tion of 4.7 g. of methyl iodide in 25 ml. of absolute ether was slowly added to the deep red colored solution with vigorous mechanical stirring. The solution was refluxed for 6.5 hours. During this time the color of the solution became light yellow. Any unreacted butyllithium was destroyed by the addition of 50 ml. of ethanol. The ether solution was washed with water until neutral and dried over calcium chloride. The ether was distilled *in vacuo* and the oil residue crystallized from benzene–methanol. Colorless crystals, m.p. 170–175°, 1.16 g., were obtained. A sample was recrystallized twice from ether–pentane. The melting point of the purified product was 163–164°. Further recrystallization failed to give material of higher m.p. A mixture of the purified material with D melted at 150–158°.

Anal. Calcd. for $C_{33}H_{26}$: C, 93.80; H, 6.20. Found: C, 93.63; H, 6.20.

Oxidation of Hydrocarbon (D). (a). To a solution of 1 g. of D in 20 ml. of pyridine was added 1.2 g. of finely powdered potassium permanganate and 1 ml. of water. The mixture was swirled and allowed to stand at room temperature for an hour. The excess permanganate was destroyed by the addition of 25 ml. of methanol. The oxides of manganese were removed by filtration through a sintered glass funnel. The filtrate was diluted with 25 ml. of water and made acid (litmus) with hydrochloric acid. A colorless solid separated; 0.7 g., m.p. 97–166°. The precipitate was dissolved in 50 ml. of ether, and the ether solution was extracted with three 20-ml. portions of saturated sodium bicarbonate solution. Acidification of the extracts failed to yield a solid acid. The neutral fraction was dried over sodium sulfate. The ether solution was concentrated and then diluted with low-boiling petroleum ether. A colorless crystalline precipitate separated, m.p. 172–173°. A mixture with the hydrolysis product below melted at 173–173.5°.

(b).—To a solution of 19 g. of D in 200 ml. of carbon tetrachloride were added 8.5 g. of N-bromosuccinimide and 0.58 g. of benzoyl peroxide. The solution was refluxed for 4 hours. The succinimide was removed by filtration. The filtrate was dried over sodium sulfate. The solvent was evaporated and the viscous residue was dissolved in 250 ml. of acetone. To the acetone solution 50 ml. of water was added and the resulting solution was refluxed for 15 hours. To this was added 8.5 g. of silver nitrate dissolved in aqueous acetone of the same concentration as the hydrolysis solution. The precipitated silver bromide was removed by filtration. The acetone solution was treated with Darco and filtered again. Ten grams of colorless crystals was obtained by dilution with water, m.p. 172–173°. The analysis corresponded to a dimeric ether.

Anal. Calcd. for $(C_{32}H_{23})_2O$: C, 92.50; H, 5.58. Found: C, 92.48; H, 5.87.

To a solution of 9.5 g. of the above ether in 100 ml. of dioxane was added a solution of 10 ml. of concd. sulfuric acid in 150 ml. of water. The mixture was refluxed for 4 days. The cooled solution was diluted with water and extracted with six 50-ml. portions of ether. The combined ether extracts were washed with 5% sodium bicarbonate solution and water. The ether was distilled and the residue crystallized from acetone. The colorless crystals had m.p. 172–173° and weighed 3.22 g. An additional 0.75 g., m.p. 174–175°, was obtained by allowing the filtrate to stand. The two crops were combined and recrystallized from acetone, m.p. 174–175°. No depression in m.p. was observed upon mixing with the carbinol obtained by permanganate oxidation of D.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.28; H, 5.87.

Nuclear Magnetic Resonance Spectra.—The nuclear magnetic resonance spectra were run at 40 megacycles and 20° on a Varian model V-4200 B instrument. Methylene chloride was employed as an external standard, and the scale was determined by the sideband method using a Hewlett–Packard model 200-CD audio oscillator. The chemical shifts are expressed in parts per million with respect to pure water, the positive values being on the side of higher frequency.

The spectrum of hydrocarbon A, run as a saturated solution in carbon tetrachloride, showed peaks at −1.82 and +3.08 p.p.m. in addition to highly split absorption below −2.22 due to the aromatic hydrogens. The ratio of the area of the +3.08 p.p.m. peak to that of the −1.82 p.p.m. peak is 3.0 to 2.1.

The spectrum of compound D as a 20% solution in carbon tetrachloride exhibited peaks at +2.10 and −0.35 p.p.m., having areas in the ratio 3.0 to 1.25, in addition to the aromatic absorption below −2.00 p.p.m. Peaks of compound E as a 20% solution in carbon tetrachloride were observed at +2.08 and +3.23 p.p.m., having areas in the ratio 3.0 to 2.0, as well as aromatic absorption below −2.15 p.p.m. The spectrum of 1,3,9-triphenylfluorene as a 20% solution in carbon tetrachloride showed only one peak above −2.00 p.p.m., a peak at −0.35 p.p.m.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MASSACHUSETTS]

O-Acylhydroxylamines. II. O-Mesitylenesulfonyl-, O-*p*-Toluenesulfonyl- and O-Mesitoylhydroxylamine[1]

BY LOUIS A. CARPINO

RECEIVED DECEMBER 5, 1959

O-Mesitylenesulfonyl- and O-*p*-toluenesulfonylhydroxylamine have been prepared by the hydrofluoric acid and perchloric acid cleavages of the corresponding *t*-butyl N-arenesulfonoxycarbamates. The structures of the O-arenesulfonylhydroxylamines were established by (a) iodometric analysis, (b) reaction with acetone which gave the corresponding O-sulfonylacetoximes and (c) infrared examination. O-Mesitoylhydroxylamine was prepared similarly from *t*-butyl N-mesitoyloxycarbamate. Reaction of O-mesitoylhydroxylamine with dibenzylamine gave 1,1-dibenzylhydrazine.

Prior to the current study the only simple N-unsubstituted O-sulfonylhydroxylamine known was hydroxylamine-O-sulfonic acid[2] (HOS, I, R = H). In connection with work on amination reactions[3] it was desirable to have available O-sulfonyl derivatives of hydroxylamine which might be soluble in organic solvents. Keller and Smith[4] attempted to prepare the methyl and ethyl esters of HOS (I, R = CH_3 and C_2H_5) with only partial success. In the present study we have succeeded in preparing O-arenesulfonylhydroxylamines by a method analogous to that which had been used in the synthesis of O-acylhydroxylamines.

H_2NOSO_2OR I

H_2NOCOR

IIa, R = C_6H_5—

IIb, R = 2,4,6-$Me_3C_6H_2$—

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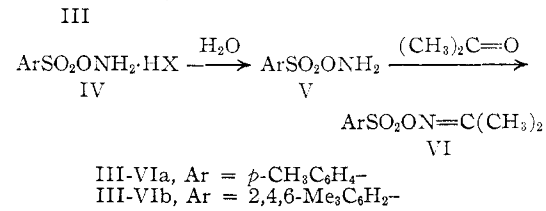
(1) Supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(603)-114. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) F. Sommer, O. F. Schulz and M. Nassau, *Z. anorg. u. allgem. Chem.*, **147**, 142 (1925).

(3) L. A. Carpino, C. A. Giza and B. A. Carpino, THIS JOURNAL, **81**, 955 (1959).

(4) R. N. Keller and P. A. S. Smith, *ibid.*, **68**, 899 (1946).

O-Benzoylhydroxylamine (IIa) was first described by Jencks[5] who found it to be the primary product of the acylation of hydroxylamine by *p*-nitrophenyl benzoate. Independently we have shown that this unique hydroxylamine derivative can be obtained by the hydrogen chloride cleavage of *t*-butyl N-benzoyloxycarbamate.[3] Attempts[3] to effect the cleavage of *t*-butyl N-*p*-toluenesulfonoxycarbamate (IIIa) by hydrogen chloride were unsuccessful because of the strong oxidizing properties of the expected cleavage product. Since the carbo-*t*-butoxy group may be cleaved by non-reducing acids such as hydrogen fluoride, trifluoroacetic acid and perchloric acid[6] these reagents have now been applied to the cleavage of *t*-butyl N-arenesulfonoxycarbamates. Both 48% aqueous hydrofluoric acid and 70% aqueous perchloric acid proved to be suitable. Treatment of IIIa with perchloric acid at room temperature gave an unstable substance which had the properties expected of *O-p*-toluenesulfonylhydroxylamine (Va), although because of its instability it was not possible to obtain samples sufficiently pure for elemental analyses.



$$\underset{\text{III}}{ArSO_2ONHCOOCMe_3} \xrightarrow{\text{HF or } HClO_4}$$

$$\underset{\text{IV}}{ArSO_2ONH_2 \cdot HX} \xrightarrow{H_2O} \underset{\text{V}}{ArSO_2ONH_2} \xrightarrow{(CH_3)_2C{=}O} \underset{\text{VI}}{ArSO_2ON{=}C(CH_3)_2}$$

III-VIa, Ar = p-$CH_3C_6H_4$–
III-VIb, Ar = 2,4,6-$Me_3C_6H_2$–

On attempted isolation and drying Va spontaneously deflagrated. Treatment of a freshly prepared sample of Va with acetone afforded the known oxime derivative VIa.

O-Mesitylenesulfonylhydroxylamine (Vb), prepared similarly from IIIb, preferably using aqueous hydrofluoric acid as the cleavage reagent, proved to be considerably more stable than Va. Spontaneous deflagrations were never noted in working with Vb although the crude material decomposed slowly on standing overnight at room temperature. Once-recrystallized samples of Vb of 96% purity (iodometric analysis) decomposed in air at room temperature within 2-3 days, but could be kept for at least two weeks upon storage in a freezer.

In contrast to the O-acylhydroxylamines (II) which form hydrochlorides stable in water solution the salts IVa-b are hydrolyzed to the free bases Va-b by virtue of the strong inductive effect of the sulfonyl group. The basicity constant (K_b) of the related compound chloramine[7] (NH_2Cl) has been estimated[8] to be 1×10^{-15}.

Examination of the infrared spectra of Va and Vb supports the suggested structures. Nerdel and Lehmann[9] have recorded the infrared spectrum of methyl benzenesulfonate and assigned strong bands at 7.33 and 8.40μ to the asymmetric and symmetric stretching frequencies of the SO_2 group. Bellamy[10] quotes the ranges 7.05–7.52 and 8.34–8.70μ for covalent sulfonates. O-Mesitylenesulfonylhydroxylamine (Vb) exhibits sharp NH stretching bands at 3.04 and 3.11μ and a medium band at 6.25μ which may be attributed to the NH_2 bending frequency. The SO_2 stretching bands for Vb and related compounds are recorded in Table I.

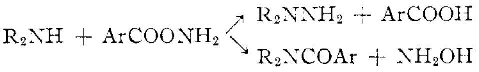
TABLE I

CHARACTERISTIC INFRARED BANDS OF O-SULFONYLHYDROXYLAMINES[a,b] (μ)

Compound	λ_{SO_2} (asymm.)	λ_{SO_2} (symm.)
$MesSO_2ONH_2$	7.43s	8.42s or 8.52s
$TsONH_2$	7.39s	8.50s
$MesSO_2ONHCOOCMe_3$	7.35s	8.38s, 8.48s or 8.66s
$MesSO_2ON{=}CMe_2$	7.39s	8.40s or 8.52s
$TsON{=}CMe_2$	7.35s	8.43s or 8.52s

[a] Mes = 2,4,6-$Me_3C_6H_2$–, Ts = p-$CH_3C_6H_4SO_2$–. [b] Spectra were recorded linearly in wave length as Nujol mulls on a Perkin–Elmer model 21 spectrophotometer, sodium chloride optics.

The significant increase in stability of Vb over Va suggested that in the O-acyl series O-mesitoylhydroxylamine (IIb) might be more easily handled than O-benzoylhydroxylamine (IIa) and therefore more useful as a model compound for comparison of the reactivity of O-acylhydroxylamines and chloramine. The O-mesitoyl derivative was prepared by the general method described previously and was indeed found to be more stable than IIa. Furthermore the steric effects exhibited by IIb allow nucleophilic displacements on nitrogen to occur without complications due to attack of the nucleophile at the carbonyl group. As an example, reaction of O-benzoylhydroxylamine with dibenzylamine gave a mixture of 1,1-dibenzylhydrazine and N,N-dibenzylbenzamide. With O-mesitoylhydroxylamine no evidence for amide formation was noted, the hydrazine being obtained in a yield of 58%. A detailed study of IIa, b and Va, b as analogs of chloramine is under way.



$$R_2NH + ArCOONH_2 \begin{array}{l} \nearrow R_2NNH_2 + ArCOOH \\ \searrow R_2NCOAr + NH_2OH \end{array}$$

Experimental[11,12]

O-*p*-Toluenesulfonylhydroxylamine (Va).—A mixture of 2.87 g. of *t*-butyl N-*p*-toluenesulfonoxycarbamate[3] and 7.5 ml. of 70% perchloric acid was stirred for 3–4 min. at room temperature until gas evolution subsided. The slurry was cooled in an ice-bath. Ice chips were added in order to keep the temperature at about 0° during subsequent dilution with water to a total volume of 40–45 ml. As the ice and water were added an oil formed which then solidified. The white amorphous solid was filtered and washed with ice-cold water and then transferred rapidly to a beaker containing 15 ml. of ice-cold sodium bicarbonate solution (1 *M*). After evolution of carbon dioxide ceased the solid was filtered and washed with ice-cold water.

O-*p*-Toluenesulfonylhydroxylamine as prepared in this manner was found to be extremely sensitive. In one case a sample which had been allowed to dry in air decomposed spontaneously and vigorously after 10–15 min., leaving a black viscous residue. In order to obtain a stable deriva-

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(5) W. P. Jencks, *Biochim. et Biophys. Acta*, **27**, 417 (1958); THIS JOURNAL, **80**, 4581, 4585 (1958).

(6) L. A. Carpino, *ibid.*, **79**, 98 (1957).

(7) Although stable in dilute aqueous solutions chloramine is considerably less stable than the O-arenesulfonylhydroxylamines. W. Marckwald and M. Willie [*Ber.*, **56**, 1319 (1923)] found free chloramine to decompose at −50°.

(8) I. Weil and J. C. Morris, THIS JOURNAL, **71**, 3123 (1949).

(9) F. Nerdel and W. Lehmann, *Ber.*, **92**, 2460 (1959).

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 300.

(11) Melting points and boiling points are uncorrected.

(12) Analyses are by Drs. Weiler and Strauss, Oxford, England.

tive for purposes of identification, a sample of the freshly prepared wet solid obtained from 2.87 g. of the carbo-*t*-butoxy precursor was added to 2–3 ml. of acetone. Dilution with 10 ml. of water after 3–5 min. followed by cooling gave 1.4 g. (61.7) of O-*p*-toluenesulfonylacetoxime, m.p. 86–88° (ethanol), lit.[13] m.p. 89°.

***t*-Butyl N-Mesitylenesulfonoxycarbamate** (IIIb).—A solution of 5.32 g. of *t*-butyl N-hydroxycarbamate[3] and 5.56 ml. of triethylamine dissolved in 20 ml. of dimethylformamide was cooled in an ice-bath and there was added in small portions over 10–15 min. 8.74 g. of mesitylenesulfonyl chloride.[14] After the mixture was allowed to stand in the ice-bath for 30 min. it was diluted with water to a volume of 250 ml. and again cooled in an ice-bath. In order to facilitate crystallization of the oil which separated, the aqueous solution was decanted from the lower layer and the residual thick oil spread about on the sides of the flask in a thin film. In this way the oil was caused to solidify within 1–2 hours. When the oil was allowed to remain below the surface of the aqueous solution, crystallization was very slow and in some cases partial decomposition occurred before the material solidified. The solid was triturated with the original aqueous solution, filtered and air-dried. There was obtained 10.5 g. (83.4%) of amorphous white powder, m.p. 99–104° dec. Recrystallization by dissolution in 10–15 ml. of warm benzene followed by precipitation with 40 ml. of ligroin (b.p. 60–90°) gave 10 g. (79.4%) of small white crystals, m.p. 102–106°. An analytical sample had m.p. 104–105.5° dec. (benzene–ligroin).

Anal. Calcd. for $C_{14}H_{21}NSO_5$: C, 53.31; H, 6.71. Found: C, 53.36; H, 6.25.

O-Mesitylenesulfonylhydroxylamine (Vb).—A suspension of 13 g. of *t*-butyl N-mesitylenesulfonoxycarbamate in 30 g. of 48% aqueous hydrofluoric acid in a polyethylene beaker was immersed in a water-bath at 65° for approximately 1 minute in order to initiate cleavage as evidenced by evolution of gas. The mixture was then removed from the bath and allowed to stand at room temperature with occasional swirling until the evolution of gas ceased and the solid was replaced by an oil (4–8 min.). The mixture was then cooled in an ice-bath and worked up essentially as given for the O-*p*-toluenesulfonyl derivative. The moist, bicarbonate-washed precipitate was dissolved in the minimum amount of ether at room temperature and the ether decanted from the lower water layer into a flat dish. Rapid evaporation of the ether by an air stream left 4.5 g. (50.7%) of white crystals which were dried briefly by pressing between filter paper. Immediate recrystallization was effected by dissolution in a small amount of ether and precipitation with five volumes of ligroin (b.p. 60–90°). After cooling in an ice-bath for 15 min. filtration gave 3 g. (33.8%) of Vb as snow-white needles, m.p. 80° dec. (when dropped into a bath heated to this temperature).

Prepared in this manner, Vb could be stored in the freezing compartment of a refrigerator (−18°) for at least 2 weeks. Decomposition occurred in 2–3 days at room temperature. Repeated crystallizations of Vb from ether–ligroin generally did not serve to yield purer samples; in fact, after 3–4 such crystallizations the material became tacky and underwent decomposition. The purest samples (96% iodometrically) were obtained by a single rapid crystallization as indicated above.

Anal. Calcd. for $C_9H_{13}NSO_3$: I.E.,[15] 107.7. Found: I.E., 112.4, 113.2, 113.4.

O-Mesitylenesulfonylacetoxime (VIb).—A solution of 1 g. of acetoxime and 1.9 ml. of triethylamine in 4 ml. of dimethylformamide was cooled in an ice-bath and treated slowly (2–3 min.) with 3 g. of mesitylenesulfonyl chloride. Dilution with 50 ml. of water after 10 min. gave 3.4 g. (97.5%) of the oxime derivative VIb. Dissolution in warm benzene and precipitation by means of ligroin (b.p. 60–90°) gave 2.8 g. (80%) of small white crystals, m.p. 95–96.5°.

Anal. Calcd. for $C_{12}H_{17}NSO_3$: C, 56.44; H, 6.71. Found: C, 56.51; H, 6.55.

There was no depression in the melting point on admixture with a sample (m.p. 95–96°) prepared by reaction of O-mesitylenesulfonylhydroxylamine with acetone.

***t*-Butyl N-Mesitoyloxycarbamate.**—A solution of 24.8 g. of *t*-butyl N-hydroxycarbamate[3] and 29.7 ml. of triethylamine in 150 ml. of methylene dichloride was cooled in an ice-bath. With mechanical stirring a solution of 34 g. of mesitoyl chloride in 75 ml. of methylene dichloride was added during 1–1.5 hours. The mixture was stirred in the ice-bath for 4 hours and at room temperature overnight and then extracted twice with 100-ml. portions of water. After removal of the solvent by distillation from a water-bath an oil remained which solidified on cooling and scratching. Recrystallization from ligroin (b.p. 60–90°) gave 44 g. (84.5%) of cream-white blocks, m.p. 72.5–76°. The analytical sample melted at 78–79.5° (ligroin, b.p. 60–90°).

Anal. Calcd. for $C_{15}H_{21}NO_4$: C, 64.49; H, 7.58. Found: C, 64.36; H, 7.79.

O-Mesitoylhydroxylamine.—A solution of 10 g. of *t*-butyl N-mesitoyloxycarbamate in 150 ml. of nitromethane was treated with a stream of anhydrous hydrogen chloride for 5–7 min. After standing for 15 min. the precipitated solid (m.p. 125–127° dec.) was filtered, washed with nitromethane, dried in air and then suspended in 100 ml. of water and treated with 1 *M* sodium bicarbonate solution until gas evolution stopped. The resulting oil was extracted with three 15-ml. portions of methylene dichloride, the extracts dried (magnesium sulfate) and the solvent removed from a water-bath at room temperature with the aid of a water aspirator. The O-mesitoylhydroxylamine remained as a clear, colorless oil, amt. 5.5 g. (86%).

Anal. Calcd. for $C_{10}H_{13}NO_2$: I.E., 89.6. Found: I.E., 92.5, 93.5.

For elemental analysis a portion of the oil was converted to the **acetyl derivative** by treatment with acetic anhydride, which rapidly precipitated a white solid. Recrystallization from ligroin (b.p. 60–90°)-benzene gave white needles, m.p. 128–130°.

Anal. Calcd. for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83. Found: C, 65.21; H, 7.16.

The free O-mesitoylhydroxylamine gave positive tests with starch–iodide paper and hydrazine (slow gas evolution). No color developed with ferric chloride in ethanol.

Conversion of O-Mesitoylhydroxylamine to 1,1-Dibenzylhydrazine.—A mixture of 5.3 g. of crude, freshly prepared O-mesitoylhydroxylamine and 17.5 g. of dibenzylamine became warm spontaneously and a solid separated after 10–15 min. The mixture was then heated in a water-bath at 70–75° for 15 min. and treated with 10 ml. of H_2O, 15 ml. of acetic acid and 3.5 g. of benzaldehyde. The resulting mixture was heated in the water-bath at 70–75° for 15 min., 250 ml. of water added and the mixture extracted with four 25-ml. portions of ether. The ether extracts were washed with water, 10% sodium hydroxide solution and dilute sodium bisulfite solution. Removal of the solvent gave 6.2 g. (70%) of the benzal derivative, m.p. 77–79°. Recrystallization from ligroin (b.p. 60–90°) gave 5.1 g. (57.5%) of faintly yellow crystals, m.p. 81–83° (lit.[16] m.p. 85°), mixture m.p. 81–83°.

AMHERST, MASS.

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[13] H. Wege, *Ber.*, **24**, 3537 (1891).

[14] E. H. Huntress and J. S. Autenrieth, THIS JOURNAL, **63**, 3446 (1941).

[15] The iodine equivalent (I.E.) was determined as follows: the sample (0.4 g.) was treated with 25 ml. of glacial acetic acid and immediately after solution occurred 2 ml. of saturated potassium iodide solution was added followed by a chip of Dry Ice. The solution was allowed to stand for 30 min. at room temperature, diluted with 25 ml. of water and titrated with sodium thiosulfate solution (0.1 *N*) using starch indicator.

[16] T. Curtius and H. Franzen, *Ber.*, **34**. 552 (1901).