m. p. above 300°. It is easily dissolved by ammonium hydroxide or concd. sulfuric acid, producing on warming with the latter a bluish fluorescence. Hydrogen sulfide is set free rapidly on heating the substance suspended in glacial acetic acid with phenylhydrazine.

1 - (*p* - Tolyl - 2,4 - dioxo - 5 - carboxy - 6 - sulfopiperidyl)-5-methylbenzothiazole.—IV dissolved quickly in cold ammonium hydroxide, a solution which was slowly run into a large volume of water containing an excess of hydrochloric acid. A bright yellow gelatinous precipitate formed. It was filtered with difficulty, washed thoroughly and dried at room temperature. The color darkened considerably, m. p. 260–261° with dec. and foaming.

Anal. Calcd. for $C_{21}H_{16}N_2O_4S_2$: C, 59.4; H, 3.8. Found: C, 59.4; H, 3.7.

The new substance is soluble in sodium carbonate solution.

1 - (*p* - Tolyl - 2,4 - dioxo - 5 - carbethoxy - 6 - sulfomethoxypiperidyl) - 5 - methylbenzothiazole.—On shaking an ammonia solution of IV with alcohol containing methyl iodide a precipitate quickly formed. The mixture, concentrated to a small volume by distillation, gave a quantitative yield of the product which was recrystallized from a large volume of alcohol. Pale yellow needles separated, m. p. 282–283°, dec.

Anal. Calcd. for $C_{24}H_{22}N_2O_4S_2$: C, 61.8; H, 4.7. Found: C, 61.7; H, 4.8.

The methyl derivative does not react with bromine or phenylhydrazine. On destructive distillation the gases blacken lead acetate paper and have a strong pyridine odor. It still is soluble in ammonia, but this is due to hydrolysis of the carbethoxy group, as an analysis of the product indicated. The product was isolated by precipitation with acid as a semi-gelatinous solid which did not discolor on standing, m. p. 260–261°, dec. The same substance was obtained by the action of concd. nitric acid or warm sulfuric acid.

Summary

It has been shown that ethyl acetonedicarboxylate reacts with one or two equivalents of *p*-tolyl isothiocyanate forming pyridones, which are soluble in alkali and are readily alkylated. An oxypiperidyl benzothiazole apparently results from the action of bromine on the pyridone containing a thioamide group.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Aromatic Amines and 3-Nitro-6-bromonitrostyrene

BY DAVID E. WORRALL AND JACK FINKEL

It has been shown previously[1] that while the additive capacity of nitrostyrene toward the so-called organic bases is comparatively weak and even more so as a rule when substituents are introduced, the nitration of 2-chloronitrostyrene produced an unsaturated compound in which this reactivity is somewhat strengthened. As we wished to determine whether its effect were general, the corresponding bromostyrene has been prepared. The two substances have almost identical chemical properties.

Experimental

α-Nitro-β-(2-bromophenyl)-ethylene (I).—This compound was obtained by the action of triethylamine[2] on bromobenzaldehyde[3] and nitromethane at 25 to 30°; yield, after steam distillation, approx. 60%. It crystallized from ligroin in bundles of yellow needles, m. p. 84°.

Anal. Calcd. for $C_8H_6BrNO_2$: C, 42.1; H, 2.6. Found: C, 42.1; H, 2.8.

α-Nitro-β-(6-bromo-3-nitrophenyl)-ethylene (II).—The product from the nitration of I, using fuming nitric acid, separated from alcohol as small pale yellow needles, m. p. 144–145°.

Anal. Calcd. for $C_8H_5BrN_2O_4$: C, 35.2; H, 1.8. Found: C, 35.1; H, 2.1.

A small portion on oxidation with potassium permanganate produced a substance that crystallized from water as long needles, m. p. 178–179°. It did not depress the melting point of an authentic sample of 6-bromo-3-nitrobenzoic acid prepared from *m*-nitrotoluene, thus indicating that the nitro group is para to the halogen.[4]

α - Bromo - α - nitro - β -(6- bromo - 3 - nitrophenyl) - ethylene (III).—Five grams of II after bromination was mixed with warm alcoholic potassium acetate. The product crystallized from alcohol in yellow needles, m. p. 146–147°.

Anal. Calcd. for $C_8H_4Br_2N_2O_4$: C, 27.3; H, 1.1. Found: C, 27.6; H, 1.3.

The corresponding chlorine derivative was obtained as yellow needles, m. p. 140–141°.

N,N′-(α,α′-Di-(2-bromophenyl)-β,β′-dinitrodiethyl)-*p*-phenylenediamine.—A small portion of I dissolved in hot alcohol was mixed with one-half the equivalent amount of the base. The yellow crystals were washed with warm alcohol, m. p. 146–147°.

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(1) Worrall, THIS JOURNAL, **60**, 2845 (1938).

(2) Worrall, *ibid.*, **56**, 1556 (1934).

(3) Adams and Vollweiler, *ibid.*, **40**, 1737 (1918).

(4) Since the corresponding chlorine derivative must contain a similar arrangement of groups, the name previously assigned to it (ref. 1) is incorrect. The substance should be listed as 3-nitro-6-chloronitrostyrene and corresponding changes made in the names of the addition products.

TABLE I

β-DERIVATIVES OF α-NITRO-β-(6-BROMO-3-NITROPHENYL)-ETHANE

Substance	Formula	M. p., °C.	Analyses, % Calcd. C	H	Found C	H
o-Toluidino	$C_{15}H_{14}BrN_3O_4$	108–109	47.4	3.7	47.8	3.8
m-Toluidino	$C_{15}H_{14}BrN_3O_4$	103–104	47.4	3.7	47.2	3.6
p-Toluidino	$C_{15}H_{14}BrN_3O_4$	132–133	47.4	3.7	47.4	4.0
o-Anisidino	$C_{15}H_{14}BrN_3O_5$	139–140	45.5	3.5	45.7	3.7
m-Anisidino	$C_{15}H_{14}BrN_3O_5$	159–150	45.5	3.5	45.2	3.5
p-Anisidino	$C_{15}H_{14}BrN_3O_5$	105–106	45.5	3.5	45.7	3.7
p-Phenetidino	$C_{16}H_{16}BrN_3O_5$	134–135	46.9	3.9	47.0	3.9
p-Dimethylaminoanilino	$C_{16}H_{17}BrN_4O_4$	140–141	47.0	4.2	47.2	4.4
Phenylhydrazino	$C_{14}H_{13}BrN_4O_4$	147–148	44.1	3.4	44.3	3.3
DERIVATIVES OF (α,α'-DI-(6-BROMO-3-NITROPHENYL)-β,β'-DINITRO-DIETHYL)						
Ammonia	$C_{16}H_{13}Br_2N_5O_8$	146–147	34.2	2.3	34.7	2.7
p-Phenylenediamine	$C_{22}H_{18}Br_2N_6O_8$	Indefinite	40.5	2.8	40.8	3.1
Benzidine	$C_{28}H_{22}Br_2N_6O_8$	Indefinite	46.0	3.0	45.8	3.5

Anal. Calcd. for $C_{22}H_{20}Br_2N_4O_4$: C, 46.9; H, 3.6. Found: C, 47.0; H, 3.9.

A similar addition product was obtained and analyzed, from III as brown crystals, m. p. indefinite. III, but not II, also formed an addition product with *p*-toluidine, yellow needles, m. p. 103–104°.

The same general procedure previously developed[1] was used in preparing the addition compounds which were obtained usually as yellow needles or narrow plates. The ammonia product was nearly colorless, while the benzidine and phenylenediamine compounds were orange in color.

Summary

3-Nitro-6-bromonitrostyrene has been prepared and also several derivatives. A number of addition products have been obtained with aromatic amines, including *o*- and *m*-anisidine.

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NOTES

The Non-interchange of Elementary Radiosulfur with Carbon Disulfide

BY ROBERT A. COOLEY, DON M. YOST AND EDWIN McMILLAN

Radioactive sulfur (half life eighty to ninety days) finds important application as a tracer in chemical and biochemical investigations,[1] and at some stages in these studies it proves convenient to use carbon disulfide as a solvent for elementary sulfur. In order to be certain that this solvent can be used without danger of loss of the radioactive sulfur, it is necessary to show that there is no interchange between elementary sulfur and carbon disulfide. Judging from the nature and structure of carbon disulfide,[2] any appreciable interchange seems unlikely, but the great solubility of sulfur in carbon disulfide (50.49 g./100 g. carbon disulfide at 25°) suggests the possible rapid reversible formation of complex compounds that might make interchange possible.

The radiosulfur used was formed by bombarding a metal sulfide with 4 Mev. deuterons in the cyclotron at the University of California radiation laboratory. Elementary sulfur was obtained from the metal sulfide by dissolving it in hydrochloric acid and passing the hydrogen sulfide formed into a 1 *N* solution of potassium iodide saturated with iodine. After warming the resulting solution to volatilize the excess iodine, and to coagulate the very fine precipitate, the sulfur was collected as small globules on a sintered glass filter. An appreciable proportion of the sulfur obtained in this manner is in the amorphous (μ) form and is slow to dissolve in carbon disulfide. It has been found by Mr. J. B. Hatcher at this

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[1] Borsook, Keighley, Yost and McMillan, *Science*, **86**, 525 (1937).

[2] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 182.