

TABLE I  
 $\beta$ -DERIVATIVES OF  $\alpha$ -NITRO- $\beta$ -(6-BROMO-3-NITROPHENYL)-ETHANE

Substance	Formula	M. p., °C.	Analyses, %			
			Calcd. C	Calcd. H	Found C	Found H
<i>o</i> -Toluidino	C <sub>15</sub> H <sub>14</sub> BrN <sub>3</sub> O <sub>4</sub>	108-109	47.4	3.7	47.8	3.8
<i>m</i> -Toluidino	C <sub>15</sub> H <sub>14</sub> BrN <sub>3</sub> O <sub>4</sub>	103-104	47.4	3.7	47.2	3.6
<i>p</i> -Toluidino	C <sub>15</sub> H <sub>14</sub> BrN <sub>3</sub> O <sub>4</sub>	132-133	47.4	3.7	47.4	4.0
<i>o</i> -Anisidino	C <sub>15</sub> H <sub>14</sub> BrN <sub>3</sub> O <sub>5</sub>	139-140	45.5	3.5	45.7	3.7
<i>m</i> -Anisidino	C <sub>15</sub> H <sub>14</sub> BrN <sub>3</sub> O <sub>5</sub>	159-150	45.5	3.5	45.2	3.5
<i>p</i> -Anisidino	C <sub>15</sub> H <sub>14</sub> BrN <sub>3</sub> O <sub>5</sub>	105-106	45.5	3.5	45.7	3.7
<i>p</i> -Phenetidino	C <sub>16</sub> H <sub>16</sub> BrN <sub>3</sub> O <sub>5</sub>	134-135	46.9	3.9	47.0	3.9
<i>p</i> -Dimethylaminoanilino	C <sub>16</sub> H <sub>17</sub> BrN <sub>4</sub> O <sub>4</sub>	140-141	47.0	4.2	47.2	4.4
Phenylhydrazino	C <sub>14</sub> H <sub>13</sub> BrN <sub>4</sub> O <sub>4</sub>	147-148	44.1	3.4	44.3	3.3
DERIVATIVES OF ( $\alpha, \alpha'$ -DI-(6-BROMO-3-NITROPHENYL)- $\beta, \beta'$ -DINITRO-DIETHYL)						
Ammonia	C <sub>16</sub> H <sub>18</sub> Br <sub>2</sub> N <sub>6</sub> O <sub>8</sub>	146-147	34.2	2.3	34.7	2.7
<i>p</i> -Phenylenediamine	C <sub>22</sub> H <sub>18</sub> Br <sub>2</sub> N <sub>6</sub> O <sub>8</sub>	Indefinite	40.5	2.8	40.8	3.1
Benzidine	C <sub>28</sub> H <sub>22</sub> Br <sub>2</sub> N <sub>6</sub> O <sub>8</sub>	Indefinite	46.0	3.0	45.8	3.5

Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: 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<sup>1</sup> 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 ben-

zidine 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,<sup>1</sup> 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,<sup>2</sup> 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 ( $\mu$ ) form and is slow to dissolve in carbon disulfide. It has been found by Mr. J. B. Hatcher at this

(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.

Institute that heating the sulfur precipitate in an autoclave is not attended with losses and that it is thereby converted into a readily soluble form.

The exchange experiments were carried out in sealed U-tubes one leg of each containing a solution of about 3 mg. of radiosulfur in 300 mg. of c. p. carbon disulfide. The filled tubes were heated in a thermostat at 100° for forty-two to sixty-eight hours, and after the heating period about one-half of the carbon disulfide was caused to distil into the empty leg of the tube by cooling it with liquid air. The contents of the two legs were subjected to a Carius combustion, and the resulting sulfuric acid was then converted into dry lithium sulfate. Thin layers of the lithium sulfate, all of equal area, about 20 sq. cm., were prepared on metal plates for the measurement of the activity. Lithium rather than the more easily prepared barium sulfate was used in the radioactivity measurements because the barium absorbs the weak (107 Kev. maximum) beta radiation<sup>3</sup> of sulfur more extensively than does lithium. The thickness of the mounted lithium sulfate samples was >0.015 g./sq. cm. and was such that the beta particles from the bottom of a sample could not penetrate to the top and from there reach the electroscopes chamber. This arrangement greatly simplifies the quantitative treatment of the results.

In our current experiments with radiosulfur it has been found possible to make the mounted samples of elementary sulfur by reducing barium sulfate to the sulfide with hydrogen at about 900°. Barium sulfide is then treated in the manner described above for the recovery of the sulfur. The reduction procedure was suggested to us by Professor J. E. Bell of this Institute, and the technique for its use was developed by Mr. J. B. Hatcher. Complete reduction of barium sulfate is not attained if the salt melts.

The activity of the lithium sulfate samples was measured with a lead shielded quartz fiber Lauritsen electroscopes. A thin aluminum foil, 0.15 mg./sq. cm., served as the window on the ionization chamber. The background was about 0.001 div./min. and varied no more than 30% in a two-week period. By taking background readings immediately before and after readings with the samples, the activities of the latter were determined to  $\pm 0.0002$  div./sec. The results, corrected for background, are shown in Table I. The same range of the electroscopes scale was used throughout in determining the effect due to the background and to the samples, and therefore no correction for linearity of scale was required.

TABLE I

RADIOACTIVITY OF DISTILLATES AND RESIDUES FROM HEATED SOLUTIONS OF RADIOSULFUR IN CARBON DISULFIDE

Expt.	Activity in div./sec.	Time soln. heated at 100°, hours
1 Distillate	0.000014	42
Residue	.0095	
2 Distillate	— .00017	48
Residue	.0028	
3 Distillate	.00009	68
Residue	.0102	

(3) W. F. Libby and D. D. Lee, *Phys. Rev.*, **55**, 245 (1939).

It is evident from the results that there is practically no interchange between sulfur and carbon disulfide even at 100°. The extent of any interchange must be less than 2%, that is, it must be less than the experimental error of the activity measurements. It is also clear that carbon disulfide may be used as a solvent for radiosulfur without fear of loss by interchange.

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### Note on the Formation of bis-( $\beta$ -Diethylaminoethyl) Sulfide

BY ELTON S. COOK AND CORNELIUS W. KREKE

In an attempt to prepare  $\beta$ -diethylaminoethyl mercaptan from 1-bromo-2-diethylaminoethane hydrobromide and sodium hydrosulfide in the presence of sodium ethylate, Lischer and Jordan<sup>1</sup> obtained  $\beta, \beta'$ -diethylaminodiethyl disulfide. We have tried to prepare the mercaptan using sodium sulfide and hydrogen sulfide by a method based on that employed by Bennett<sup>2</sup> for the preparation of monothioethylene glycol. We did not obtain the desired mercaptan but isolated *bis*-( $\beta$ -diethylaminoethyl) sulfide.

### Experimental Part

**1-Bromo-2-diethylaminoethane hydrobromide** was prepared by heating redistilled  $\beta$ -diethylaminoethyl alcohol and 66% hydrobromic acid at 135° according to the method of Meyer and Hopff.<sup>3</sup> We found that 40% hydrobromic acid could not be used satisfactorily. The presence of a trace of free bromine greatly facilitated the reaction.

**bis-( $\beta$ -Diethylaminoethyl) Sulfide Dihydrochloride.**—One hundred and fifty grams of sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) was heated to 130° for fifteen minutes and saturated with hydrogen sulfide. The solution was cooled to 60–65°, the passage of hydrogen sulfide being continued during the cooling. Then 10.2 g. of 1-bromo-2-diethylaminoethane hydrobromide was added slowly with stirring and the mixture was kept at 55° for fifteen minutes. The mixture was cooled and extracted immediately three times with 100-cc. portions of ether. The ether solution was dried over anhydrous sodium sulfate, the ether removed, and the dried oily residue was taken up in absolute ether. Dry hydrogen chloride was passed in and the dihydrochloride precipitated readily. It was crystallized from absolute alcohol by the addition of absolute ether:

(1) C. F. Lischer and C. N. Jordan, *THIS JOURNAL*, **59**, 1623 (1937).

(2) G. M. Bennett, *J. Chem. Soc.*, **119**, 418 (1921).

(3) K. H. Meyer and H. Hopff, *Ber.*, **54B**, 2274 (1921).