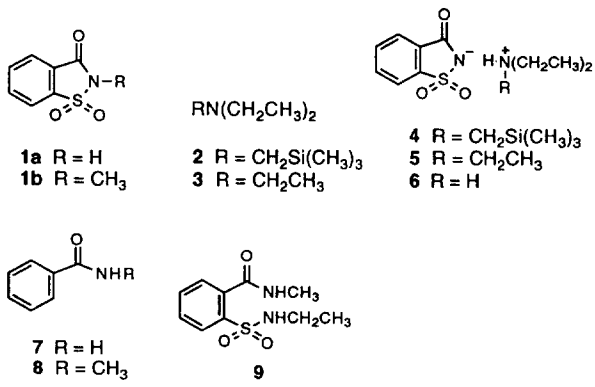
Table 1. Results of Photochemical Reactions of Saccharin-Tertiary Amine Systems

Reactant	Concentration (mM)	Solvent	Reaction Time(h)	%Conversion of Saccharin	Product(s) (% Yields)[a]
1a+**2**, **(4)**	8.2+24.6	CH_3CN	14	70	**6** (55%), **7**[b] (25%)
1a+**2**, **(4)**	13.7+41.0	CH_3OH	4	80	**6** (40%), **7**[b] (37%)
1a+**3**, **(5)**	13.7+41.0	CH_3OH	3.5	37	**7**[b] (95%)
1b+**2**	10.2+50.7	CH_3OH	3.5	100	**8**[b] (15%), **9** (53%)

[a]Yields are based on consumed saccharins. [b]All physical properties are consistent with those of authentic samples.

electron donor groups undergo efficient and high yielding photocyclizations to provide midium to large ring heterocycles.[4] In contrast to the many papers[1] reporting on the photochemistry of phthalimides, reports on the photochemistry of its sulfoimide derivatives, the saccharins, are rare. Recently Kamigata[5] showed that alkylsaccharins undergo photochemical reactions *via* homolytic N-S bond cleavage. This result suggests that the sulfone groups in saccharins can introduce different photoreactivity to these systems as compared to the related phthalimides.

In a continuation of an exploration of new SET-induced photochemical reactions of synthetic utility, we have investigated photochemical reactions of saccharins with tertiary amines including N-trimethylsilylmethyl-N,N-diethylamine (**2**). Below are described the results of these studies which demonstrate that these substances participate in novel SET-induced photochemical reaction pathways.



Results

Formation of salts between saccharin and *tert.* amines, and their photochemical reactions. Saccharin (**1a**) undergoes rapid and quantitative acid-base reactions with N-trimethylsilylmethyl-N,N-diethylamine (**2**)[6] and triethylamine (**3**) in CH_3CN or CH_3OH to form ammonium saccharin salts **4** and **5**, respectively. Photochemical reactions of saccharin (**1a**) with N-trimethylsilylmethyl-N,N-diethylamine (**2**) and triethyl amine (**3**), *i.e.* ammonium saccharins **4** and **5**, were explored first to examine whether SET-induced photoaddition reactions similar to those observed[3] in the photochemical reactions of phthalimides with α-silyl amine **2** take place. Preparative reactions were performed by irradiation (Vycor filter) of CH_3CN and CH_3OH solutions of salt **4** and **5** (8.2-16.4 mM), generated by combining saccharin (**1a**) with 3-fold excesses of the amines **2** and **3**. The nature of products generated and gross chemical efficiencies were evaluated for the photoprocesses conducted at ammonium saccharin salt conversions ranging from 37% to 80%. Product separation employed silica gel chromatographic methods (see the Experimental Section). Products distributions and yields along with the solvents used are given in Table 1.

Irradiation of N-trimethylsilylmethyl-N,N-diethyl ammonium saccharin (**4**) in CH_3CN or CH_3OH results in the formation of N,N-diethyl ammonium saccharin **6** as the major product along with benzamide (**7**). The yields of **6** and **7** do not very significantly with solvent. However the reaction efficiency appears to greatly incerase in CH_3OH *vs.* CH_3CN, judging from the times required to bring about comparable conversions of saccharin salt **4** (Table 1).

Photoreaction of triethyl ammonium saccharin (**5**) in either CH_3CN or CH_3OH produces only benzamide (**7**) with a qualitatively determined lower efficiency than that of **4**. These results indicate that dealkylation similar to desilylmethylation observed in the photoreaction with N-trimethylsilylmethyl-N,N-diethyl amine (**2**) does not occur in the photoreaction with the tertiary amine, triethyl amine (**3**). Thus, the trimethylsilylmethyl group appears to be a requisite for dealkylation process. The ammonium saccharins, **4** and **5**, can be isolated and purified by silica gel chromatography. Irradiation of the isolated ammonium saccharins **4** and **5** in CH_3OH or CH_3CN give similar products distributions as those obtained from irradiations of *in situ* generated ammonium saccharins.

Structural assignments to ammonium saccharin salts **4-5**[7] and photoproduct **6** were made on the basis of characteristic spectroscopic data. IR spectra of the ammonium saccharin salts **4-6** contain characteristic bands for NH^+ groups at 2200-3600 cm^{-1}, imide carbonyl groups at 1615-1635 cm^{-1}, and imide sulfonyl groups at 1260-1280 cm^{-1} and 1150-1180 cm^{-1}.

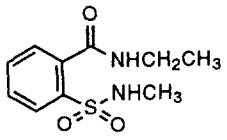
Their ^1H NMR and ^{13}C NMR spectra clearly show resonances which correspond to their alkyl ammonium groups and aromatic rings of saccharin moieties. The ^1H NMR spectrum of **4** contains singlets for methylene hydrogens at 2.56 ppm and for trimethyl hydrogens of N-trimethylsilylmethyl group at 0.11 ppm respectively. Further its ^{13}C NMR spectrum shows resonances at 43.2 ppm for methylene carbon and −1.47 ppm for trimethyl carbons of N-trimethylsilylmethyl group. In contrast, the resonances for trimethylsilylmethyl group in ^1H NMR and ^{13}C NMR spectra of the starting ammonium saccharin **4** are not present in those of the desilylmethylated product **6**. Resonances for alkyl ammonium moieties in ^1H NMR and ^{13}C NMR spectra of the ammonium saccharin salts **4-6** appear in downfield-shifted regions from those of the free amines, N-trimethylsilylmethyl-N,N-diethylamine (**2**), triethylamine (**3**) and diethylamine which support

their ammonium structures. All of the other spectroscopic features of these substances are in complete accord with their assigned structures.

Photochemical reaction of N-methylsaccharin with α-silylamine. Photochemical reaction of N-methylsaccharin (**1b**) with N-trimethylsilyl-methyl-N,N-diethyl amine (**2**) was explored to examine if the photoinduced desilylmethylation process observed in the photochemical reaction of saccharin (**1b**) with N-trimethylsilylmethyl-N,N-diethyl amine (**2**) was form ammonium saccharin salt.

Preparative irradiation was conducted on CH_3OH solution of N-methylsaccharin (**1b**, 10.2 mM) and α-silylamine (**2**, 50.7 mM) by using Vycor-filtered light. Products were separated by chromatography (see the Experimental Section) and the products yields are shown in Table 1. This photoreaction results in the formation of an unexpected product, *o*-(N-methylcarbamoyl)-N-ethylbenzenesulfonamide (**9**) along with a minor quantity of N-methylbenzamide (**8**).

Structural assignment to photoproduct **9** was made by analysis of its characteristic spectroscopic data (see the Experimental Section). The ^1H NMR spectra of **9** shows a triplet for three hydrogens at 1.10 ppm, a quartet for two hydrogens at 2.83 ppm and a singlet for three hydrogens at 2.76 ppm which indicate that it contains one ethyl and one methyl group. Its ^{13}C NMR spectrum contains resonances which correspond to a methyl carbon and a methylene carbon at 10.8 and 41.4 ppm respectively. Especially characteristic are two closely related resonances at 25.9 and 26.0 ppm in ^{13}C NMR spectrum which correspond to two nonequivalent methyl carbons caused by hindered rotation around C-N amide bond. Furthermore, the mass spectrum of **9** shows a base peak at m/z 134 which corresponds to a fragment M^+-SO_2NHCH_2-CH_3. All of these data show that photoproduct **9** is *o*-(N-methylcarbamoyl)-N-ethylbenzenesulfonamide instead of *o*-(N-ethylcarbamoyl)-N-methylbenzenesulfonamide (**10**).



10

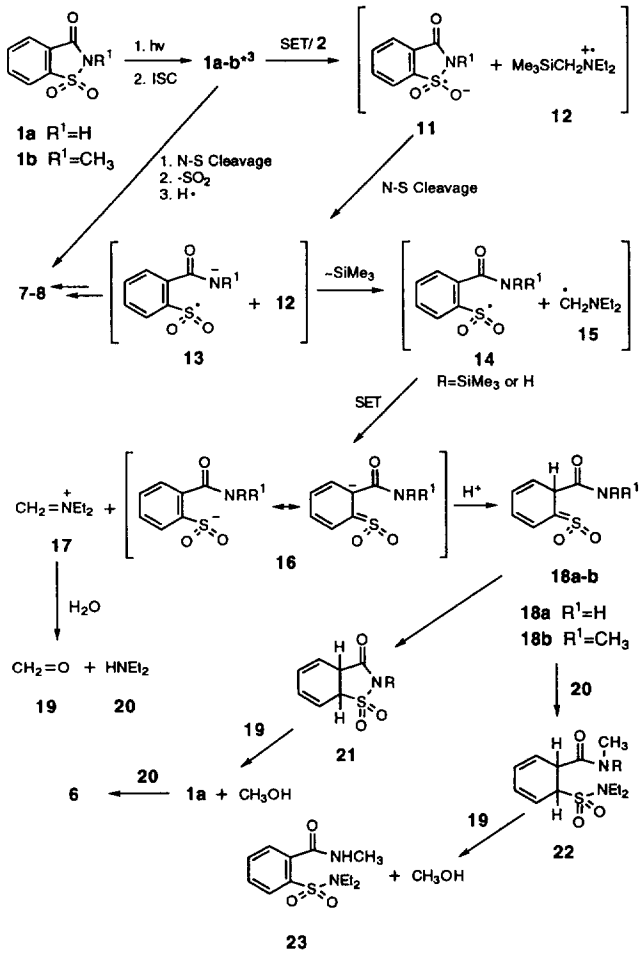
Quenching of photoreactions of ammonium saccharins and of N-methylsaccharin with α-silylamine by oxygen. In order to obtain information about the reactive excited states of saccharin (**1a**) and N-methylsaccharin (**1b**) responsible for formations of products **6**, **7**, and **8**, **9**, oxygen quenching experiments were performed. Oxygen was found to result in almost complete quenchings of the production of **6** and **7** for photoreactions of saccharin (**1a**) with the tertiary amine **2-3** in CH_3OH or CH_3CN, and the formation of **8** and **9** in photoreaction of **1b** with α-silylamine **2** in CH_3OH. These observations suggest that the reactive excited states of saccharin (**1a**) and N-methylsaccharin (**1b**) are triplets.

Discussion

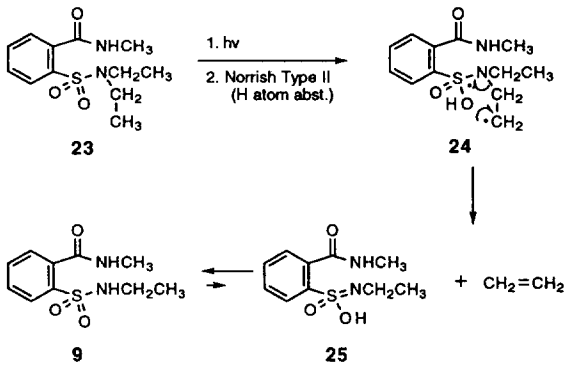
Photoreaction of saccharin (**1a**) with N-trimethylsilylmethyl-N,N-diethyl amine (**2**) in CH_3OH or CH_3CN results in the formation of diethyl ammonium saccharin (**6**) as the major product along with benzamide (**7**). The formation of benzamide (**7**) has precedent in the photochemical reactions of saccharin derivatives[5] and is believed to occur *via* homolytic N-S bond cleavage. In contrast, photoreaction of saccharin (**1a**) with triethyl amine (**3**) does not lead to the formation of product, diethyl ammonium saccharin (**6**) but to the generation of benzamide (**7**) as the exclusive product. The photoreaction with triethyl amine (**3**) is qualitatively less efficient (based on irradiation time *vs.* percent conversion) than that with α-silylamine **2**. The results indicate that α-trimethylsilyl substitution is crucial for the novel dealkylation pathway which competes with the unimolecular cleavage pathway of the triplet excited saccharin.

Interestingly photoreaction of N-methylsaccharin (**1b**) with α-silylamine **2** results in the production of *o*-(N-methylcarbamoyl)-N-ethylbenzenesulfonamide (**9**) as the major product along with N-methylbenzamide (**8**). Although the predominant product, *o*-(N-methylcarbamoyl)-N-ethylbenzenesulfonamide (**9**) differs from the diethyl ammonium saccharin (**6**) which is produced in the photoreaction of saccharin (**1a**) with α-silylamine **2** and appears to be generated through a complex and multiphotochemical reaction pathway, the both photoproducts show that photoinduced desilylmethylations occur in reaction of both N-methylsaccharin (**1b**) and saccharin (**1a**). Further, the desilylmethylation processes of saccharins **1a-b** with α-silylamine **2** appear to involve two-electron oxidations. Electron transfer from α-silylamine **2** ($E_{1/2(+)}$=*ca.*+0.7 V *vs* $Ag/AgNO_3$)[8] to excited saccharin ($E^*_{1/2(-)}$=*ca.*+2.2 V *vs* $Ag/AgNO_3$)[9] is thermodynamically favorable and, thus, rapid.[10] The oxygen quenching results presented earlier support the assignment of saccharin triplet states **1a-b**^{*3} as the reactive species in these photochemical reactions. Accordingly, electron transfer from **2** to triplet excited of saccharins **1a-b**^{*3} results in generation of radical ion pairs **11**+**12** (Scheme 1). Homolytic cleavage of the arylsulfonamide radical anion[11] **11** should be rapid and occur to produce the radical ion pair **13**+**12**. Also, desilylation of the α-silylamine radical cation **12** by the nucleophilic radical anion **13** or the nucleophilic solvent takes place to generate radical pair **14**+**15**.

Subsequent electron transfer from the strong reducing agent, α-amino radical **15** ($E_{1/2(+)}$=*ca.*−1.4 V *vs* $Ag/AgNO_3$)[12] to the sulfonyl radical ($E_{1/2(-)}$=*ca.*+0.2 V *vs* $Ag/AgNO_3$)[13] should be both rapid and efficient and result in production of the hydrolytically unstable formaldiminium ion (**17**) and anion intermediate **16**. Hydrolysis of formaldiminium (**17**) by water present in solution generates formaldehyde (**19**) and diethyl amine (**20**), and protonation of anion **16** in solution occurs to give sulfene **18**[14]. Cyclization by addition of the amide to the sulfene group in **18a** (R^1=H) yields dihydrosaccharin **21** which is oxidized to saccharin (**1a**) by formaldehyde (**19**). The generated saccharin (**1a**) undergoes salt formation reaction with diethyl amine (**20**) present in solution to give the observed product, diethyl ammonium saccharin **6**. On the other hand, the sulfene intermediate **18b** (R^1=CH_3) undergoes intermolecular nucleophilic addition with diethyl amine (**20**) present in solution to produce dihydrosulfonamide **22**. Similarly oxidation of dihydrosulfonamide **22** by formaldehyde (**19**) occurs to produce *o*-(N-methylcarbamoyl-N,N-diethylbenzenesulfonamide **23**. The benzenesulfonamide **23** is presumed to undergo Norrish type II cleavage



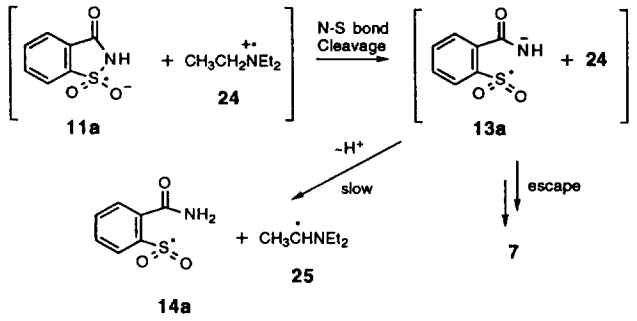
Scheme 1.



Scheme 2.

under the photochemical reaction condition to give the observed product **9** (Scheme 2).

The N-S bond homolysis pathway from triplet excited saccharin **1a-b**^{*3} seems to compete with the SET reaction pathway. Following homolysis, the resulting biradical intermediate undergoes elimination of SO_2 and subsequent hydrogen atom abstraction to produce benzamide **7-8**. In addition to direct homolysis of N-S bond in triplet excited saccharin **1a-b**^{*3}, the radical anion **13** generated by sequential SET-N-S bond cleavage pathway can escape from the radical ion pair **13**+**12** cage and produce benzamide **7-8** after ensuing



Scheme 3.

elimination of SO_2, protonation and hydrogen atom abstraction.

Electron transfer from triethylamine (**3**) to triplet excited saccharin **1a**^{*3} is also expected to be rapid and to occur to generate the radical ion pair **11a**+**24** (Scheme 3). However α-deprotonation of triethylamine radical cation **24** by the attack of radical anion **13a** or by solvent should much less efficient[2] compared to the desilylation of radical cation **12**. Thus most of generated radical anion **13a** escapes from the radical ion pair **13a**+**24** cage to produce benzamide **7** as the major product.

Although saccharin (**1a**) undergoes rapid and quantitative acid-base reaction with tertiary amines **2-3** to form ammonium saccharin salts **4-5** in CH_3OH or CH_3CN, the initial single electron transfer processes in the photoreaction of saccharin (**1a**) with amines **2-3** are believed to occur from the free amines to triplet excited state saccharin **1a**^{*3}. In summary this study has demonstrated that saccharins exhibit diverse SET-promoted photoreactivities in addition to the homolytic N-S bond cleavage process. We are continuing to explore for new photochemical reactions of saccharin derivatives and to probe interesting mechanistic issue associated with these reactions.

Experimental Section

General procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded by using Varian EM-360 or Bruker AF-200 spectrometers. Chemical shifts are reported in parts per million relative to Me_4Si as an internal standard. For compounds containing Me_3Si groups, $CHCl_3$ was used as an internal standard. ^{13}C NMR resonances were assigned by use of the DEPT technique to determine the numbers of attached hydrogens. IR spectra were recorded on a Matton IR-10410E spectrometer. Preparative photochemical reactions were conducted with an apparatus consisting of a 450W Hanovia medium pressure mercury vapor lamp (Ace) surrounded by a Vycor filter in a water-cooled quartz immersion well surrounded by the solution being irradiated. The photolysis solutions were purged with nitrogen both before and during irradiations, and solvent used for photolysis was removed under reduced pressure after reactions. Preparative TLC was performed on 20×20 cm plate coated with E-Merck silica gel PF_{254}. Low resolution mass spectral analyses were performed at 70 eV on Hitachi RMU-6 mass spectrometer and high resolution mass spectral analyses were performed at 70 eV on Hitachi VG-7070 mass spectrometer. N-Trimethyl-

silylmethyl-N,N-diethyl amine (**2**) was prepared by the reported method.[6]

Irradiation of saccharin (1a) and N-trimethylsilylmethyl-N,N-diethyl amine (2) in CH_3CN. A solution containing saccharin (**1a**, 300 mg, 1.64 mmol) and N-trimethylsilyl-methyl-N,N-diethyl amine (**2**, 780 mg, 4.91 mmol) in 200 m*l* of CH_3CN was irradiated for 14 h resulting *ca.* 70% conversion. After removal of solvent, the residue was subjected to preparative TLC (8% CH_3OH in CH_2Cl_2) to yield 35 mg (25%) of benzamide (**7**) and 162 mg (55%) of N,N-diethyl ammonium saccharin (**6**). Spectral data for **6**; ^1H NMR ($CDCl_3$) 1.35 (t, 6H, J=7.3 Hz, $N(CH_2\underline{CH_3})_2$), 2.80 (s, 2H, N^+H_2), 3.20 (q, 4H, J=7.3 Hz, $N(\underline{CH_2}CH_3)_3$), 7.52-7.58 (m, 2H, aromatic), 7.72-7.77 (m, 2H, aromatic); IR (neat) 3600-2100 (broad N^+H stretching), 1620 (C=O stretching), 1582, 1457, 1260 (SO_2 asymmetric stretching), 1150 cm^{-1} (SO_2 symmetric stretching); ^{13}C NMR ($CDCl_3$) 8.5 ($NCH_2\underline{CH_3}$), 46.0 ($N\underline{CH_2}CH_3$), 120.0, 123.4, 131.8 and 132.1 (CH aromatic), 133.8 and 144.2 (C aromatic), 170.5 (C=O); mass spec., (rel. intensity) 189 (15), 188 (68), 183 (13), 174 (10), 159 (19), 149 (29), 129 (18), 128 (16), 105 (16), 104 (16), 101 (15), 91 (20), 86 (100), 83 (60); high resolution mass spec., 183.0004 (M^+-$C_4H_{11}N$ requires 182.9990). All physical properties of the isolated **6** were identical to those of diethyl ammonium saccharin (**6**) which was independently prepared by acid-base reaction between saccharin (**1a**) and diethyl amine.

Irradiation of saccharin (1a) and N-trimethylsilylmethyl-N,N-diethyl amine (2) in CH_3OH. A solution containing saccharin (**1a**, 500 mg, 2.73 mmol) and N-trimethylsilylmethyl-N,N-diethyl amine (**2**, 1300 mg, 8.18 mmol) in 200 m*l* of CH_3OH was irradiated for 4 h resulting *ca.* 80% conversion. After similar work-up to the photolysis in CH_3CN, 90 mg (37%) of benzamide (**7**) and 222 mg (40%) of product **6** were obtained.

Irradiation of saccharin (1a) and triethyl amine (3) in CH_3OH. A solution containing saccharin (**1a**, 500 mg, 2.73 mmol) and triethyl amine (**3**, 828 mg, 8.20 mmol) in 200 m*l* of CH_3OH was irradiated for 3.5 h resulting *ca.* 37% conversion. After removal of solvent and preparative TLC (8% CH_3OH in CH_2Cl_2) of the residue gave 115 mg (95%) of benzamide (**7**).

Irradiation of N-methylsaccharin (1b) with N-trimethylsilylmethyl-N,N-diethyl amine (2). A solution of N-methylsaccharin (**1b**, 400 mg, 2.03 mmol) and N-trimethylsilylmethyl-N,N-diethyl amine (**2**, 1620 mg, 10.14 mmol) in 200 m*l* of CH_3OH was irradiated for 3.5 h resulting almost complete conversion of N-methylsaccharin (**1b**). After removal of solvent, the residue was subjected to column chromatography (AcOEt : CH_2Cl_2 : CH_3OH = 1 : 2 : 1) to yield 42 mg (15%) of N-methylbenzamide (**8**) and 320 mg (53%) of photoproduct **9**. Spectral data for **9**; ^1H NMR (CD_3OD) 1.58 (t, 3H, J=7.3Hz, $NCH_2\underline{CH_3}$), 3.26 (s, 3H, $NH\underline{CH_3}$), 3.32 (q, 2H, J=7.3 Hz, $NH\underline{CH_2}CH_3$), 7.75-7.95 (m, 3H, aromatic), 8.26-8.31 (m, 1H, aromatic); ^1H NMR (DMSO-d_6) 1.10 (t, 3H, J=7.2 Hz, $NCH_2\underline{CH_3}$), 2.76 (s, 3H, $NH\underline{CH_3}$), 2.83 (q, 2H, J=7.2 Hz, $NH\underline{CH_2}CH_3$), 7.28-7.72 (m, 4H, aromatic), 8.69 (br.s, 1H, NH), 9.67 (br.s, 1H, NH); ^{13}C NMR (DMSO-d_6) 10.8 ($SO_2NHCH_2\underline{CH_3}$), 25.9 and 26.0 ($CONH\underline{CH_3}$), 41.1 ($SO_2NH\underline{CH_2}CH_3$), 123.4, 128.0, 129.3 and 129.7 (CH aromatic), 133.2 and 156.5 (C aromatic), 167.9 (amide C=O); IR (KBr) 1650 (amide C=O stretching), 1330 (SO_2 asymmetric stretching), 1035 (SO_2 symmetric stretching), 965 cm^{-1}; mass spec., m/z (rel. intensity) 242 (M^+, 9), 227 (M^+-CH_3, 9), 212 (M^+-$NHCH_3$, 8), 209 (19), 181 (81) 165 (30), 152 (24), 134 (M^+-$SO_2NHCH_2CH_3$, 100), 121 (31), 105 (54); high resolution mass spec., m/z 242.0735 ($C_{10}H_{14}N_2O_3S$ requires 242.0725).

Quenching of photoreactions of saccharuin (1a) and of N-methylsaccharin (1b) with amines 2-3 by oxygen. Two solutions containing saccharin (**1a**, 80 mg, 0.44 mmol) and N-trimethylsilylmethyl-N,N-diethyl amine (**2**, 350 mg, 2.20 mmol) or triethyl amine (**3**, 225 mg, 2.22 mmol) in 30 m*l* of CH_3OH were irradiated simultaneously in a Rayonet reactor with RUL-2537 lamps while one was purged with a stream of N_2 and the other with a stream of O_2. During irradiation, two reaction mixtures were intermittently qualitatively analyzed by TLC (AcOEt : CH_2Cl_2 : CH_3OH = 1 : 2 : 1) to examine their gross conversion to products. Oxygen was observed to quench almost completely the conversion of ammonium saccharin **4** or **5** and the formation of product **6** and **7**, while more than 50% of ammonium saccharin **4** or **5** was reacted to produce **6** and **7**. A similar oxygen quenching experiment on the photoreaction of N-methylsaccharin (**1b**, 80 mg, 0.41 mmol) with N-trimethylsilylmethyl-N,N-diethyl amine (**2**, 320 mg, 2.03 mmol) showed that oxygen results in the almost complete quenching of conversion of **1b** and formation of product **8** and **9**.

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7. Spectral data for **4** : ^1H-NMR ($CDCl_3$) 0.11 (s, 9H, $Si(CH_3)_3$), 1.23 (t, 6H, J=7.3 Hz, $N(CH_2\underline{CH_3})_2$), 2.56 (s, 2H, $-CH_2Si$), 3.11 (br.s, 1H, N^+H), 3.25 (q, 4H, J=7.3 Hz, N ($\underline{CH_2}CH_3)_2$), 7.42-7.50 (m, 2H, aromatic), 7.60-7.67 (m, 2H, aromatic); IR (neat) 3600-2200 (broad N^+H stretching), 1615 (C=O stretching), 1270 (SO_2, asymmetric stretching), 1150 cm^{-1}

(SO_2 symmetric stretching); ^{13}C NMR ($CDCl_3$)-1.5 (Si(CH_3)$_3$), 8.3 ($NCH_2\underline{C}H_3$), 43.2 ($N\underline{C}H_2Si$), 49.4 ($N\underline{C}H_2CH_3$), 119.6, 123.0, 131.6 and 131.9 (CH aromatic), 133.3 and 144.0 (C aromatic), 170.2 (C=O); mass spec., m/z (rel. intensity) 183 (saccharin M^+, 32), 158 (9), 143 (15), 119 (14), 118 (17), 104 (9), 103 (7), 92 (14), 86 (100), 76 (38), 74 (9), 73 (11); high resolution mass spec., m/z 182.9991 (M^+-$C_8H_{21}NSi$ requires 182.9990).

Spectral data for **5**; ^1H NMR ($CDCl_3$) 1.34 (t, 9H, J=7.3 Hz, $N(CH_2\underline{C}H_3)_2$), 3.19 (q, 6H, J=7.3 Hz, $N(\underline{C}H_2CH_3)_2$), 7.50-7.90 (m, 4H, aromatic); IR (neat) 3600-2200 (broad N^+H stretching), 1635 (C=O stretching), 1280 (SO_2 asymmetric stretching), 1180 cm^{-1} (SO_2 symmetric stretching); ^{13}C NMR ($CDCl_3$) 8.5 ($NCH_2\underline{C}H_3$), 45.9 ($N\underline{C}H_2CH_3$), 120.0, 123.3 131.8 and 132.1 (CH aromatic), 133.5 and 144.3 (C aromatic), 170.3 (C=O); mass spec., m/z (rel. intensity) 183 (saccharin M^+, 100), 120 (35), 119 (25), 104 (26), 103 (16), 101 (16), 92 (23), 86 (80), 82 (25), 74 (13), 64 (17), 58 (20); high resolution mass spec., m/z 182.9990 (M^+-$C_6H_{15}N$ requires 183.0003).

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Effect of Ureas on the Hydrophobic Properties of Aqueous Poly(ethylene oxide) Solutions by Viscometry

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Poly(ethylene oxide) (PEO) in aqueous solutions has a hydrophobic character which can induce the hydrophobic interaction between its nonpolar parts. The hydrophobic properties of aqueous PEO solutions are studied by the viscometry in terms of the water structure-making and -breaking capabilities of added solutes of ureas. The results show that the contracted conformation of PEO of low molecular weight, namely poly(ethylene glycol) (PEG), does not result from the hydrophobic interaction between the nonpolar parts of PEO but it can participate in a hydrophobic interaction between the nonpolar parts of PEO and added ureas solutes with nonpolar groups, which can induce a large hydrodynamic volume and increase the viscosity. On the other hand, the PEO of large molecular weight seems to behave like any other water soluble polymers with nonpolar parts and its conformation in aqueous solutions is well explained in terms of water structure perturbing capabilities of added ureas.

Introduction

Poly(ethylene oxide) is an important water-soluble polymer of industrial and biological interests,[1,2] and a crystalline state has helical conformation that is maintained to a greater or lesser extent in aqueous solutions.[3-5] Furthermore it displays some basic features of proteins so that it can be thought as a simple model compound.[6] The most important feature is that it contains nonpolar hydrophobic region (-CH_2-CH_2-) and polar hydrogen bonding site (-O-). Recent studies suggest that PEO chain has a hydrophobic character,[7-11] which can induce a hydrophobic interaction between the nonpolar groups. The conformation of the PEO chain in aqueous solution will be influenced by the interaction of the hydrophobic nature between the ethylene groups and the polar solvent molecules.

Aqueous solutions of urea and substituted ureas are found to be effective denaturants of proteins.[12,13] The denaturants play a role in the denaturation process by changing the water structure. The change of water structure is explained in terms of water structure-breaking and -making of solutes.[14] The concept of water structure-breaking and -making effect of solutes has been used as a powerful indirect tool for interpreting solute-water interactions in aqueous solution.[15,16]

The hydrophobic groups of PEO can participate in a hydrophobic interaction which is a nonelectrostatic, through the