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Photodecomposition of N-*t*-Butyl-N-chloro-ω-phenylalkanesulfonamides in the Presence of Oxygen

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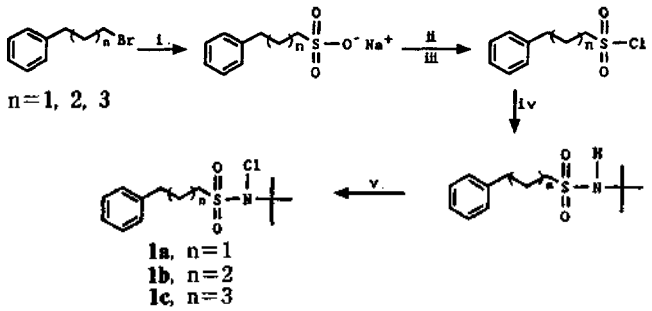
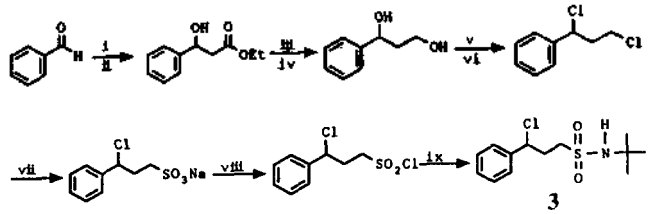
Irradiation of N-*t*-butyl-N-chloro-3-phenylpropanesulfonamide (**1a**) in benzene at 20℃ using 450 W high pressure mercury arc lamp in the presence of oxygen affored N-*t*-butyl-3-phenylpropanesulfonamide (**2**), N-*t*-butyl-3-chloro-3-phenylpropanesulfonamide (**3**), and N-*t*-butyl-3-oxo-3-phenylpropanesulfonamide (**4**). Similarly, N-*t*-butyl-4- (**5**), N-*t*-butyl-4-chloro-4- (**6**), and N-*t*-butyl-4-oxo-4-phenylbutanesulfonamides (**7**) were obtained from N-*t*-butyl-N-chloro-4-phenylbutanesulfonamide (**1b**). However, irradiation of N-*t*-butyl-N-chloro-5-phenylpentanesulfonamide (**1c**) under the same conditions gave complex mixtures. These results indicate that sulfonamidyl radical generated from each of **1a** and **1b** can abstract intramolecularly a hydrogen atom from the benzylic position only by forming six and seven-membered transition states, respectively.

Introduction

Photodecomposition of N-alkyl-N-haloalkanesulfonamides has recently received much attention owing to the chemistry of N-alkylalkanesulfonamidyl radicals formed by the homolysis of halogen-nitrogen bond of the N-alkyl-N-haloalkanesulfonamides.[1] Komori *et al.*[1c] studied photodecomposition of N-*t*-butyl-N-chloroalkanesulfonamides in benzene, aqueous acetic acid, aqueous t-butyl alcohol, and a mixture of acetic acid, water and sulfuric acid using 150 W high pressure mercury arc lamp at 28 to 30℃ under nitrogen atmosphere and isolated N-*t*-butylalkanesulfonamide, γ-, δ-, and ε-chloroalkanesulfonamides, of which yields were dependent on the reaction conditions. The formations of γ-, δ-chloroal-



Scheme 1. Reagents and conditions: i. Na_2SO_3, 150-160℃, 9 h: ii. PCl_5, 100℃, 30 min; iii. PhH, 100℃, 1 h; iv. $(CH_3)_3CNH_2$, PhH, 90-100℃, 1 h; v. Cl_2, H_2O, NaOH, 5-10℃:



Scheme 2. Reagents and conditions: i. Zn, $BrCH_2CO_2Et$, PhH, Δ, 2 h; ii. aq. HCl, 0℃; iii. $LiAlH_4$, Et_2O, Δ; iv. 10% H_2SO_4; v. PCl_5, 100℃, 30 min; vi. PhH, 100℃, 1 h; vii. $NaHSO_3$, H_2O, 150-160℃, 1 h; viii. PCl_5 100℃, 30 min; ix. $(CH_3)_3CNH_2$, PhH, 90-100℃, 1 h.

kanesulfonamides were explained in terms of a hydrogen abstraction from γ-, δ-carbon atoms of the alkanesulfonamides by N-*t*-butylalkanesulfonamidyl radical whereas those of ε-chloroalkanesulfonamides a hydrogen abstraction by chlorine radical. However, Neale[1d] reported that no N-*t*-butyl-δ-chlorobutanesulfonamide was observed in the decomposition of N-*t*-butyl-N-chlorobutanesulfonamide. The generations and reactions of the sulfonamidyl radicals reported were mostly carried out under inert atmosphere. There is one report[1(d)] which described photolysis of N-chloro-N-methylmethanesulfonamide in the presence of styrene in the air. However only a complex mixture was obtained. Since most of radicals are quenched by a triplet state of oxygen molecules, we were interested in the investigation on the fate of the sulfonamidyl radicals in the presence of a triplet state of oxygen molecules, particulary in the hope of obtaining the information about the possible formation of sulfonamidylperoxy radicals and the development of the synthetic method of γ-and/or δ-ketosulfonamides of which general synthetic routes have not been reported. Herein we report the preliminary results.

Results and Discussion

N-*t*-butyl-N-chloro-ω-phenylalkanesulfonamides (**1**) were synthesized according to the literature method[2-4] as shown in Scheme 1.

N-Chlorosulfonamides (**1**) dissolved in an appropriate solvent were irradiated with 450 W Ace-Hanovia high pressure mercury are lamp (see experimental section). From the photodecomposition of **1a** were isolated a mixture of N-*t*-butyl-3-phenylpropanesulfonamide (**2**) and N-*t*-butyl-3-chloro-3-phenylpropanesulfonamide (**3**), and N-*t*-butyl-3-oxo-3-phenylpropanesulfonamide (**4**).

Table 1. Photodecomposition of N-*t*-butyl-N-chloro-3-phenylpropanesulfonamide (**1a**)

entry	solvent	**1a** (g)	Time (min)	Concentration (mM)	Yield(%) **1a**	**2**	**3**	**4**
1	Benzene	0.839	5	9.657	11	0.392*		31.8
2	Benzene	0.839	10	9.657		0.422*		33.6
3	Benzene	0.839	30	9.657		45.2	4.39	39.1
4	Benzene	0.786	60	9.681		46.0	2.46	31.5
5	CH_3CN	0.840	30	9.657		64.2	4.21	24.2

For entry 1 and 2, yields based on the isolation by chromatography but the separation of a mixture of **2** and **3** was unsuccessful. * Yields in grams. For entry 3-5, yields of **2** and **3** based on HPLC analyses. Yields of **4** based on the isolation by chromatography.

Table 2. Photodecomposition of N-*t*-butyl-N-chloro-4-phenylbutanesulfonamide (**1b**) in benzene

Entry	**1b** (g)	Time (min)	Concentration (mM)	Yield (g) **5+6**	Yield (%) **7**
1	0.917	10	9.888	0.392	37.7
2	1.121	30	9.681	0.388	37.9
3	0.744	60	8.560	0.321	40.4

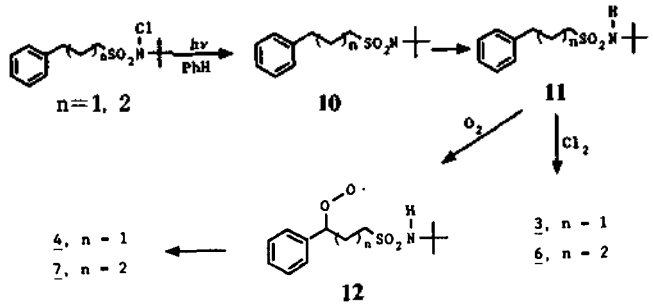
Yield based on the isolation by chromatography.

The structural identifications of **2** and **3** were achieved by a comparison of the retention times of **2** and **3** in the mixture on HPLC with those of the authentic samples, which were synthethized independently by the literature methods[2,3,5] as shown in Scheme 2.

Photodecomposition of **1a** was performed under different conditions and the results are summarized in Table 1.

Table 1 shows that 5 min-irradiation time of **1a** in benzene is not long enough for the complete photodecomposition in view of the recovery of **1a** (11%). However, **1a** disappeared completely after 10 min-irradiation. A noteworthy is the formation of ketosulfonamide (**4**) of which yield seems to be essentially independent of the irradiation time (Entry 1, 2), considering the experimental errors. To our best knowledge, this is the first report for the synthesis of γ-ketosulfonamide although there have been a few reports on the synthesis of β-ketosulfonamides.[6] Prolonged irradiation of **1a** for 30 min under the same conditions, followed by chromatography gave **4** (39%). Analyses of other inseparable mixtures using HPLC gave **2** and **3** in 45% and 4% yields, respectively (Entry 3). Similar result was obtained from the irradiation of **1a** for 60 min (Entry 4). However, in acetonitrile, which is a polar aprotic solvent, yield of **4** decreased remarkably with the increase of **2** (Entry 5).

In order to know the selectivity between γ- and δ-hydrogens toward hydrogen abstraction, N-*t*-butyl-N-chloro-4-phenylbutansulfonamide (**1b**) in benzene was irradiated under the same conditions. From the reaction were isolated N-*t*-butyl-4-phenylbutanesulfonamide (**5**), N-*t*-butyl-4-chloro-4-phenylbutanesulfonamide (**6**), and N-*t*-butyl-4-oxo-4-phenylbutansulfonamide (**7**) of which synthesis has not been reported. No N-*t*-butyl-3-chloro- and N-*t*-butyl-3-oxo-4-phenylbutanesulfo-



Scheme 3.

namide were isolated. The results are tabulated in Table 2.

The yields of **7** were *ca.* 38%, essentially independent of the irradiation time as in the photodecomposition of **1a** under the same conditions. The fact that no N-*t*-butyl-3-chloro-4-phenylbutanesulfonamide was isolated is in contrast with the previous report in which the isomer ratio of N-*t*-butyl-3-chloro to 4-choro-butanesulfonamide was 4.10 to 6.29, depending on N_2 flow rate in the photodecomposition of N-*t*-butyl-N-chlorobutanesulfonamide in benzene.[1c] The regiospecific formations of **6** and **7** without the formations of N-*t*-butyl-3-chloro- and N-*t*-butyl-3-oxo-4-phenylbutanesulfonamides may be rationalized by the presence of a phenyl group which stabilizes radical formed at C-4 of **1b**.

Since oxo groups are introduced at only benzylic positions of **1a** and **1b** to give γ-ketosulfonamide (**4**) and δ-ketosulfonamide (**7**), respectively, N-*t*-butyl-N-chloro-5-phenylpentanesulfonamide (**1c**) was subjected to the same reaction condition in order to see the formation of ε-ketosulfonamide (**8**). However, the reaction was very complicated and only N-*t*-butyl-5-phenylpentanesulfonamide (**9**) was isolated. The failure for the detection of **8** indicates that the compounds **4** and **7** are formed *via* an intramolecular hydrogen abstraction by sulfonamidyl radicals (**10**) through the formation of six and seven membered transition states, followed by the reaction with a triplet state of oxygen molecules to give peroxy radicals (**12**)[7] which were eventually converted to **4** and **7**, respectively.

However, in the case of **10** ($n=3$), eight-membered transition state should be formed to abstract a benzylic hydrogen atom which is highly energetic. Therefore the formation of benzylic radical is unlikely. In addition, the sulfonamidyl radical **10** ($n=3$) did not show the regioselectivity on the hydrogen abstraction at either γ- or δ-position of **1c**, which is contrast with Komori's result[1c] but somewhat in accord, with the report describing the failure for the isolation of N-*t*-butyl-5-halobutanesulfonamide.[1d]

It is uncertain whether sulfonamidylperoxy radical is formed or not. However, our observations can be rationalized better in terms of the intramolecular hydrogen atom abstractions by sulfonamidyl radicals through forming a six or seven-membered transition state to give benzylic radical.

Experimental

All chemicals were obtained from Aldrich Chemical Company, Inc., USA and various solvents were from Duksan Pharm. Company, Inc, and distilled befor use. Infrared spectra were recorded using Perkin-Elmer Model 782 Spectrometer. ^{1}H-NMR spectra were recorded on a Varian EM 360A (60 MHz) unless otherwise specified using tetramethylsilane as an internal standard. Mass spectra were obtained using VG 12-250 Spectrometer. Ultraviolet spectra were recorded on a Shimadzu UV-Visible Spectrometer UV-260. HPLC analyses were performed on Millipore model 510 from Waters Company, Inc.. Detector was Millipore Differential refractomer R_{410} and μ Bondpac™ C18 reverse column from Waters was used. Acetonitrile and methanol for HPLC were from Aldrich Chemical Company, Inc., Melting points were measured using a Fisher-Johns melting point apparatus and are uncorrected.

General Synthetic Method for Sodium 1-Bromo-ω-phenylalkanesulfonate

A mixture of 1-bromo-ω-phenylalkane, sodium sulfite, and water was heated at 150℃ to 160℃ for 9 h and the mixture was worked up according to the literature method.[2]

Sodium 3-phenylpropanesulfonate. 1-bromo-3-phenylpropane (75.24 g, 0.38 mol), sodium sulfite (83.30 g, 0.66 mol), and water (150 m*l*) were used. Yield: 63%; mp. 168-169℃ (EtOH): ^{1}H-NMR (D_2O) δ 2.00 (q, 2H, CCH_2C), 2.75 (m, 4H, $PhCH_2$, CH_2SO_2), 7.26 (s, 5H, Ph).

Sodium 4-phenylbutanesulfonate. 1-Bromo-4-phenylbutane (60.01 g, 0.28 mol), sodium sulfite (72.01 g, 0.57 mol), and water (150 m*l*) were used. Yield: 60%; mp. 248℃ (dec): ^{1}H-NMR (D_2O) δ 1.63-2.20 (m, 4H, C-CH_2CH_2-C) 2.90 (t, 2H, $PhCH_2$), 3.10 (t, 2H, CH_2SO_2), 7.56 (s, 5H, Ph); IR (KBr) 3095, 3030, 2930, 2860, 1625, 1500, 1465, 1455, 1310, 1250, 1200, 1180, 1060, 1050, 795, 785, 745, 715, 700, 615, 590, 540, 470 cm^{-1}.

Sodium 5-phenylpentanesulfonate. 1-Bromo-5-phenylpentane (19.37 g, 0.085 mol), sodium sulfite (23.91 g, 0.190 mol), and water (100 m*l*) were used. Yield: 56%.

General Synthetic Method for ω-phenylalkanesulfonyl Chloride

A mixture of sodium ω-phenylalkanesulfonate and phosphorus pentachloride was heated at 100℃ for 30 min. The reaction mixture was cooled to room temperature, followed by addition of benzene (100 m*l*), which was refluxed for 1 h. The reaction mixture was worked up as in the literature procedure.[3]

3-Phenylpropanesulfonyl Chloride. Sodium 3-phenylpropanesulfonate (55.10 g, 0.25 mol), phosphorus pentachloride (60.6 g, 0.29 mol), and benzene (150 m*l*) were used. Yield: 64%; ^{1}H-NMR ($CDCl_3$) δ 2.30 (q, 2H, C-CH_2-C), 2.7 (t, 2H, $PhCH_2$), 3.50 (t, 2H, CH_2SO_2), 7.23 (s, 5H, Ph); IR (KBr) 3080, 3050, 3020, 2920, 2850, 1600, 1490, 1450, 1370, 1250, 1200, 1180, 1080, 1070, 1030, 965, 750, 710, 700, 600, 565, 500 cm^{-1}.

4-Phenylbutanesulfonyl Chloride. Sodium 4-phenylbutanesulfonate (67.31 g, 0.29 mol), phosphorus pentachloride (70.00 g, 0.34 mol), and benzene (150 m*l*) were used. Yield: 70% (liquid); ^{1}H-NMR ($CDCl_3$) δ 2.00 (m, 4H, C-CH_2CH_2-C), 2.85 (t, 2H, $PhCH_2$), 3.73 (t, 2H, CH_2SO_2), 7.25 (s, 5H, Ph); IR (KBr) 3090, 3070, 3030, 2900, 2870, 1605, 1500, 1455, 1375, 1170, 1080, 1030, 915, 750, 705, 600, 580, 550, 525 cm^{-1}.

5-Phenylpentanesulfonyl Chloride. Sodium 5-phenylpentanesulfonate (15.61 g, 0.062 mol), phosphorus pentachloride (16.86 g, 0.081 mol), and benzene (150 m*l*) were used. Yield: 78% (liquid); ^{1}H-NMR ($CDCl_3$) δ 1.16-2.20 (m,

6H, C-$CH_2CH_2CH_2$-C), 2.63 (t, 2H, $PhCH_2$), 3.56 (t, 2H, CH_2SO_2), 7.24 (s, 5H, Ph); IR (KBr) 3050, 3020, 2930, 2350, 1600, 1495, 1460, 1450, 1370, 1165, 1030, 750, 700, 600, 545, 520 cm^{-1}.

General Synthetic Method for N-*t*-Butyl-ω-phenylalkanesulfonamide

t-Butylamine was added to ω-phenylalkanesulfonyl chloride in benzene, followed by refluxing for 1 h. The reaction mixture was worked up according to the literature method.[4]

N-*t*-Butyl-3-phenylpropanesulfonamide. 3-Phenylpropanesulfonyl chloride (35.32 g, 0.16 mol), *t*-butylamine (88.31 g, 1.21 mol), and benzene (60 m*l*) were used. Yield: 70%: mp. 58-59℃ (*n*-hexane) (lit.[8] 61.5-62.5℃); ^{1}H-NMR ($CDCl_3$) δ 1.30 (s, 9H, $C(CH_3)_3$), 2.13 (m, 2H, C-CH_2-C), 2.88 (m, 4H, $PhCH_2$, CH_2SO_2), 4.56 (s, 1H, NH), 7.23 (s, 5H, Ph); IR (KBr) 3290, 3030, 2970, 2920, 2880, 1500, 1450, 1435, 1395, 1375, 1365, 1305, 1145, 1130, 1020, 1010, 880, 755, 730, 705, 600, 555, 500 cm^{-1}.

N-*t*-Butyl-4-phenylbutanesulfonamide. 4-Phenylbutanesulfonyl chloride (54.24 g, 0.23 mol), *t*-butylamine (21.70 g, 0.30 mol), and benzene (60 m*l*) were used. Yield: 75%: mp. 41-42℃ (*n*-hexane); ^{1}H-NMR ($CDCl_3$) δ 1.33 (s, 9H, $C(CH_3)_3$), 1.55-1.97 (t, 4H, C-CH_2CH_2-C), 2.70 (t, 2H, $PhCH_2$), 3.10 (t, 2H, CH_2SO_2), 4.56 (s, 1H, NH), 7.15 (s, 5H, Ph); IR (KBr) 3280, 2980, 2960, 2940, 2880, 1500, 1455, 1440, 1395, 1375, 1320, 1260, 1250, 1235, 1215, 1170, 1145, 1130, 1025, 1015, 895, 870, 785, 740, 700, 595, 565, 500 cm^{-1}. Anal. Calcd for $C_{14}H_{23}NO_2S$: C, 62.42; H, 8.61; N, 5.20. Found: C, 62.59; H, 8.83; N, 5.18.

N-*t*-Butyl-5-phenylpentanesulfonamide. 5-Phenylpentanesulfonyl chloride (11.29 g, 0.046 mol), *t*-butylamine (27.02 g, 0.37 mol), and benzene (50 m*l*) were used. Yield: 83%: mp. 55-57℃ (*n*-hexane); ^{1}H-NMR ($CDCl_3$) δ 1.38 (s, 9H, $C(CH_3)_3$), 1.05-2.23 (m, 6H, C-$CH_2CH_2CH_2$-C), 2.67 (t, 2H, $PhCH_2$), 3.08 (t, 2H, CH_2SO_2), 4.60 (s, 1H, NH), 7.33 (s, 5H, Ph); IR (KBr) 3250, 2960, 2935, 2860, 1450, 1390, 1365, 1315, 1290, 1270, 1150, 1130, 980, 945, 625, 600 cm^{-1}. Anal. Calcd for $C_{15}H_{25}NO_2S$: C, 66.88; H, 8.89; N, 4.94. Found: C, 66.94; H, 8.94; N, 4.86.

General Synthetic Method for N-*t*-Butyl-N-chloro-ω-phenylalkanesulfonamide (1)

Chlorine gas was bubbled into the suspension of N-*t*-butyl-ω-phenylalkanesulfonamide in aqueous sodium hydroxide at 5℃ to 10℃ until the yellow color persisted. The reaction mixture was worked up according to the literature method.[1c]

N-*t*-Butyl-N-chloro-3-phenylpropanesulfonamide (1a). N-*t*-butyl-3-phenylpropanesulfonamide (3.58 g, 0.014 mol), water (50 m*l*), and sodium hydroxide (0.50 g, 0.013 mol) were used. Yield: 2.23 g (0.077 mol, 55%); mp. 63-64℃ (petroleum ether); UV λ_{max}^{MeCN} 258 (ε=382) nm; ^{1}H-NMR δ 1.50 (s, 9H, $C(CH_3)_3$), 2.20 (m, 2H, C-CH_2C), 2.80 (t, 2H, $PhCH_2$), 3.30 (t, 2H, CH_2SO_2), 7.20 (s, 5H, Ph); IR (KBr) 3300, 2980, 2940, 2880, 1600, 1500, 1460, 1400, 1370, 1320, 1240, 1230, 1180, 1150, 890, 840, 810, 760, 710, 600, 580, 505, 480 cm^{-1}. Anal. Calcd for $C_{13}H_{20}ClNO_2S$: C, 53.88; H, 6.96; N, 4.83; Cl, 12.2. Found: C, 53.97; H, 6.89; N, 4.79; Cl, 12.4.

N-*t*-Butyl-N-chloro-4-phenylbutanesulfonamide (1b). N-*t*-Butyl-4-phenylbutanesulfonamide (1.09 g, 4.05 mmol), sodium hydroxide (0.18 g, 4.50 mmol), and water (50 m*l*) were used. Yield: oily liquid (0.738 g, 2.43 mmol, 60%); UV λ_{max}^{MeCN} 259 (ε=327) nm: ^{1}H-NMR ($CDCl_3$) δ 1.45 (s, 9H, $C(CH_3)_3$), 1.60-1.93 (m, 4H, C-CH_2CH_2-C), 2.63 (t, 2H, $PhCH_2$), 3.20 (t, 2H, CH_2SO_2) 7.20 (s, 5H, Ph); IR (neat) 2990, 2940, 1565, 1500, 1400, 1370, 1340, 1240, 1180, 1150, 890, 750, 700, 620 cm^{-1}. Anal. Calcd for $C_{14}H_{22}ClNO_2S$: C, 55.34; H, 7.30; N, 4.61; Cl, 11.7. Found: C, 55.56; H, 7.49; N, 4.76; Cl, 11.9.

N-*t*-Butyl-N-chloro-5-phenylpentanesulfonamide (1c). N-*t*-Butyl-5-phenylpentanesulfonamide (0.86 g, 3.03 mmol), sodium hydroxide (0.15 g, 3.75 mmol), and water (40 m*l*) were used. Yield: oily liquid (0.63 g, 1.98 mmol, 65%); ^{1}H-NMR ($CDCl_3$) δ 1.50 (s, 9H, $C(CH_3)_3$), 1.13-2.31 (m, 6H, C-$CH_2CH_2CH_2$-C), 2.64 (t, 2H, $PhCH_2$), 3.08 (t, 2H, CH_2SO_2), 7.35 (s, 5H, Ph); IR (neat) 2990, 2940, 1565, 1500, 1400, 1370, 1340, 1240, 1180, 1150, 890, 750, 700, 620 cm^{-1}. Anal. Calcd for $C_{15}H_{24}ClNO_2S$: C, 56.68; H, 7.61; N, 4.41; Cl, 11.12. Found: C, 56.92; H, 7.83; N, 4.59; Cl, 11.3.

Photodecomposition of N-*t*-Butyl-N-chloro-ω-phenylakanesulfonamide (1)

N-*t*-Butyl-N-chloro-ω-phenylalkanesulfonamide (1) dissolved in an appropriate solvent was irradiated with 450 W Ace-Hanovia high pressure mercury arc lamp through quartz immersion well which was cooled by circulating cooling water at 20℃. Oxygen gas was bubbled through the reaction. The yellow reaction mixture was concentrated under reduced pressure and the residue showed two spots on TLC, which was separated by chromatography. Elution with chloroform gave a mixture of N-*t*-butyl-ω-phenylalkanesulfonamide and N-*t*-butyl-ω-chloro-ω-phenylalkanesulfonamide, which were identified by comparison with the retention time of the authentic samples on HPLC (see Table 1, 2). Elution next with ether gave N-*t*-butyl-ω-oxo-ω-phenylalkanesulfonamide.

N-*t*-Butyl-3-oxo-3-phenylpropanesulfonamide (4). mp. 99-100℃ (*n*-hexane); ^{1}H-NMR ($CDCl_3$) δ 1.36 (s, 9H, $C(CH_3)_3$), 3.36 (s, 4H, $COCH_2$, CH_2SO_2), 4.30 (s, 1H, NH), 7.43 (m, 3H, Ph), 7.90 (m, 2H, Ph); IR (KBr) 3300, 2980, 1690, 1600, 1450, 1430, 1420, 1395, 1370, 1355, 1320, 1260, 1200, 1145, 1125, 1005, 880, 745, 690, 550 cm^{-1}. Anal. Calcd for $C_{13}H_{19}NO_3S$; C, 57.97; H, 7.11; N, 5.20. Found: C, 58.02; H, 7.03; N, 5.18.

N-*t*-Butyl-4-oxo-4-phenylbutanesulfonamide (7). ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 1.36 (s, 9H, $C(CH_3)_3$), 2.26 (quintet, 2H, CCH_2C), 3.20 (2t, 4H, $COCH_2$, CH_2SO_2), 4.17 (s, 1H, NH), 7.43 (m, 3H, Ph), 7.90 (m, 2H, Ph); IR (KBr) 3280, 2970, 1690, 1390, 1365, 1310, 1140, 1000, 930, 870, 760 cm^{-1}. Anal. Calcd for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.47; N, 4.94. Found: C, 59.03; H, 7.65; N. 4.78.

HPLC Analysis of a Mixture of N-*t*-Butyl-ω-phenylalkanesulfonamides (2, 5) and N-*t*-Butyl-ω-chloro-ω-phenylalkanesulfonamides (3, 6)

A mixture of two compounds **2** and **3** showed two peaks (retention time, 5.7 min and 5.8 min, respectively) by elution with a mixture of CH_3CN and water (v/v, 5 : 1) when the flow rate was 1.0 m*l*/min. The structural identifications of **5** and **6** were achieved by the same method as described above.

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Electrochemical Oxidation of Benzidine and Hydrazobenzene

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The electrochemistry of benzidine and hydrazobenzene was studied in water-acetonitrile mixed solutions at various pHs and the results are reported. The cyclic voltammetric peak for the oxidation of benzidine shows a pH dependency of −62 mV/pH in the pH range of 0-3.5, no pH dependency between pH values of 3.5 and about 10.5, and of about −50 mV/pH between pH = 10.50 and 14.0, indicating that oxidation mechanisms differ depending on the pH of the medium. However, the CV peak for the hydrazobenzene oxidation is shown to be independent of pH of the medium, suggesting that the proton is not involved in the rate limiting step of the electrochemical oxidation of hydrazobenzene to azobenzene. Results of *in situ* spectroelectrochemical experiments indicate that the oxidation products obtained during the oxidation of benzidine and hydrazobenzene depend on the result of dynamic equilibria taking place at various pHs.

Introduction

The electrochemistry of benzidine and hydrazobenzene is an important component in understanding and controlling electrochemical polymerization reactions of aniline in acidic aqueous media, because various dimers of aniline have been identified during the early stage of the oxidation of aniline at low concentrations.[1-6] These dimers have been shown to proceed to produce polyaniline; some dimers are more important than others.[7] Of three possible dimers produced, a head-to-tail dimer, *p*-aminodiphenylamine (or N-phenyl-*p*-phenylene diamine), would be the most desirable intermediate for preparing polyaniline. Both benzidine and hydrazobenzene have been shown to polymerize to polyaniline,[7] although physical properties of polyanilines prepared from different precursors have not been characterized.

The electrochemistry of benzidine has been studied by several groups of investigators for different reasons. It has been studied as an indicator for redox titrations[8,9] and as a model to study the oxidation mechanisms involved in primary, secondary, and tertiary aromatic amines.[10-12] Only a few studies on the electrochemistry of hydrazobenzene has been reported due to its instability in an acidic medium owing to the benzidine rearrangement reaction.[13,14] The reduction of azobenzene to hydrazobenzene in acidic media, which was shown to be reversible on polarographic time scale, has been used as a model for studying electrochemical-chemical (EC) reaction mechanisms to develop electrochemical techniques.[15-18] The electrochemically reduced product of azobenzene, *i.e.*, hydrazobenzene, undergoes a benzidine rearrangement reaction[19] and thus served as a model reaction for developing electrochemical techniques for studying EC reactions.

In this study, we have conducted cyclic voltammetric and *in situ* spectroelectrochemical studies on the electrochemistry of benzidine as well as hydrazobenzene in a wide range of pHs and report the results. The results indicate that benzidine undergoes a two electron transfer in acidic solutions to form a deprotonated dication, benzidinequinonediimine. In the medium pH range, it undergoes two one electron step reactions as in nonaqeous solvents. The chemical reversibility of the electrochemical reaction of the hydrazobenzene-azobenzene pair is also demonstrated by *in situ* spectroelectrochemical techniques.

Experimental

Aldrich's hydrazobenzene and Matheson's benzidine were used after sublimation. Other chemicals of ACS reagent grade were used without further purification. Stock solutions