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THE CHEMISTRY OF ALIPHATIC NITROSULFONATES. IV. COUPLING WITH DIAZONIUM SALTS

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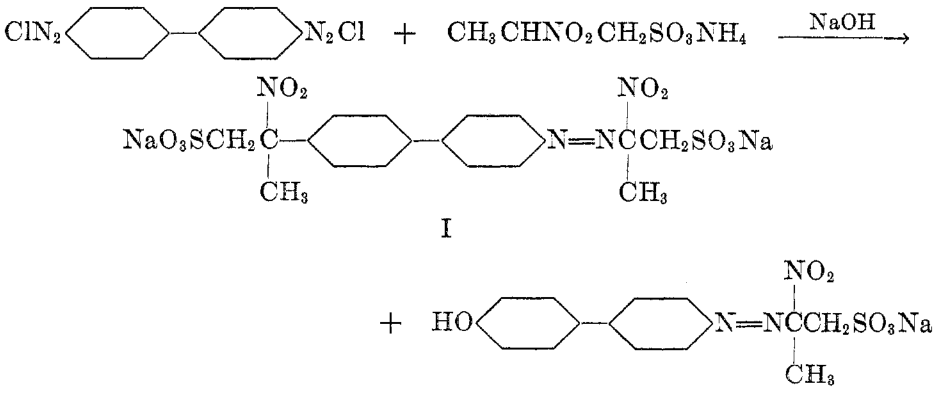
The coupling of nitroparaffins with diazonium salts has been reviewed by Hass and Riley (1) and more recently has been described by Feasley and Degering (2) and by Nygaard, McCracken, and Hamilton (3). The present report deals with similar condensations using the aliphatic nitrosulfonates (4) in place of the nitroparaffins. The products are stable yellow dyes which are usually water-soluble or soluble in aqueous alcohol mixtures (5). They act as direct dyes on protein fibres such as silk and wool and may be precipitated in other materials by means of polybasic amines.

The previous investigators used the sodium salts of the enolized form of the nitroparaffins. Inasmuch as nitrosulfonates are water-soluble, they offered a means of determining whether the reaction in homogeneous solution requires the aci-nitro salt as such, or whether it is primarily for the purpose of producing a soluble reagent. (Such might possibly have been the case in the coupling with nitroparaffins.) Inasmuch as solubility is necessary for reaction in either case, the results of this work indicate that once homogeneity is achieved the coupling reaction must occur through the aci-nitro form. The diazo coupling with the aci-nitro salts of the nitrosulfonates was found to be practically instantaneous by frequent spot tests with β-naphthol on the reaction mixture. This was not the case where the non-enolic nitrosulfonate was used.

Using the normal or non-enolic nitrosulfonate, the coupling was not at all sharp or clear cut. The diazonium compound precipitated considerable self-coupled product. However at higher reaction temperatures where the rate of



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enolization is more rapid, some of the desired product was obtained. The dyes obtained in this way were quite unstable and often decomposed upon drying in a vacuum desiccator. In some cases several other reaction products were obtained. For example: when tetrazotized benzidine was coupled with ammonium 2-nitropropane-1-sulfonate, two compounds were isolated. One of the compounds (I) showed the loss of azo nitrogen with direct coupling of the aromatic nucleus to the nitrosulfonate group. The second product (II) showed the loss of one of the diazonium groups with subsequent replacement by hydroxyl.

Where the aci-nitro salt was used, no such side reactions were noted and the dyes appeared to have much greater stability to heat and light.

EXPERIMENTAL

COUPLING REACTION OF DIAZONIUM COMPOUNDS WITH THE ACI-NITRO NITROSULFONATES

One-tenth mole of the aromatic amine was thoroughly wetted with 200 ml. of water and then converted to the hydrochloride with 50 ml. of concentrated hydrochloric acid. After cooling the resulting solution to 0–5°, the diazotization was carried out by the addition of 0.1 mole of sodium nitrite, either in solution or as the solid salt, depending upon the ease with which the amine self-coupled. During the diazotization, 0.1 mole of potassium 2-nitrobutane-1-sulfonate was converted to the aci-nitro salt by stirring with 0.1 mole potassium hydroxide in about 200–500 ml. of water (At least 20 minutes is required to insure complete enolization and rapid neutralization of the nitro group.) The excess nitrous acid in the diazotization was then destroyed with sulfamic acid and the solution filtered. The filtered diazonium solution was then added rapidly with stirring to the aci-nitro sulfonate solution. Frequent checks on the *p*H of the solution were made and potassium hydroxide was added to maintain *p*H 7–9. Coupling was instantaneous. In most cases the coupled products separated out during the reaction in relatively pure form or else they could be precipitated by the addition of salt. The dyes were then removed and dried in a vacuum desiccator overnight.

Potassium 2-nitro-2-(p-nitrophenylazo)butane-1-sulfonate was prepared in 51.4% yield from the coupling with diazotized *p*-nitroaniline. It explodes at 148°.

Anal. Calc'd for $C_{10}H_{11}KN_4O_7S$: N, 15.1; S, 8.6.
Found: N, 15.4; S, 9.4.

Potassium 2-nitro-2-[1-azo-(4-azophenyl)phenyl]butane-1-sulfonate was prepared in 56% yield from the coupling with diazotized *p*-aminoazobenzene. It melts with decomposition at 123–126°.

Anal. Calc'd for $C_{16}H_{16}KN_5O_5S$: N, 16.3; S, 7.5.
Found: N, 15.9; S, 8.0.

p,p'-Bis-[potassium 2-nitro-2-(azo)butyl-1-sulfonate]m,m'-dimethoxybiphenyl was prepared in 77% yield by the coupling of tetrazotized dianisidine with the potassium enolate of potassium 2-nitrobutane-1-sulfonate. It melted with decomposition at 114–116°.

Anal. Calc'd for $C_{22}H_{26}K_2N_6O_{12}S_2$: S, 9.0; K, 11.2.
Found: S, 9.3; K, 11.5.

COUPLING REACTIONS WITH NON-ENOLIZED NITROSULFONATES

A. Tetrazotized benzidine. A slurry of 9.2 g. of benzidine, 30 ml. of hydrochloric acid, and 200 ml. of water, after cooling to 4°, was tetrazotized with 7.2 g. of sodium nitrite. The excess nitrous acid was removed with sulfamic acid and the solution filtered. The tetrazonium solution was then added at 50° to a solution containing 27.9 g. of ammonium 2-nitropropane-1-sulfonate in 200 ml. of water. The reaction medium was maintained on the alkaline side by additions of sodium hydroxide as required. When the addition and coupling were complete, the product was thrown out of solution by the addition of salt. A gummy precipitate formed which hardened upon cooling to 10°. The material was filtered, dried, and then extracted in a Soxhlet extractor with methanol to separate it from inorganic salts. Concentration of the methanol solution and fractional crystallization gave two products I and II. Fraction I was determined to be disodium 2-{*p*′-[-2-(2-nitropropyl-1-sulfonate)-*p*-azodiphenyl]}-2-nitropropane-1-sulfonate.

Anal. Calc'd for $C_{18}H_{18}N_4Na_2O_{10}S_2$: Na, 8.2; N, 10.0.
Found: Na, 8.2; N, 9.4.

Fraction II was determined to be sodium 2-[*p*-(*p*-hydroxydiphenyl)azo]-2-nitropropane-1-sulfonate.

Anal. Calc'd for $C_{15}H_{14}N_3NaO_6S$: Na, 5.9; N, 10.9.
Found: Na, 6.4; N, 10.9.

SUMMARY

Diazonium salts couple readily with the aci-nitro salts of nitrosulfonates to form stable yellow dyes. When the coupling reaction is carried out with the non-enolized nitrosulfonate, although it may be in alkaline solution, side reactions appear to take precedence and only a small fraction of the desired dye is obtained.

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REFERENCES

(1) HASS AND RILEY, *Chem. Revs.*, **32**, 373 (1943).
(2) FEASLY AND DEGERING, *J. Org. Chem.*, **8**, 12 (1943).
(3) NYGAARD, MCCRACKEN, AND HAMILTON, U. S. Patent 2,392,611 (January 8, 1946).
(4) GOLD, *et al.*, *J. Org. Chem.*, **16**, this issue, Paper I.
(5) GOLD AND LEVINE, U. S. Patent 2,526,218 (October 17, 1950).