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Reactions of Nitroparaffins with Sulfur Dioxide and Amines

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The reaction of a primary or secondary nitroparaffin with sulfur dioxide and amines yields salts of imidodisulfonic acid. Other products of the reaction are Schiff bases and enamines. The reaction of an oxime with sulfur dioxide and amines yields sulfamic acid salts, Schiff bases and enamines.

A study of the reaction of nitroparaffins with sulfur dioxide was made in an attempt to prepare oximes or their rearrangement products according to equation 1.

$$R_1R_2CHNO_2 + SO_2 \longrightarrow R_1R_2C{=}NOH + SO_3 \quad (1)$$

When this reaction was carried out with 2-nitropropane in the presence of *n*-butylamine, no oxime was obtained. Instead, a good yield of crystalline bis(*n*-butylammonium) imidodisulfonate (I), was obtained.

$$HN(SO_3)_2^{=}2C_4H_9N\overset{+}{H}_3$$

I

The identity of this material was established by elementary analysis, titration in nonaqueous media, and by comparison of infrared spectra and melting points with an authentic sample prepared from triammonium imidodisulfonate[1] by the method of Boatman and Sisler.[2]

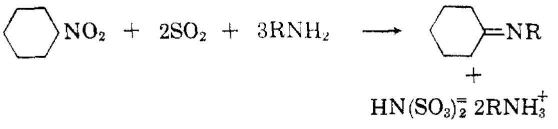
Nitrocyclohexane and 1-nitropropane on reaction with *n*-butylamine and sulfur dioxide also gave bis(*n*-butylammonium) imidodisulfonate.

The reaction of cyclohexylamine with sulfur dioxide and either 2-nitropropane or nitrocyclohexane yielded, analogously, bis(cyclohexylammonium) imidodisulfonate. A similar product, dimorpholinium imidodisulfonate was obtained on reaction of nitrocyclohexane with sulfur dioxide and morpholine.

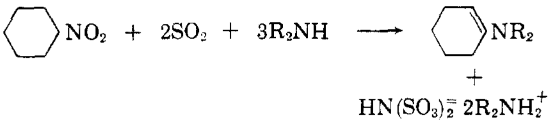
No imidodisulfonate was obtained by the reaction of a tertiary nitroparaffin, 2-methyl-2-nitropropane, with sulfur dioxide and cyclohexylamine. Amine-sulfur dioxide reaction products were isolated instead.

The reaction of nitroparaffins with sulfur dioxide and *tert*-butylamine or *tert*-octylamine yielded no imidodisulfonates. The nature of the various products obtained in these cases was not established with certainty.

The reaction leading to imidodisulfonates yielded in addition, Schiff bases from primary amines and enamines from secondary amines. These products were isolated only in low yield. Assuming that these products along with the imidodisulfonates are formed initially, the over-all reaction may be written as in Equation 2 or 3 using nitrocyclohexane as an example.



(2)



(3)

Several reaction paths may be considered. Two of these are shown.

SCHEME I

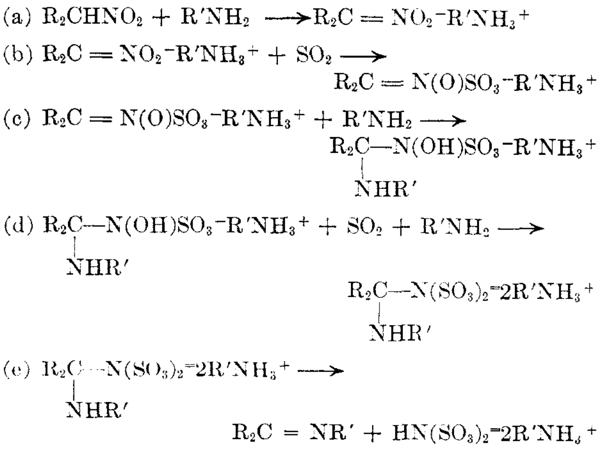
(a) $R_2CHNO_2 + SO_2 \longrightarrow R_2C = NOH + SO_3$

(b) $R_2C = NOH + SO_2 + R'NH_2 \longrightarrow R_2C = NSO_3^-R'NH_3^+$

(c) $R_2C = NSO_3^-R'NH_3^+ + R'NH_2 \longrightarrow H_2NSO_3^-R'NH_3^+ + R_2C = NR'$

(d) $H_2NSO_3^-R'NH_3^+ + SO_3 + R'NH_2 \longrightarrow HN(SO_3)_2^{=}2R'NH_3^+$

SCHEME II



(a) $R_2CHNO_2 + R'NH_2 \longrightarrow R_2C = NO_2^-R'NH_3^+$

(b) $R_2C = NO_2^-R'NH_3^+ + SO_2 \longrightarrow R_2C = N(O)SO_3^-R'NH_3^+$

(c) $R_2C = N(O)SO_3^-R'NH_3^+ + R'NH_2 \longrightarrow \underset{\displaystyle NHR'}{\underset{|}{R_2C}}{-}N(OH)SO_3^-R'NH_3^+$

(d) $\underset{\displaystyle NHR'}{\underset{|}{R_2C}}{-}N(OH)SO_3^-R'NH_3^+ + SO_2 + R'NH_2 \longrightarrow \underset{\displaystyle NHR'}{\underset{|}{R_2C}}{-}N(SO_3)_2^{=}2R'NH_3^+$

(e) $\underset{\displaystyle NHR'}{\underset{|}{R_2C}}{-}N(SO_3)_2^{=}2R'NH_3^+ \longrightarrow R_2C = NR' + HN(SO_3)_2^{=}2R'NH_3^+$

Reaction I(a) is the originally desired reaction, the feasibility of which is unknown. The feasibility of the combined reactions I(b) + I(c) was established by a study of the reaction of cyclohexanone oxime with sulfur dioxide and amines. Good yields

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[1] H. H. Sisler and L. F. Audrieth, *Inorganic Syntheses*, Vol. II, W. C. Fernelius, ed., McGraw-Hill Book Co., Inc., New York, 1946, p. 180.

[2] C. E. Boatman and H. H. Sisler, *J. Am. Chem. Soc.*, **73**, 559 (1951).

of alkylammonium sulfamate were obtained along with the Schiff base or the enamine.

An attempt to establish the feasibility of the combined reactions I(b) + I(c) + I(d) was unsuccessful. Addition of sulfur trioxide to the mixture produced by the reaction of sulfur dioxide with cyclohexanone oxime and cyclohexylamine resulted in a very dark mixture from which the only solid isolated and purified was cyclohexylammonium sulfamate. While this experiment does not disprove the feasibility of Scheme I, the likelihood of sulfur trioxide reacting preferentially with the sulfamate in the presence of high concentrations of amines appears doubtful.

Scheme II is presented as a reasonable possibility. Other schemes involving similar reaction steps, but in different sequence, can also be written. The failure of a tertiary nitroparaffin to yield an imidodisulfonate is to be expected on the basis of any of the reaction schemes considered. The fact that tertiary alkylamines failed to yield imidodisulfonates may be due to steric prevention of one of the C = N addition reactions required in all the schemes considered.

EXPERIMENTAL[3]

Bis(cyclohexylammonium) imidodisulfonate. (a) *From nitrocyclohexane.* To a well stirred mixture of 65 g. of nitrocyclohexane and 149 g. of cyclohexylamine in 300 ml. of petroleum ether (b.p. 30–60°) was added 65 g. of sulfur dioxide in 1 hr. 45 min. at a temperature of 30–40°. An additional 200 ml. of petroleum ether was added and stirring was continued for 2 hr. 15 min. The solid (*A*) was collected by filtration, washed first with petroleum ether, then with ethyl ether and with acetone to yield 143 g. of crude product. Two recrystallizations from methanol yielded material for analysis, m.p. 234–239°. The reported melting point is 239.2°.[2]

Anal. Calcd. for $C_{12}H_{29}N_3S_2O_6$ (mol. wt. 375.5): C, 38.38; H, 7.78; N, 11.19; S, 17.08. Found: C, 38.84, 38.29; H, 8.14, 7.89; N, 11.03, 10.77; S, 17.63, 18.07.

To the original petroleum ether mother liquor was added 20 g. of anhydrous sodium carbonate. After standing at room temperature overnight, the mixture was filtered and the filtrate was distilled. There was obtained 16.8 g. of product (*B*), b.p. 92–94°/2 mm., n_D^{20} 1.4966.

Anal. Calcd. for *N*-cyclohexylidenecyclohexylamine, $C_{12}H_{21}N$ (mol. wt. 179.3): N, 7.81. Found: N, 8.34. Neut. equiv. (nonaqueous titration), 182.0.

The reported refractive index and boiling point are: n_D^{21} 1.4972, b.p. 117–118°/9 mm.[4]

(b) *From 2-nitropropane.* In a manner essentially similar to (a) there was obtained 101 g. of crude bis(cyclohexylammonium) imidodisulfonate from 250 g. of 2-nitropropane, 62 g. of sulfur dioxide, and 99 g. of cyclohexylamine. No reaction solvent other than the excess 2-nitropropane was used in this instance.

Anal. Found: C, 38.68; H, 7.83; N, 10.93; S, 16.72, 16.80.

Bis(n-butylammonium) imidodisulfonate (I). Bis(*n*-butylammonium) imidodisulfonate was prepared in 50–61% yields by the reaction of a nitroparaffin (250 g. of either 2-nitropropane, 1-nitropropane, or nitrocyclohexane) with *n*-butylamine (73 g.) and sulfur dioxide (51–63 g.) essentially by the procedure described above for the cyclohexylamine derivative. The melting range of the recrystallized products varied from 183–187° to 195–199°. The material appears to be hygroscopic. The lower melting products were obtained under humid conditions. The reported melting point is 204.5°.[2]

Anal. Calcd. for $C_8H_{25}N_3S_2O_6$ (mol. wt. 323.4): C, 29.71; H, 7.79; N, 12.99; S, 19.82. Found: C, 30.16, 29.91; H, 7.99, 8.04; N, 12.94, 13.04; S, 19.75, 19.50. Equivalent weight by nonaqueous titration, 324.9. Infrared spectrum (potassium bromide): principal bands at 3.40 (vs), 6.26 (m), 6.62 (s), 7.17 (s), 7.89 (vs), 8.12 (vs), 9.13 (s), 9.61 (vs), and 11.25 μ (vs).

An authentic sample of bis(*n*-butylammonium) imidodisulfonate was prepared by the reaction of *n*-butylamine with triammonium imidodisulfonate in methanol essentially by the procedure of Boatman and Sisler.[2] The crude product, m.p. 179–184°, was recrystallized from methanol and from ethanol to yield material for analysis, m.p. 186–191°.

Anal. Found: N, 12.90; S, 20.14.

The melting points of the nitroparaffin derived products were not depressed on admixture with this authentic sample of imidodisulfonate. The infrared spectra are identical.

Dimorpholinium imidodisulfonate. (a). A mixture of 65 g. of nitrocyclohexane and 131 g. of morpholine was stirred for 15 min. and then left at room temperature for 1.5 hr. Gaseous sulfur dioxide was added to the stirred mixture at a temperature of 32–42°. After 1 hr. 45 min., benzene[5] (100 ml.) was added to the thick mixture and the sulfur dioxide addition was continued for 15 min. until a total of 60.3 g. had been added. The mixture was stirred at 30° for 15 min., cooled to 20°, and filtered. The gummy filter cake was washed with benzene (100 ml.) and acetone (300 ml.) to yield 158 g. of product m.p. 125–135°. Further washing with acetone (600 ml.) yielded 128 g. of product, m.p. 138–140°. Two recrystallizations from methanol yielded material for analysis, m.p. 155–157°.

Anal. Calcd. for $C_8H_{21}N_3S_2O_8$ (mol. wt. 351): C, 27.34; H, 6.03; N, 11.96; S, 18.25. Found: C, 27.72; H, 6.05; N, 11.94; S, 17.53.

The benzene mother liquor was washed with water, dried with sodium sulfate and distilled to yield 7.7 g. of product, b.p. 110–115.5°/10 mm. This material was redistilled to yield 3.8 g. of product, b.p. 99–102/2 mm.

Anal. Calcd. for *N*-(1-cyclohexenyl)morpholine, $C_{10}H_{17}NO$ (mol. wt. 167.3): N, 8.38. Found: N, 8.93. Neut. equiv. (nonaqueous titration), 171.9.

The reported boiling point of *N*-(1-cyclohexenyl)morpholine is 117–120°/10 mm.[6]

To 1.1 g. of crude enamine in 10 ml. of carbon tetrachloride was added 40 ml. of an approximately 0.7*N* solution of bromine in carbon tetrachloride. The precipitate was collected and washed with 20 ml. of carbon tetrachloride. The dried product melted at 56–58°.

Anal. Found: N, 3.73; Br, 53.99.

The structure of this product has not been established.

(b) In another experiment similar to (a), recrystallized dimorpholinium imidodisulfonate was obtained, m.p. 160–164°.

Anal. Found: C, 27.47, 27.38; H, 6.16, 6.08; N, 11.78; S, 17.94, 17.44, 17.82.

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(3) All melting points were taken on a Fisher-Johns melting point apparatus.

(4) G. Mignonac, *Ann. chim.* [11], **2**, 224 (1934); *Chem. Abstr.*, **29**, 1074 (1935).

(5) Various solvents were investigated for the reaction of nitrocyclohexane with sulfur dioxide and morpholine. In general, the more nonpolar solvents such as cyclohexane, benzene, and ethyl ether gave high yields of solid product but these were quite crude and low melting requiring extensive washing and recrystallization. Methanol and ethanol can be used as reaction media. Relatively low yields of relatively pure imidodisulfonate were obtained readily.

(6) S. Hünig, E. Benzing, and E. Lücke, *Chem. Ber.*, **90**, 2833 (1957).

Reaction of 2-methyl-2-nitropropane with sulfur dioxide and cyclohexylamine. (a) To a well stirred mixture of 52 g. of 2-methyl-2-nitropropane and 50 g. of cyclohexylamine in 250 ml. of petroleum ether (b.p. 30–60°) was added 66 g. of gaseous sulfur dioxide in 2 hr. at a temperature of 30–44°. Stirring was continued for an additional 1.5 hr. The solid was collected by filtration, washed with petroleum ether, and dried in a vacuum desiccator to yield 62 g. of product m.p. 294–>300°. This material is believed to be the crude 1:1 cyclohexylamine–sulfur dioxide reaction product.

Anal. Calcd. for $C_6H_{13}NSO_2$: N, 8.58; S, 19.64. Found: N, 8.25; S, 18.27.

(b) An experiment similar to (a) but using 149 g. of cyclohexylamine, 52 g. of 2-methyl-2-nitropropane, and 66 g. of sulfur dioxide yielded 157.5 g. of crude solid decomposing at 270–294°. This material is believed to be the crude 2:1 cyclohexylamine–sulfur dioxide reaction product.

Anal. Calcd. for $C_{12}H_{26}N_2SO_2$: N, 10.68; S, 12.22. Found: N, 9.75; S, 12.73.

(c) A mixture produced in a manner similar to (a) from 99 g. of cyclohexylamine, 35 g. of 2-methyl-2-nitropropane, and 43 g. of sulfur dioxide in 300 ml. of petroleum ether was cooled and poured onto 500 g. of ice, and the flask was rinsed with 300 ml. of ice water. The layers were separated and the aqueous layer was extracted with 2 × 200 ml. of petroleum ether. The organic layer and the extracts were combined, washed with water, dried with sodium carbonate, and distilled. There was obtained 22.2 g. of material, b.p. 125–126°, assumed to be the starting material, 2-methyl-2-nitropropane, b.p. 127°.[7]

Cyclohexylammonium sulfamate. (a) *From cyclohexanone oxime.* To a well stirred mixture of 113 g. of cyclohexanone oxime and 198 g. of cyclohexylamine in 300 ml. of ether was added 65 g. of sulfur dioxide in 1 hr. 38 min. at a temperature of 44–47°. Stirring at 42–44° was continued for 1.5 hr. The cooled mixture was filtered and the solid was washed with 400 ml. of ether to yield 165 g. of dried product (*A*), m.p. 145–148°. Recrystallization of this material three times from ethanol yielded a product for analysis, m.p. 156–158°.

Anal. Calcd. for $C_6H_{16}N_2SO_3$: N, 14.27; S, 16.33. Found: N, 14.21; S, 16.95. Infrared spectrum (potassium bromide): principal bands at 3.07 (m), 3.43 (s), 3.74 (w), 3.81 (w), 3.90 (w), 3.96 (w), 4.05 (w), 5.00 (m), 6.26 (m), 6.51 (m), 6.72 (m), 6.84 (m), 6.89 (m), 6.93 (m), 7.21 (m), 8.19 (vs), 8.66 (m), 8.90 (s), 9.49 (vs), 9.83 (m), 10.50 (m), and 12.40 μ (s).

The filtrate from *A* was distilled finally at reduced pressure to yield 24.6 g. of product, b.p. 113–116°/9 mm., n_D^{20} 1.4996, neut. equiv., 174.8. The reported boiling point and refractive index of *N*-cyclohexylidenecyclohexylamine are: n_D^{21} 1.4972, b.p. 117–118°/9 mm.[4] The theoretical equivalent weight is 179.3.

(b) *From sulfamic acid.* An authentic sample of cyclohexylammonium sulfamate was prepared by the reaction of cyclohexylamine with sulfamic acid in methanol. The sample for analysis, m.p. 155–158°, was obtained by repeated recrystallizations from methanol. A mixture of this material and the product prepared in (a) melted at 155–158°.

Morpholinium sulfamate. (a) *From cyclohexanone oxime.* To a well stirred mixture of 113 g. of cyclohexanone oxime and 174 g. of morpholine in 300 ml. of ether was added 65 g. of sulfur dioxide in 1 hr. 25 min. at a temperature of 42–46°. Stirring was continued for an additional 0.5 hr. and the cooled mixture was filtered. The solid was washed with ether (400 ml.) and with acetone (800 ml.) to yield 196 g. of product (*A*), m.p. 103–107°. Recrystallization of this material three times from ethanol and once from a mixture of methanol and ethanol yielded material for analysis, m.p. 113–115.5°.

Anal. Calcd. for $C_4H_{12}N_2SO_4$: N, 15.21; S, 17.40. Found: N, 15.09; S, 16.95.

The ether mother liquor from *A* was distilled finally at reduced pressure to yield 46.7 g. of product, b.p. 112–114°/10 mm.

Anal. Calcd. for *N*-(1-cyclohexenyl)morpholine, $C_{10}H_{17}NO$ (mol. wt. 167.3): C, 71.79; H, 10.24; N, 8.37. Found: C, 71.12; H, 10.09; N, 8.55. Neut. equiv. (nonaqueous titration), 166.8.

The reported boiling point of *N*-(1-cyclohexenyl)morpholine is 117–120/10 mm.[6]

(b) *From sulfamic acid.* An authentic sample of morpholinium sulfamate was prepared by the reaction of morpholine with sulfamic acid in methanol. The product was recrystallized from methanol and from ethanol to yield material, m.p. 114–117°.

Anal. Found: N, 15.37; S, 17.01.

Reaction of cyclohexanone oxime with sulfur dioxide, sulfur trioxide, and cyclohexylamine. To a well stirred mixture of 57 g. of cyclohexanone oxime and 149 g. of cyclohexylamine was added 34.7 g. of sulfur dioxide in 1 hr. 20 min. at a temperature of 30–42°. Stirring was continued at 30–40° for 3 hr. Sulfur trioxide (Sulfan "B") was added dropwise to the stirred and cooled (30–42°) mixture until 14.3 g. had been added. The mixture at this point was very viscous and unstirrable. The mixture was cooled and 100 ml. of acetone was added. The solid was collected by filtration, washed with acetone (500 ml.), and dried to yield 131 g. of product, m.p. 117–123°. Recrystallization of this material twice from isopropyl alcohol and twice from ethanol yielded the product, m.p. 150–154°, shown by mixed melting point to be cyclohexylammonium sulfamate. No imidodisulfonate was isolated though its absence has not been proved.

Acknowledgment. The author is indebted to Mr. R. A. Jewell for the infrared determinations.

TERRE HAUTE, IND.

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[7] E. E. Toops, Jr., *J. Phys. Chem.*, **60**, 304 (1956).