

Table III. Analyses of Sulfones—C₆H₅SO₂R

R	M.P., °C. ^a	Recrystallization from	Calcd., %			Found, % ^b		
			C	H	S	C	H	S
—(CH ₂) ₁₀ —	72-73	Benzene-hexane	62.56	7.11	15.16	62.17	7.31	14.94
—CH ₂ CH ₂ OCH ₂ CH ₂ —	176.5-180	1,1,1-Trichloroethane-hexane ^c	54.23	5.08	18.07	54.14	4.75	18.06
3,4-Dimethylbenzyl—	93.5-95.5	2-Propanol-water	69.23	6.15	12.31	69.12	6.33	11.89
2-Pyridyl—	87-89	1,1,1-Trichloroethane-hexane ^c	60.27	4.10	14.61	60.28	4.18	14.34

^a Melting points are those of analytical samples, determined with a Mel-Temp heated aluminum block in capillaries, and are corrected.

^b Performed under the direction of L. A. Small in this laboratory. ^c With use of Darco KB carbon.

by means of a rotary evaporator. Extraction of the residue with 25 ml. of hot 1,1,1-trichloroethane and dilution of the extract with hexane gave the analytical sample (Table III). $\nu_{\text{min}}^{\text{KBr}}$ 3050, 2980, 2920, 1580, 1475, 1450, 1420, 1290, 1220, 1140, 1080, 1030, 1000, 930, 775, 742, 683 cm.⁻¹.

3,4-Dimethylbenzyl Phenyl Sulfone. The crude reaction mixture obtained as in Run 10, Table II, was diluted with 50 ml. of water and 20 ml. of 1,1,1-trichloroethane. The lower layer was freed of solvent, and the oil remaining was crystallized from ethyl acetate-hexane and recrystallized as in Table III. $\nu_{\text{min}}^{\text{KBr}}$ 2910, 1445, 1285, 1260, 1240, 1155, 1125, 1083, 885, 795, 775, 750, 735, 707, 685 cm.⁻¹.

2-(Phenylsulfonyl)pyridine. The reactants in methoxyethanol were boiled under reflux for 16 hours. Longer reaction time up to 3 days caused no further apparent change. Extraction of the mixture, after removal of solvent, with 25 ml. of 1,1,1-trichloroethane and dilution with hexane and ethyl acetate gave material which was recrystallized as in Table III. $\nu_{\text{min}}^{\text{KBr}}$ 3080, 1578, 1448, 1427, 1303, 1252, 1162, 1127, 1089, 1071, 990, 785, 777, 758, 744, 733, 706, 680 cm.⁻¹.

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Nitration of 1,3-Dibromobenzene

Synthesis of 1,5-Dibromo-2,4-dinitrobenzene and 1,3-Dibromo-2,4,6-trinitrobenzene

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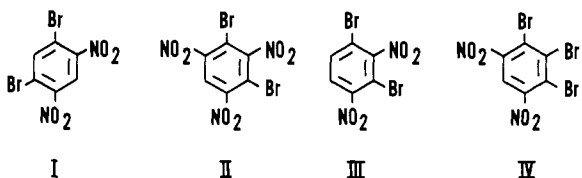
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Nitration of 1,3-dibromobenzene has been effected in mixed acids and in solutions of potassium nitrate in 30% oleum. Simplified procedures for the preparation of 1,3-dibromo-2,4-dinitrobenzene and 1,3-dibromo-2,4,6-trinitrobenzene have been developed. In each case, the yield was 75% or higher, and the products were isolated easily from the reaction mixture.

METHODS for the preparation of 1,5-dibromo-2,4-dinitrobenzene (I) and 1,3-dibromo-2,4,6-trinitrobenzene (II) have either involved time-consuming multistep procedures or produced complex mixtures from which the products have been difficult to isolate. Jackson and Cohoe (3) prepared I by the nitration of 1,3-dibromobenzene in fuming nitric acid and mixtures of fuming nitric and sulfuric acids at elevated temperatures. The yields and detailed description of products were not given. However, Korner and

Contardi (6) found that a similar procedure using fuming nitric acid gave I along with 1,3-dibromo-2,4-dinitrobenzene (III) and two mononitro derivatives. They also reported that I was converted to II when reheated in this medium. Jackson and Earle (4) found that by treating 1,3-dibromo-2,4,6-trinitrobenzene and 1,3,5-tribromo-2,4,6-trinitrobenzene with alcoholic sodium sulfite, they were reduced to I and II, respectively. However, their effort to find a more facile synthesis for II by nitrating I in boiling mixtures of fuming nitric and sulfuric acids was not successful. Along with II, this procedure gave 1,3-dinitro-4,5,6-tribromobenzene (IV) as the main product.

¹ Deceased.



RESULTS AND DISCUSSION

This investigation was undertaken to develop improved synthesis for I and II, and to eliminate the confusion concerning the preparation of these compounds. Simple one-step procedures involving the nitration of 1,3-dibromobenzene have been developed. Attempts to nitrate the parent compound in mixed acids at elevated temperatures resulted in mixtures which were difficult to resolve. However, by using a mixture of 90% nitric and 97% sulfuric acids at temperatures not exceeding 40° C. for one hour, I was easily isolated in yields as high as 76%. The residue remaining after evaporation of the combined mother liquors melted over an extended range, starting at about 60° C., and could not be resolved by fractional crystallization.

In view of the success of Hill and Taylor (2) in converting 1,3,5-tribromo-2,4-dinitrobenzene to the trinitro derivative using potassium nitrate in 30% oleum, this medium was explored in efforts to convert 1,3-dibromobenzene to II. By starting the reaction below 60° C., then heating to 125° C. for 7 to 9 hours, a suitable one-step process was developed. As was the case in the synthesis of I, the residue from the combined mother liquors could not be resolved by fractional crystallization.

The unresolved fractions from both of the above syntheses were examined by thin-layer chromatography, using the method of Yasuda (7), and the mixtures were subsequently resolved by chromatography on columns of metasilicic acid. The residue from I proved to be a mixture of I and III, and that from II was a mixture of II, IV and a very small amount of picryl bromide. The identities of I and IV were established by melting points, elemental analyses, and molecular weight determinations.

The predominance of I over III in the milder nitration procedure is as would be expected, since the 2-position in 1,3-dibromobenzene is hindered by bromines at the two adjacent positions. The relative ease with which both the 4- and 6-positions in the parent compound are nitrated is reflected by the absence of mononitro derivatives among the products.

The so-called bromine migration has often been a problem in the nitration of certain polybromobenzenes. In the nitration of 1,3-dinitro-2,4,6-tribromobenzene in mixed acids, Jackson and Wing (5) found 1,3-dinitro-2,4,5,6-tetrabromobenzene among the products and presented evidence to show that the added bromine for its formation came from the starting material. Hill and Taylor (2) also found this product, and Hill (1) has presented evidence to show that the additional bromine came, at least in part, from 1,3,5-tribromo-2,4,6-trinitrobenzene. During this investigation, samples of pure II were heated at 125° C. for 16 hours in potassium nitrate-oleum mixtures and recovered by drowning in crushed ice. The material recovered was high-purity II, but 20 to 22% had been lost. Near the end of the heating period, brown fumes appeared above the reaction mixture. The formation of silver bromide rather than silver nitrite when these fumes were swept through an aqueous solution of silver nitrate indicated they were bromine, rather than oxides of nitrogen. It therefore appears likely that II is the source of bromine for the formation of IV from I.

EXPERIMENTAL

CAUTION! The compound 1,3-dibromo-2,4,6-trinitrobenzene is explosive in nature and appropriate precautions should be taken in its handling.

1,5-Dibromo-2,4-dinitrobenzene (I). To a stirred mixture of 100 ml. of concentrated sulfuric acid and 100 ml. of 90% nitric acid cooled on an ice bath were added slowly 94.4 grams (0.4 mole) of 1,3-dibromobenzene. The rate of addition was such as to maintain a temperature of 30° to 40° C. Precipitation occurred soon after the addition started. A temperature of 35° to 40° C. was maintained for 40 minutes after the addition was complete, and the reaction mixture was then drowned in an excess of crushed ice. The solids were recovered by filtration through sintered glass, washed with water until the filtrates were neutral, then dried in the oven at 50° C. The crude product, weighing 131.5 grams, was dissolved in a solution containing 400 ml. of absolute ethanol and 85 ml. of acetone, filtered, and cooled in the refrigerator overnight. On filtering, washing with 100 ml. of cold ethanol, and drying at 80° C., the bright yellow crystalline I, m.p. 117–18° C., weighed 80.6 grams. When the filtrate was concentrated to about 300 ml. and cooled in the refrigerator, a second crop of 16.0 grams, m.p. 112–17° C., resulted. A final crop of 5.7 grams, m.p. ca. 104° C., was obtained by concentrating the filtrate from crop 2 to 200 ml. and repeating the isolation process. The second and third crops were dissolved in a minimal amount (ca. 80 ml.) of hot absolute ethanol, and the solution was cooled in the freeze compartment for one hour. On filtering and drying, an additional 18.9 grams of pure I, m.p. 116.5–8° C., were obtained. The total yield of pure I, melting at 116.5–8° C. (lit. 117° C.), was 99.5 grams, 76.4%.

1,3-Dibromo-2,4,6-trinitrobenzene (II). Six hundred grams of reagent grade potassium nitrate were slowly stirred into 1500 ml. of 30% oleum cooled on an ice bath. Two hundred and fifty grams of 1,3-dibromobenzene were added in a steady stream. There was a slight evolution of heat, and the rates of addition and cooling were adjusted so as to keep the temperature below 60° C. When the addition was complete and there was no further evolution of heat, the mixture was heated to 125° C. on an oil bath for 9 hours. After cooling, it was drowned in an excess of crushed ice. The solid phase consisted of a mixture of dense yellow equant crystals (A) and very pale yellow needles (B). The mixture was stirred, the dense product A was allowed to settle, and the supernatant liquor, in which B remained suspended, was decanted and filtered through sintered glass. By adding water and repeating this process several times, a good preliminary separation was effected. Both A and B were washed with water until the filtrates were neutral, and dried. The yields of A and B were 314 and 45 grams, respectively. Product B was dissolved in 500 ml. of boiling carbon tetrachloride and allowed to stand at room temperature for several hours. On filtering, a pale yellow crystalline solid, m.p. 132–34° C., weighing 23.3 grams, was recovered. This was combined with A and dissolved in 1500 ml. of boiling chloroform. The solution was then cooled in the freezer to –20° C. and filtered. The yield was 297 grams (75%) of II, m.p. 136–37° C. (lit. 135° C.).

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