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THE CHEMISTRY OF ALIPHATIC NITROSULFONATES. III. HALOGENATED NITROSULFONATES

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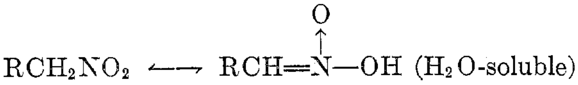
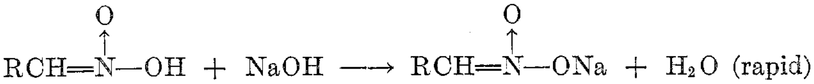
The aliphatic nitrosulfonates (1) offer an interesting opportunity for the study of reactions of aliphatic nitro compounds in a single-phase aqueous system. Heretofore, nitroparaffin reactions with aqueous reagents have always involved two liquid-phase systems. In such cases the reactions are stepwise and involve first, the slow, first order enolization of the nitro group. The aci-form is usually more water-soluble than the non-enolized nitro form and in contact with an aqueous reagent such as a strong base reacts very rapidly. The nitrosulfonates being water-soluble both as the aci-nitro or nitro isomers have an advantage over the nitroparaffins in determining whether it is the nitro or aci-nitro structure which is involved in the reaction.

In the normal reaction of nitroparaffins with the halogens it is quite possible to isolate halogenated nitroparaffins when the halogen and aqueous alkali are added simultaneously to an aqueous suspension of nitroparaffin (2). On the other hand, in this laboratory it was found that the simultaneous addition of alkali and halogen to a solution of an aliphatic nitrosulfonate gives only unchanged starting material plus oxidative degradation products of the nitrosulfonate. In order to obtain the halogenated nitrosulfonate it is first necessary to prepare the aci-nitro salt (3) and then addition of the halogen gives instant formation of the halogenated product. The explanation for the formation of halonitroparaffins when nitroparaffin is contacted simultaneously with base and halogen is shown by the following equations:

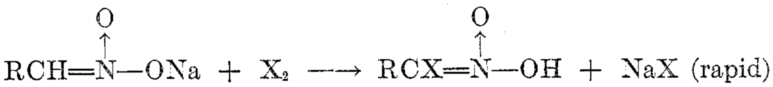
a. $$\mathrm{RCH_2NO_2\ (H_2O\text{-insoluble}) + NaOH + X_2 \longrightarrow \text{no reaction}}$$

b.


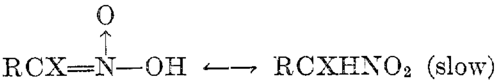
$$\mathrm{RCH_2NO_2 \longleftrightarrow RCH{=}\overset{\substack{O\\ \uparrow}}{N}{-}OH\ (H_2O\text{-soluble})}$$

c.


$$\mathrm{RCH{=}\overset{\substack{O\\ \uparrow}}{N}{-}OH + NaOH \longrightarrow RCH{=}\overset{\substack{O\\ \uparrow}}{N}{-}ONa + H_2O\ (rapid)}$$

d.


$$\mathrm{RCH{=}\overset{\substack{O\\ \uparrow}}{N}{-}ONa + X_2 \longrightarrow RCX{=}\overset{\substack{O\\ \uparrow}}{N}{-}OH + NaX\ (rapid)}$$

e.


$$\mathrm{RCX{=}\overset{\substack{O\\ \uparrow}}{N}{-}OH \longleftrightarrow RCXHNO_2\ (slow)}$$

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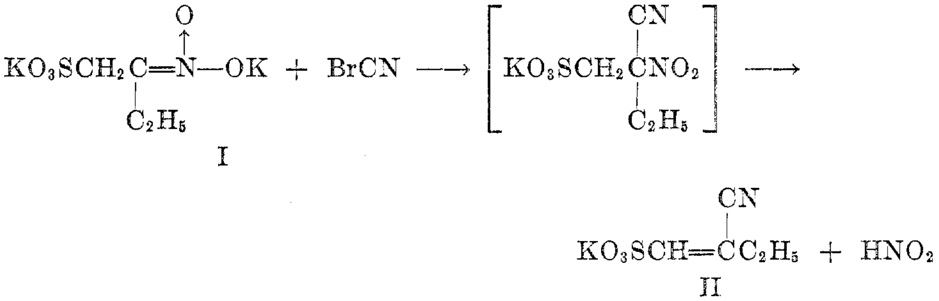
This report describes the addition of chlorine, bromine, and iodine to several aliphatic nitrosulfonates. In addition, bromocyanogen was used as a halogenoid (4) with the intention of introducing the cyano radical in the same manner as a chlorine or bromine. When bromocyanogen was added to the aci-nitro potassium salt of potassium 2-nitrobutane-sulfonate (I) a product was isolated which no longer contained the nitro group. Apparently the presence of a nitro and a cyano group on the same carbon atom creates a highly unstable system. The effect of this is to eliminate the elements of nitrous acid and form the corresponding potassium 2-cyano-1-butene-1-sulfonate (II).



$$KO_3SCH_2\underset{C_2H_5}{C}{=}\overset{\overset{O}{\uparrow}}{N}{-}OK + BrCN \longrightarrow \left[KO_3SCH_2\overset{CN}{\underset{C_2H_5}{C}}NO_2\right] \longrightarrow KO_3SCH{=}\overset{CN}{C}C_2H_5 + HNO_2$$

I

II

EXPERIMENTAL

Potassium 2-nitro-2-bromobutane-1-sulfonate. A well-stirred suspension of 442 g. of potassium 2-nitrobutane-1-sulfonate (1) in 2 l. of water was cooled to 0–5° and 132 g. of 85% potassium hydroxide in 200 ml. of water was added all at once. The nitrosulfonate dissolved and the solution gradually began to drop in *p*H. After 20 minutes the solution was at *p*H 7.5. Then 320 g. of bromine was added over a period of 100 minutes. The bromine was absorbed rapidly and the solution remained at constant *p*H over most of the reaction. Towards the end of the addition the solution was finally down to *p*H 6. As the bromination proceeded a white crystalline precipitate separated from solution. At the end of the reaction a slight excess of bromine was removed with sulfur dioxide. The crystalline product after filtration and air-drying weighed 534 g. (89%). The compound was purified for analysis by recrystallization from aqueous alcohol. It melted with decomposition at 199.5–200° (uncorr.).

Anal. Calc'd for $C_4H_7BrKNO_5S$: K, 13.0; Br, 26.7.
Found: K, 13.5; Br, 27.5.

Potassium 2-nitro-2-iodobutane-1-sulfonate. A solution of the potassium aci-nitro salt of potassium 2-nitrobutane-1-sulfonate was prepared as above. Then an equivalent amount of iodine dissolved in carbon tetrachloride was added to the reaction mixture. The light yellow crystalline product which separated was removed, sucked dry, and washed with ether to remove traces of iodine. The yield was 70% without working up the mother liquors. The compound was purified for analysis by recrystallization from aqueous alcohol; m.p. 156° (uncorr., dec.).

Anal. Calc'd for $C_4H_7IKNO_5S$: K, 11.2; I, 36.6.
Found: K, 11.0; I, 36.4.

Potassium 2-nitro-2-chlorobutane-1-sulfonate. Using the method for the bromo compound, except that chlorine instead of bromine was bubbled into the solution to *p*H 6, a yield of 73.6% was obtained without working up the mother liquors. After recrystallization from water the compound melted with decomposition at 208°.

Anal. Calc'd for $C_4H_7ClKNO_5S$: K, 15.3; Cl, 13.9.
Found: K, 15.2; Cl, 14.1.

Potassium 1-nitro-1-bromo-2-phenylethane-2-sulfonate. A potassium aci-nitro salt of 6.2 g. of potassium 1-nitro-2-phenylethane-2-sulfonate was prepared as described in the first experiment. After stirring 20 minutes the solution was down to *p*H 7.3. To this solution, cooled to 3°, was added 1.28 ml. of bromine over a period of 20 minutes. The white crystalline product which separated was isolated, washed, and dried to yield 6.0 g. (54.8%) of product. No attempt was made to work up the mother liquors. The product was recrystallized from water; m.p. 226–227° (uncorr., dec.).

Anal. Calc'd for $C_8H_7BrKNO_5S$: Br, 23.0; S, 9.2.
Found: Br, 23.0; S, 9.0.

Potassium 1-nitro-1,1-dibromo-2-phenylethane-2-sulfonate. A solution of the enol salt of 2.7 g. of potassium 1-nitro-1-bromo-2-phenylethane-2-sulfonate, prepared above, was effected by dissolving in water and 10.9 ml. of 0.854 *N* potassium hydroxide. The mixture was cooled to 3–5° and stirred 20 minutes to *p*H 7.5. Then 0.40 ml. of bromine was added dropwise and the product separated upon strong cooling and scratching of the sides of the container. Recrystallization from water gave 0.55 g. of white crystals melting with decomposition at 195–195.2° (uncorr.).

Anal. Calc'd for $C_8H_6Br_2KNO_5S$: Br, 37.5; K, 9.1.
Found: Br, 36.2; K, 9.0.

Potassium 2-bromopropane-1-sulfonate. This compound was prepared from potassium 2-nitropropane-1-sulfonate in the same manner as the corresponding butane derivative in 72% yield. Recrystallization from aqueous ethanol gave white crystals melting with decomposition at 211–211.5° (uncorr.).

Anal. Calc'd for $C_3H_5BrKNO_5S$: Br, 28.0; S, 11.2.
Found: Br, 27.2; S, 10.8.

Potassium 1-nitro-1,1-dibromoethane-2-sulfonate. A solution of the aci-nitro salt from 19.3 g. of potassium 1-nitroethane-2-sulfonate in 50 ml. of water prepared by the addition of an equimolecular quantity of potassium hydroxide was cooled to 3–5° and stirred for 25 minutes. The solution was adjusted with a little acid to *p*H 7.0–7.5 and then 16.0 g. of bromine was added dropwise over a period of 15 minutes. The resulting solution was concentrated under reduced pressure and, after cooling, a crystalline product separated. The precipitate, recrystallized several times from water, melted with decomposition at 209–209.5° (uncorr.). The analysis indicates that two atoms of bromine had been substituted in the molecule rather than the one, which had been expected.

Anal. Calc'd for $C_2H_2Br_2KNO_5S$: Br, 45.6; K, 11.1.
Found: Br, 44.3; K, 11.2.

Potassium 2-cyano-1-butane-1-sulfonate. A solution of 55.2 g. of potassium 2-nitrobutane-1-sulfonate, 16.5 g. of 85% potassium hydroxide, and 250 ml. of water was stirred and cooled to 0–5°. After 20 minutes the solution was in the range of *p*H 7–7.5. Then a solution of cyanogen bromide, (prepared by the addition of a cold solution of 17.1 g. of 95% potassium cyanide in 85 ml. of water to 12.8 ml. of bromine in 50 ml. of water) was added dropwise to the reaction mixture. The resulting solution was filtered and concentrated under reduced pressure. Potassium bromide was removed in several crops and then the remaining concentrate was precipitated by pouring into ethanol. The resulting product, after several recrystallizations from alcohol-water mixtures, was light tan in color. It melted with decomposition at 186–191° and indicated its unsaturation by absorption of bromine and reduction of potassium permanganate.

Anal. Calc'd for $C_5H_6KNO_3S$: N, 7.0; S, 16.1.
Found: N, 7.4; S, 15.5.

SUMMARY

The aliphatic nitrosulfonates are halogenated in aqueous solution only after prior conversion to the corresponding aci-nitro salt. Upon addition of cyanogen bromide in a similar manner for the introduction of the cyano group, the carbon

atom is so overloaded with negative groups that the nitro radical is eliminated as nitrous acid.

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REFERENCES

(1) GOLD, *et al.*, *J. Org. Chem.*, **16,** this issue, Paper I.
(2) VANDERBILT, U. S. Patent 2,181,411 (Nov. 28, 1939); TINDALL, U. S. Patent 2,309,806 (Feb. 2, 1943); U. S. Patent 2,365,981 (Dec. 26, 1944).
(3) POLEN, U. S. Patent 2,521,307 (Sept. 5, 1950).
(4) MOUREAU AND DELANGE, *Bull. soc. chim.*, **25,** 99 (1901); MOUREAU AND LOZENNEC, *Compt. rend.*, **142,** 211 (1906); GRIGNARD, BELLET, AND COURTOT, *Ann. chim.*, [9] **4,** 28 (1915).