$S_3(CS.SC_2H_5)_2 \longrightarrow S_3(C_2H_5)_2$. The intermediate product could be isolated after a short action of a 5% solution of alcoholic ammonia.

A side reaction in the decomposition with alcoholic ammonia resulted in the formation of ethyl mercaptan: $S_x(CS.SC_2H_5)_2 + 4NH_3 = 2C_2H_5SH + H_2S + (x - 1)S + 2NH_4SCN$.

My thanks are due to Dr. P. E. Verkade of the Commercial University in Rotterdam, Holland, for his valuable suggestions.

Summary

The mono-, di-, tri- and tetrasulfides of ethyl formate, ethyl thioformate and ethyl dithioformate have been prepared and some of their reactions studied. The four sulfides show the same reactions in each group. Substitution of sulfur in the terminal groups intensifies the color of each series. Replacement of oxygen by sulfur in the terminal groups stabilizes the polysulfides. For example, the polysulfides of ethyl formate decompose spontaneously into the disulfide; in the ethyl thioformate series the group of sulfur atoms between the terminal groups is destroyed on heating; whereas, under the same conditions in the ethyl dithioformate series this group of sulfur atoms remains intact.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES. VI. 2-AMINO-6-NITRO-PARA-CYMENE AND CERTAIN NEW AZO DYES

BY ALVIN S. WHEELER AND C. R. HARRIS[1]

RECEIVED NOVEMBER 1, 1926 PUBLISHED FEBRUARY 5, 1927

2-Amino-6-nitro-*p*-cymene has not hitherto been described. We obtained it by the partial reduction of 2,6-dinitro-*p*-cymene with ammonium sulfide. This involved considerable study of the nitration of cymene. Kraut[2] first made dinitrocymene by dropping cymene into a mixture of concd. sulfuric and fuming nitric acids. Mazzara[3] prepared it from 3-amino-2,6-dinitro-*p*-cymene by direct substitution of hydrogen for the amino group. In 1916, Aschan[4] studied the nitration of cymene but his method was improved upon by Alfthan.[5] This was similar to Kraut's method but a better yield (38%) was obtained. We tried many variations to better this yield, employing several concentrations of acids and different

---

[1] This paper is an abstract of a thesis submitted by C. R. Harris in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of North Carolina in June, 1926.

[2] Kraut, *Ann.*, **92**, 67 (1854).

[3] Mazzara, *Gazz. chim. ital.*, **20**, 146 (1890).

[4] Aschan, *Finska Kemistsamfundets Medd.*, **25**, 122 (1916).

[5] Alfthan, *Ber.*, **53**, 78 (1920).

temperatures, and also by nitrating nitrocymene. The method adopted was essentially that of Alfthan, but we improved his method of purifying the product.

Constitution of the Dinitro-*p*-cymene

The dinitrocymene obtained in the nitration of cymene has been regarded as the 2,6-dinitro form. Mazzara so regarded it, having obtained it from a dinitrothymol and a bromonitrothymol, in which cases the nitro groups and the bromo and nitro groups were regarded as necessarily in *meta* positions. We have fully established this location of the nitro groups by converting the compound (1) into 2,6-dinitro-*p*-toluic acid and (2) into 2,6-dinitroterephthalic acid. The melting point of the pure 2,6-dinitro-*p*-cymene is 54°.

The Reduction of Dinitrocymene

The partial reduction of dinitrocymene was effected with ammonium sulfide, giving yellow needles of 2-amino-6-nitro-*p*-cymene; m. p., 53°. The hydrochloride, hydrobromide, sulfate and nitrate were found to be unstable in the air but could easily be kept in closed vessels. The acetate and benzoate were prepared and a number of azo and disazo dyes, by coupling the diazotized amine with certain phenols, such as phenol, resorcinol, thymol, carvacrol, 2-naphthol, 1-naphthol-2-sulfonic acid, 1-naphthol-4-sulfonic acid, and 1,8-dihydroxynaphthalene-3,6-disulfonic acid. Suitable conditions were not found for coupling with anisole and *o*- and *p*-nitrophenol. Crystalline compounds were obtained with aniline and 1- and 2-naphthylamine but their study was not completed. The dyes gave very good shades of browns, reds and yellows, the sulfonic acid dyes being particularly rich and brilliant.

The nitro group in the *meta* position acts as a hypsochrome group as shown by the fact that the dye from cymidine and R-salt gives a red color on wool while that from aminonitrocymene gives an orange. The dyes are quite fast under the usual tests, though the acid dyes are not fast to washing and alkali. The colors were named according to Ridgway.[6] The names given to the dyes are based on analogy and not upon any special orientation study.

Experimental Part

Preparation of 2,6-Dinitro-*p*-cymene.—Two hundred g. of cymene was dropped into a mixture of 400 g. of fuming nitric acid (d., 1.52) and 800 g. of sulfuric acid (d., 1.84). The mixture was mechanically stirred and kept below 0°. Four hours was required for the introduction of the cymene. After stirring for an additional hour the reaction mixture was poured over a large quantity of cracked ice. The oily product seemed to solidify and had a melting point of about 20°. After washing free from acid with water and dil. sodium carbonate solution, it was dried on a steam-bath; yield, 290 g. It was then refrigerated overnight, separating into a solid and an oily portion. The

---

[6] Ridgway, "Color Standards and Color Nomenclature," Washington, D. C., 1912.

solid was filtered off and washed with a little alcohol; yield, 190 g. The oily portion was fractionally distilled but no more solid could be separated from it. The solid was dissolved in 700 cc. of hot alcohol, and 68 g. of fairly pure dinitrocymene crystallized on cooling. Upon concentrating the mother liquor, a mixture of dinitrocymene and dinitrotoluene began to crystallize, therefore the alcohol was completely evaporated and the residue dissolved in 100 cc. of carbon tetrachloride. On the addition of 200 cc. of petroleum ether, 34 g. of dinitrotoluene separated out. The filtrate was evaporated to dryness and the residue taken up with 400 cc. of alcohol from which another portion of dinitrocymene was obtained. The process was repeated with the mixed solvents. In this manner the final yield of dinitrocymene was 114 g., and of dinitrotoluene 40 g. There still remained an oily portion which was not investigated. However, during the distillation of the nitration product at 100–105° and 3 mm., we obtained 7 g. of *p*-nitrotoluene which crystallized in the condenser. Two hundred g. of cymene had been nitrated. This product has not hitherto been reported.

Reduction of Dinitrocymene

2-Amino-6-nitro-*p*-cymene, $C_6H_2CH_3NH_2C_3H_7NO_2$.—Five g. of pure dinitrocymene was dissolved in 20 cc. of warm alcohol. On cooling, a portion crystallized; 3 g. of concd. ammonium hydroxide was added and the solution rapidly saturated with hydrogen sulfide. After boiling under a reflux for an hour the solution was cooled and again treated with hydrogen sulfide. It was warmed again, cooled and poured into 500 cc. of cold water. A liquid separated which soon solidified. It was filtered off, washed with water and boiled with 200 cc. of 1 *N* hydrochloric acid. After filtering off some undissolved portion, the hydrochloride crystallized on cooling. The free base was obtained by dissolving 3 g. of the salt in 15 cc. of alcohol and adding 2 g. of ammonium hydroxide. This was poured into 200 cc. of cold water. The yellow crystals which separated were recrystallized by dissolving in 15 cc. of alcohol at 50°, adding 5 cc. of water and cooling the solution with ice. The amine consists of short, bright yellow needles; m. p., 53°. It is very soluble in alcohol, ether and benzene, slightly soluble in petroleum and insoluble in water. As the melting point was only one degree below that of dinitrocymene, the substance was repurified through the hydrochloride and also through the acetate. The melting point remained unchanged. The amine is very stable, remaining unchanged several months, exposed to the air.

Anal. Subs., 0.1878: N_2, 25 cc. (28°, 752.6 mm.). Calcd. for $C_{10}H_{14}O_2N_2$: N, 14.43. Found: 14.39.

HYDROCHLORIDE, $C_{10}H_{14}O_2N_2.HCl$.—This salt obtained in the preparation of the amine consists of fine, fluffy, white needles which turn yellow and melt at 207–208°, though some decomposition is noticeable at 175°. It is hydrolyzed by water and slowly turns yellow in the air.

Anal. Subs., 0.3250: 19.22 cc. of 0.0741 *N* NaOH. Calcd. for $C_{10}H_{15}O_2N_2Cl$: HCl, 15.81. Found: 15.79.

HYDROBROMIDE, $C_{10}H_{14}O_2N_2.HBr$.—The amine was dissolved in warm, 1 *N* hydrobromic acid, the salt crystallizing out on cooling in long, slender, white needles which turn reddish-brown at 210–230°, melt at 233°, are hydrolyzed by water and are unstable in the air.

Anal. Subs., 0.2868: 14.17 cc. of 0.0741 *N* NaOH. Calcd. for $C_{10}H_{15}O_2N_2Br$: HBr, 29.42. Found: 29.63.

SULFATE, $C_{10}H_{14}O_2N_2.H_2SO_4$.—The amine was dissolved in warm, dil. sulfuric acid, the salt crystallizing out on cooling in long, slender, white needles which are unstable in the air and melt to a viscous, orange-colored liquid at 115–140°.

Anal. Subs., 0.2746: 25.7 cc. of 0.0741 *N* NaOH. Calcd. for $C_{10}H_{16}O_6N_2S$: H_2SO_4, 33.56. Found: 34.01.

NITRATE, $C_{10}H_{14}O_2N_2.HNO_3$.—Three g. of the amine was dissolved in 60 cc. of dil. nitric acid. It gave thin, white plates, some rectangular but mostly ill-defined. It softens, turning brown at 155°; m. p., 165°.

Anal. Subs., 0.3068: 16.18 cc. of 0.0741 *N* NaOH. Calcd. for $C_{10}H_{15}O_5N_3$: HNO_3, 24.50. Found: 24.47.

ACETATE, $C_6H_2CH_3C_3H_7NHCOCH_3NO_2$.—Five g. of the amine was refluxed two hours with 10 cc. of acetic anhydride and poured into 300 cc. of cold water. After recrystallizing from 25 cc. of benzene four times, it gave slender, white needles; m. p., 115°; yield, 90%.

Anal. Subs., 0.2008: N_2, 21.2 cc. (23°, 751.9 mm.). Calcd. for $C_{12}H_{16}O_3N_2$: N, 11.86. Found: 11.69.

BENZOATE, $C_6H_2CH_3C_3H_7NHCOC_6H_5NO_2$.—Three g. of the amine was mixed with 30 cc. of 0.5 *N* sodium hydroxide solution and 2 g. of benzoyl chloride and shaken for an hour. After recrystallizing thrice from alcohol it gave very slender needles, insoluble in water, readily soluble in hot alcohol and sparingly soluble in ether; m. p., 179°.

Anal. Subs., 0.2538: N_2, 21.7 cc. (25°, 756.9 mm.). Calcd. for $C_{17}H_{18}O_3N_2$: N, 9.39. Found: 9.45.

The Constitution of Dinitrocymene

2,6-Dinitro-*p*-toluic Acid.—This acid was obtained by boiling 3 g. of dinitrocymene in 50 cc. of fuming nitric acid (d., 1.6) for 48 hours. On pouring the solution into cold water, 2.5 g. of a yellow solid separated. After several recrystallizations from water it melted at 160°, forming fine, nearly white needles which slowly changed to thin plates in water. This corresponds to 2,6-dinitro-*p*-toluic acid, described by Claus and Joachim,[7] who also describe the other three isomers.

2,6-Dinitroterephthalic Acid.—This acid was obtained by boiling 2 g. of dinitrocymene with 200 cc. of fuming nitric acid (d., 1.52) for ten hours at 130° in a sealed tube. The precipitate which formed on pouring the solution into water weighed 0.4 g. and after recrystallizing from water melted at 255°, with decomposition. It crystallized in small octahedrons. This corresponds to the 2,6-dinitroterephthalic acid described by Haeussermann and Martz,[8] who also describe the other two isomers.

Azo Dyes Derived from 2-Amino-6-nitro-*p*-cymene

These dyes were prepared by diazotizing the aminonitrocymene at 0°, adding the phenol dissolved in alkali, precipitating the dye with acetic acid and recrystallizing the product from a suitable solvent.

TABLE I

NEW AZO DYES

No.	Coupler	Solvent	Color of crystals	M. p., °C.
1	Phenol	Hot acetic acid	Claret brown	240
2	Resorcinol	Hot acetone	Nopal red	253
3	Thymol	Hot acetic acid	Chocolate	242
4	Carvacrol	Hot acetic acid	Blue-black	216
5	2-Naphthol	Hot acetic acid	Carmine	251

---

[7] Claus and Joachim, *Ann.*, **266**, 211 (1891).

[8] Haeussermann and Martz, *Ber.*, **26**, 2982 (1893).

TABLE I (*Concluded*)

No.	Coupler	Solvent	Color of crystals	M. p., °C.
6	1-Naphthol-2-sulfonic acid	Hot acetic acid	Grenadine red	243
7	1-Naphthol-4-sulfonic acid	Hot 50% alcohol	Carmine	256
8	1,8-Dihydroxynaphthalene-3,6-disulfonic acid	Ether and alcohol	Purple	Not at 325

TABLE II

NAMES, BASED ON ANALOGY

No.	
1	2,4(6-Nitrocarvacryldisazo)-phenol
2	2,6(6-Nitrocarvacryldisazo)-resorcinol
3	2,6(6-Nitrocarvacryldisazo)-thymol
4	3,5(6-Nitrocarvacryldisazo)-carvacrol
5	1(6-Nitrocarvacrylazo)-2-naphthol
6	4(6-Nitrocarvacrylazo)-1-naphthol-2-sulfonic acid
7	2(6-Nitrocarvacrylazo)-1-naphthol-4-sulfonic acid
8	2,7(6-Nitrocarvacrylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid

TABLE III

ANALYSES

No.	Formula	Subs., g.	N_2, cc.	N calcd., %	N found, %
1	$C_{26}H_{28}O_5N_6$	0.1424	21.4 (22°, 754.8 mm.)	16.67	16.82
2	$C_{26}H_{28}O_6N_6$	.1992	27.6 (18°, 755.5 mm.)	16.15	15.82
3	$C_{30}H_{36}O_5N_6$	.1654	22.6 (22°, 750.8 mm.)	15.00	15.21
4	$C_{30}H_{36}O_5N_6$	.1700	23.3 (22°, 752.7 mm.)	15.00	15.26
5	$C_{20}H_{19}O_3N_3$	.2476	26.4 (23°, 753.9 mm.)	12.03	11.86
			$BaSO_4$, g.	S calcd., %	S found, %
6	$C_{20}H_{19}O_6N_3S$	.1258	0.0668	7.47	7.30
7	$C_{20}H_{19}O_6N_3S$	.1306	.0704	7.47	7.41
8	$C_{30}H_{30}O_{12}N_6S_2$	.2200	.1426	8.78	8.91

TABLE IV

DYEING COLORS

No.	Wool	Silk	Cotton
1	Maize yellow	Empire yellow	Maize yellow
2	Salmon orange	Orange chrome	Salmon orange
3	Yellow ocher	Yellow ocher	Ochraceous buff
4	Deep chrome	Yellow ocher	Ochraceous buff
5	Orange chrome	Orange chrome	Bittersweet orange
6	Flame scarlet	Cadmium orange	Strawberry pink
7	Scarlet	Scarlet	La France pink
8	Bordeaux	Bordeaux	Pale rose purple

TABLE V

BEHAVIOR WITH CONCENTRATED SULFURIC ACID

No.	1	2	3	4	5	6	7	8
Cold	red-brown	brown-red	deep cherry	light cherry	bright crimson	deep violet	cherry-red	deep purple
Hot	dull brown	dark brown	dark brown	light brown	deep brown	dark brown	brown	colorless
Dilute	lemon-yellow	straw color	brown ppt.	brown ppt.	orange	light straw	orange-red ppt.	violet

The dyes were found to be quite fast under the usual tests, exception being made for the sulfonic acid dyes which were not fast to washing and alkali.

Summary

1. The preparation of 2,6-dinitro-*p*-cymene has been improved upon and its nitro groups have been fully established in positions indicated.

2. 2-Amino-6-nitro-*p*-cymene was made by reducing the dinitro compound with ammonium sulfide. It was characterized by its hydrochloride, hydrobromide, sulfate, nitrate, acetate and benzoate.

3. Eight new dyes were made by coupling the amine with the following phenols: phenol, resorcinol, thymol, carvacrol, 2-naphthol, 1-naphthol-2-sulfonic acid, 1-naphthol-4-sulfonic acid and 1,8-dihydroxynaphthalene-3,6-disulfonic acid. Crystalline compounds were also obtained with a few amines.

4. The dyes color textiles reds, browns and yellows. The sulfonic acid dyes are particularly beautiful.

5. A new by-product, *p*-nitrotoluene, was discovered among the nitration products of cymene.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM DYSON-PERRINS LABORATORY, OXFORD UNIVERSITY]

A SYNTHESIS OF SUBSTITUTION DERIVATIVES OF INDIGO

II. ETHYL NITROTRIMETHYLGALLYL ACETATE AND RELATED COMPOUNDS

BY CALVIN J. OVERMYER

RECEIVED NOVEMBER 2, 1926 PUBLISHED FEBRUARY 5, 1927

Further application of the synthesis previously described[1] was made in the attempted formation of a hexamethoxy indigo, using gallic acid as the starting point. This hydroxy acid was methylated by a process which offers advantages over those employed by Will,[2] Graebe and Martz[3] and Perkin and Weizmann.[4]

Harding[5] secured nitrotrimethylgallic acid in small yield by the nitration of trimethylgallic acid directly, 5-nitrotrimethylpyrogallol (I) being the chief product of the reaction. That the nitro group replaced the carboxyl group directly was shown by the fact that no trimethylpyrogallol (II) with its attendant 3,5-dimethoxy-*p*-benzoquinone (III) was formed, a

---

[1] Overmyer, THIS JOURNAL, **48**, 454 (1926).

[2] Will, *Ber.*, **21**, 2022 (1888).

[3] Graebe and Martz, *Ann.*, **340**, 219 (1905).

[4] Perkin and Weizmann, *Trans. Chem. Soc.*, **89**, 1655 (1906).

[5] Harding, *ibid.*, **99**, 1586 (1911).