with saturated aqueous sodium bicarbonate. After drying ($CaSO_4$) and concentrating, the resulting crude product was recrystallized from 95% ethanol to afford 0.6 g (65%) of N-methyl-2,3,3-triphenylpropenamide hemihydrate (**8**): mp 172.5-174°; ir 3250 (NH), 1620 (C=O), 770 (C=C), and 685 (ArH).

Anal. Calcd for $C_{44}H_{40}N_2O_3$: C, 81.96; H, 6.25; N, 4.34. Found: C, 82.32; H, 6.55; N, 4.27.

Dehydration of β-Hydroxyamide 3.—Solid adduct **3** (2.0 g) was added in small portions to 45.6 g of polyphosphoric acid maintained at a sufficiently high temperature to allow magnetic stirring. After 5 min, the brown-green solution was treated with 50 g of ice, and the cold solution was extracted several times with a total of 400 ml of ether. After work-up as in the dehydration of adduct **2b**, the resulting residue was recrystallized from benzene to give 1.47 g (80%) of 2-(9-fluorenyl)-2-phenylacetamide (**9**), mp 229-231°.

Anal. Calcd for $C_{21}H_{15}NO$: C, 84.82; H, 5.09; N, 4.71. Found: C, 84.52; H, 5.25; N, 4.48.

Registry No.—*n*-Butyllithium, 109-72-8; **2b**, 2683-62-7; **3**, 17510-68-8; **4a**, 17510-69-9; **4b**, 17510-70-2; **4c**, 17510-71-3; **5a**, 17510-72-4; **5c**, 17510-73-5; N-methyl-2,3,3-triphenylpropenamide, 2683-63-8; **9**, 17510-75-7.

Metalation at Methyl Group of N-Substituted *o*-Toluenesulfonamides by Excess *n*-Butyllithium. Condensation with Benzophenone[1]

HAMAO WATANABE AND CHARLES R. HAUSER

Department of Chemistry, Duke University, Durham, North Carolina 27706

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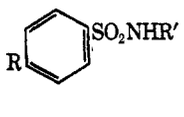
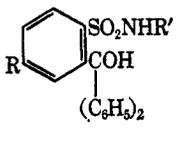
N-Substituted benzenesulfonamides **1** (R = H; R′ = CH_3 or C_6H_5) and also *p*-toluenesulfonanilide (**1**, R = CH_3; R′ = C_6H_5) have previously[2] been shown to undergo *ortho* metalation, as well as N metalation, with excess *n*-butyllithium, as evidenced by condensations of the resulting dilithiosulfonamides with benzophenone to form *ortho* derivatives **2**; these products underwent thermal cyclodehydration to give the sultams **3**.



1



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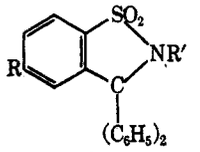
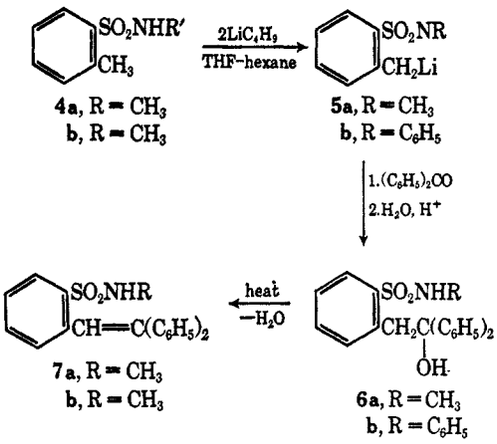


3

N-Substituted *o*-toluenesulfonamides **4a, b** have now been found to undergo metalation at the methyl group, as well as N metalation, with excess *n*-butyllithium to form dilithiosulfonamides **5a, b**, as evidenced by condensation with benzophenone to give carbinol sulfonamides **6a, b**; these products underwent thermal dehydration to afford unsaturated sulfonamides **7a** and **b**, respectively (Scheme I).

The carbinol sulfonamides **6a, b** and their dehydration products **7a, b** were obtained in high yields (73–96%). Their structures were supported by analyses and absorption spectra. Surprisingly, carbinol sulfonamide **6b** appeared to undergo a change in structure on standing at room temperature, especially in the presence of polyphosphoric acid, as evidenced by a change in the nmr spectrum. That the second structure was still essentially carbinol sulfonamide **6b** was supported, not only by analysis and absorption spectra, but also by dehydration to form the unsaturated sulfonamide **7b** (see Experimental Section).

SCHEME I



The difference in the courses of metalation of the *o*- and *p*-toluenesulfonamides appears to be due to initial coordination of the lithium of the *n*-butyllithium with the nitrogen of the monolithio intermediate to form a complex in which the potential *n*-butyl carbanion is directed to a methyl hydrogen in the 2-methyl compounds **4a, b** but to an *ortho* hydrogen in the 4-methyl compound **1** (R = CH_3; R′ = C_6H_5). Thus, although a nucleophilic mechanism probably operates to form a weaker base in both cases, the lithium cation also plays an important role especially in the latter case where an *ortho* hydrogen rather than the probably more acidic 4-methyl hydrogen is ionized.[3]

The difference in the courses of thermal dehydration of the benzophenone adducts of the *o*- and *p*-toluenesulfonamides is evidently due to the presence of methylene hydrogen β to the hydroxyl group in the former compounds, but not in the latter. Thus, whereas the carbinol sulfonamides **2** can undergo only cyclodehydration, the carbinol sulfonamides **6a, b** can, and do, exhibit linear dehydration involving their methylene hydrogen. Although **6a, b** also underwent linear dehydration with acid catalysts in refluxing acetic acid or benzene, they might possibly exhibit cyclodehydration with acids at lower temperatures since the corresponding carbinol carboxamides **8**, which have methylene hydrogen, have recently been observed to undergo cyclodehydration with cold sulfuric acid to form **9**.[4] Unfortunately, cold sulfuric acid has now been found

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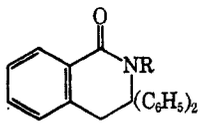
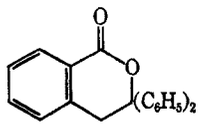


9



10

(1) Supported by Army Research Office (Durham).

(2) H. Watanabe, R. L. Gay, and C. R. Hauser, *J. Org. Chem.*, **33**, 900 (1968).

(3) See K. P. Klein and C. R. Hauser, *ibid.*, **32**, 1479 (1967); also see A. A. Morton, "Solid Organoalkali Reagents," Gordon and Breach, Inc., New York, N. Y., 1964.

(4) I. T. Barnish, C. L. Mao, and C. R. Hauser, *Chem. Commun.*, 564 (1968).

to convert carbinol sulfonamides **6a, b** into water-soluble products under similar conditions.

Incidentally, the courses of the thermal reactions of carbinol sulfonamides **6a, b** and **2** differ, not only from each other, but also from that of carbinol carboxamides **8** which undergo thermal deamination to form lactone **10**.[5]

Experimental Section[6]

Metalations of 4a, b with *n*-Butyllithium to Form Dilithiosulfonamides 5a, b.—A solution of 0.020 mol of N-methyl- or N-phenyl-*o*-toluenesulfonamides (**4a** and **4b**, respectively) in 70 ml of tetrahydrofuran[7] in a dry flask under nitrogen was cooled to 0°, and 30 ml of (0.046 mol) of a solution of 1.6 *M* *n*-butyllithium in hexane[8] was added during 4–5 min. After stirring for 30 min at 0°, the clear, deep orange solution from **4a** and the clear, dark red solution from **4b** were considered to contain 0.020 mol of the dilithiosulfonamides **5a** and **5b**, respectively. These solutions were employed at 0° described below.

Condensations of Dilithiosulfonamides with Benzophenone to Form Carbinol Sulfonamides. A. Condensation of 5a to Form 6a.—To the stirred, cold solution of dilithiosulfonamide **5a** was added under nitrogen with stirring, during 4–5 min, a solution of 4.74 g (0.026 mol) of benzophenone in 30 ml of tetrahydrofuran,[7] and the stirring continued for 1 hr at 0°. To the resulting clear, yellow solution (at 0°) was added with stirring 30 ml of distilled water and then 35–40 ml of 5% hydrochloric acid. The two layers were separated. After saturation with sodium chloride, the aqueous layer was extracted three times with ether, and the extracts were combined with the organic layer. After washing twice with a saturated solution (30 ml) of sodium chloride and drying ($MgSO_4$), the solvent was removed under reduced pressure on the steam bath to give a slightly yellow, viscous liquid, which was stirred with a little methanol and then left to stand in a current of air under a hood for a few hours. The resulting crystals were collected, washed with a little cold methanol, and dried in air; more crystals were recovered from the filtrate to which the washings had been added. The combined crystals were recrystallized from methanol, giving 6.64 g (91%) of carbinol sulfonamide **6a** (prismatic crystals): mp 161–163°, and mp 163.5–164.5° after further recrystallization; ir 3495 (OH), 3315 (NH), 1295 (SO_2), 1145 (SO_2), 840, 780, 756, 740, and 695 cm^{-1}; nmr (acetone-d_6) δ 8.13–6.26 (m, 15.40, aromatic H and OH or NH), 5.04 (s, 0.7, NH or OH), 4.20 (s, 1.8, CH_2), and 2.55 ppm (d, 2.8, J = 5.3 cps, N–CH_3).

Anal. Calcd for $C_{21}H_{21}NSO_3$: C, 68.64; H, 5.76; N, 3.81. Found: C, 69.00; H, 5.51; N, 3.64.

B. Condensation of 5b to Form 6b.—This condensation was effected essentially as described above under A to give a clear, yellow-orange solution which, on work-up, afforded 7.06 g (82%) of carbinol sulfonamide **6b**, mp 149–151.5°. Recrystallization from methanol gave 5.73 g (67%) (large prismatic crystals, sample A): mp 152–153°; ir 3500, 3400 and 3265 (OH, broad), 3160 (NH), 1312 and/or 1290 (SO_2), 1150 and/or 1140 (SO_2), 934, 778, 757, 740, 690 cm^{-1}; nmr (acetone-d_6) δ 9.27 (s, 0.9, OH or NH), 8.67–6.42 (m, 19.4, aromatic H), 5.05 (s, 0.9, NH or OH), 4.21 ppm (s, 2.0, CH_2). After standing at room temperature for 3 months, the ir spectrum was unchanged; the nmr spectrum (acetone-d_6) showed δ 7.50–6.00 (m, 20.4, aromatic H and OH), 4.56 (broad, NH), and 3.73 ppm (s, 1.8, CH_2).

Anal. Calcd for $C_{26}H_{23}NSO_3$: C, 72.70; H, 5.40; N, 3.26. Found: C, 72.81; H, 5.24; N, 3.17.

A 1-g sample of this compound was mixed well with 40 g of polyphosphoric acid. After standing at room temperature (25–30°) for 24 hr the mixture was poured, with stirring, onto 100 g of ice–water. The resulting solid was collected and recrystallized from methanol to give 0.96 g of recovered carbinol sulfonamide **6b** (fine crystals, sample B): mp 156–157.5°; with sample A, mmp 156–157°; ir 3500 (OH), 3265 (NH), 1315 and/or 1285 (SO_2), 1150 (SO_2), 918, 777, 753, 740, and 696 cm^{-1}; nmr (acetone-d_6) δ 8.00–6.33 (m, 21.4, aromatic H, OH and NH), and 4.17 ppm (s, 1.9, CH_2); nmr ($CDCl_3$) δ 8.03–6.80 (m, 18.7, aromatic H), 6.27 (broad, 0.9, NH), 4.05 (s, 2.2 CH_2), and 3.35 ppm (s, 1.0, OH). After standing at room temperature for 6 months, the ir spectrum was unchanged; the nmr spectrum (acetone-d_6) showed δ 7.50–6.00 (m, 20.0, aromatic H and OH), 4.50 (broad 0.6, NH), and 3.73 ppm (s, 2.1, CH_2).

Anal. Calcd for $C_{26}H_{23}NSO_3$: C, 72.70; H, 5.40; N, 3.26. Found: C, 72.90; H, 4.97; N, 3.15.

Dehydration of Carbinol Sulfonamides to Form *o*-Sulfamyltriphenyl ethylenes. A. Thermal Method.—A 1-g sample of carbinol sulfonamide **6a** was heated under a slow stream of nitrogen in a round-bottomed flask on a Wood's metal bath (220–230°) for 5 hr. The flask was removed from the bath, and the molten mass was allowed to come to room temperature. The resulting solid was recrystallized from methanol to give 0.77 g (81%) of **7a** (fine prismatic crystals): mp 107.5–109.5°; ir 3300 (NH), 1315 (SO_2), 1155 (SO_2), 843, 777, 764, 759, 744, and 695 cm^{-1}; nmr ($CDCl_3$) δ 8.17–6.88 (m, 14.2, aromatic H), 7.57 (s, 1.0, vinyl H), 4.53 (broad, 0.7, NH), and 2.57 ppm (d, 2.6, J = 5.1 cps, N–CH_3).

Anal. Calcd for $C_{21}H_{19}NSO_2$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.38; H, 5.37; N, 3.89.

Similarly, a 1-g sample of carbinol sulfonamide **6b** (sample A) was dehydrated at 235–245°. The resulting mass was recrystallized from methanol to give 0.92 g (96%) of **7b** (fine needles): mp 128.5–130°; ir 3240 (NH), 1315 (SO_2), 1150 (SO_2), 920, 829, 779, 757, 751, 738, 725, and 690 cm^{-1}; nmr ($CDCl_3$) δ 8.28–7.65 and 7.45–6.50 (m, 20.0, aromatic H and NH) and 7.25 ppm (s, 0.7, vinyl H).

Anal. Calcd for $C_{26}H_{21}NSO_2$: C, 75.88; H, 5.14; N, 3.40. Found: C, 75.76; H, 5.27; N, 3.45.

B. Acetic–Sulfuric Acid Method.—A solution of a 1-g sample of carbinol sulfonamide **6a** in 30 ml of glacial acetic acid containing 0.015 ml of concentrated sulfuric acid was refluxed for 24 hr and then cooled to room temperature. The clear, colorless solution was poured onto 100 ml of ice–water. The mixture was made basic with sodium carbonate. The resulting white solid was collected and dissolved in hot methanol. After separation of insoluble material (0.14 g), the filtrate was evaporated to give 0.69 g (73%) of **7a** (fine prismatic crystals): mp 106.5–108°; mixture melting point with **7a** obtained under A, 106–108°; the ir spectra of the two samples were identical.

C. *p*-Toluenesulfonic Acid Method.—A solution of 0.60 g of carbinol sulfonamide **6b** (sample B) in 30 ml of benzene containing 0.03 g of *p*-toluenesulfonic acid (hydrate) was refluxed for 10 hr, during which a Dean–Stark water trap was used to remove water as an azeotrope of benzene–water. The hot, colorless, clear solution was allowed to evaporate in a current of air under a hood. The resulting sticky liquid was scratched to solidify. The solid was washed with dilute sodium carbonate solution and water, and then recrystallized from methanol to give 0.56 g (89%) of **7b** (fine needles): mp 128.5–130°; mixture melting point with **7b** obtained under A, 128.5–130°; ir spectra of the two samples were identical.

Registry No.—*n*-Butyllithium, 109-72-8; benzophenone, 119-61-9; **6a**, 17510-55-3; **6b**, 17510-56-4; **7a**, 17510-57-5; **7b**, 17510-58-6.

(5) R. L. Vaulx, W. H. Puterbaugh, and C. R. Hauser, *J. Org. Chem.*, **29**, 3514 (1964).

(6) Melting points are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich. Ir spectra (KBr method) were produced on Perkin-Elmer Infracord Model 137 and Model 237. Nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane (δ 0 ppm) as an internal standard.

(7) Freshly distilled from lithium aluminum hydride.

(8) Foote Mineral Co., Exton, Pa.

Fluorination of Methyl Isobutyrate with Perchloryl Fluoride[1]

WALTER J. GENSLER, QUAZI A. AHMED, AND MERVYN V. LEEDING

Department of Chemistry, Boston University, Boston, Massachusetts 02215

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Enolates react with perchloryl fluoride to give α-fluoro carbonyl derivatives. This kind of fluorination

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