

The 2,4-dinitrophenylhydrazone<sup>4</sup> of the distillate melted initially at 175–180°, but after two recrystallizations from ethyl acetate it melted at 196–197°. The 2,4-DNP prepared from authentic diacetone alcohol exhibited the same melting point behavior. The mixed melting point between the two recrystallized samples was not depressed. A mixed melting point with the 2,4-DNP prepared from I (m.p. 196–197°) was also not depressed.

SHELL DEVELOPMENT CO.  
EMERYVILLE, CALIF.

(4) Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York 1948, p. 143.

## Bromination of Naphthalene with Dioxane Dibromide

ROBERT W. BAYER AND EDWARD J. O'REILLY, JR.

Received August 16, 1957

Yanovskaya<sup>1,2</sup> has reported the quantitative preparation of 1,4-dibromonaphthalene by the reaction of naphthalene with dioxane dibromide in a one to two mole ratio, at 40°. We have attempted this preparation and find that it is neither quantitative nor specific for the 1,4-dibromonaphthalene, 1,5-dibromonaphthalene and 2-bromonaphthalene also being formed.

### EXPERIMENTAL

The bromination was studied varying the temperature and the time of the reaction. In two runs, solutions of the products were analyzed by means of infrared spectrophotometry. The absorption frequencies (in wave numbers) used for analysis are: naphthalene, 782, 955, 1010; 1-bromonaphthalene, 768, 794; 2-bromonaphthalene, 742, 812, 887; 1,4-dibromonaphthalene, 760, 823; 1,5-dibromonaphthalene, 704, 782.

Bromine, 17.0 g. was added to 9.5 g. of dioxane (0.106 moles of dioxane dibromide) in a 100 ml. round-bottom flask. To this solid complex, 6.4 g. (0.05 moles) of naphthalene was added. The reaction began immediately, the mixture turned a deep red, the temperature rose to 39° and HBr fumes were evolved. The mixture was stirred periodically for 3 hr. and some solid formed; it was left standing overnight. After being made basic to litmus with 10% NaOH, white crystals formed and were filtered, washed with water, and recrystallized from 95% ethanol. The yield was 9.9 g. of crude material, (70%) and had a melting point of 77–80°. It contained about 78% of the 1,4-isomer, the balance being the 1,5-isomer with a trace of 1-bromonaphthalene.

The above crude product was recrystallized twice from absolute methanol. The melting point was 83–83.5°. The infrared spectrum showed trace amounts of impurities.

Dioxane dibromide, 24.8 g. (0.1 moles) was added to 6.4 g. of naphthalene (0.05 moles) in a 300 ml., three neck round-bottom flask. Two of the necks were left open so that there was ample room for the HBr to escape. After standing

(1) L. A. Yanovskaya, *Doklady Akad. Nauk SSSR*, **17**, 693 (1950).

(2) A. P. Terent'ev, L. I. Belen'kii, and L. A. Yanovskaya, *Zhur. Obshchei Khim.*, **24**, 1265 (1954).

an hour, the liquid mixture was stirred and maintained at 40° for 6 hr. by means of a water bath. It was then allowed to stand overnight. The reaction mixture was neutralized with 10% NaOH and filtered. A white crystalline residue (7.240 g.) was air dried. It contained about 95% 1,4-dibromonaphthalene, the remainder being the 1,5-isomer and 1-bromonaphthalene. The oil, (3.6068 g.) from the above filtration, was washed with water, and taken up in ether. A qualitative analysis showed it to be mainly 1-bromonaphthalene and 1,4-dibromonaphthalene. There was estimated to be about 10% 1,5-dibromonaphthalene and about 5% 2-bromonaphthalene in the oil.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF NORTH DAKOTA  
GRAND FORKS, N. D.

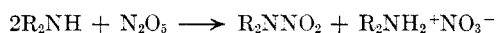
## Nitration of Amines with Dinitrogen Pentoxide<sup>1</sup>

WILLIAM D. EMMONS,<sup>2</sup> ANGELO S. PAGANO,<sup>3</sup>  
AND TRAVIS E. STEVENS<sup>3</sup>

Received August 16, 1957

In spite of the fact that dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>, has been known for many years, its use as an alkaline nitration reagent for amines has not been investigated generally. A number of aromatic amines have been converted to the corresponding nitramines with dinitrogen pentoxide<sup>4,5</sup> but other than a report that triethylamine and dinitrogen pentoxide form an unstable explosive complex,<sup>6</sup> aliphatic amines do not appear to have been investigated.

It has been found that secondary aliphatic amines react smoothly with dinitrogen pentoxide to give secondary nitramines in excellent yields.



The reactions were carried out by addition of dinitrogen pentoxide in carbon tetrachloride solution to excess amine also in carbon tetrachloride at –25°. Yields obtained with a number of amines are summarized in Table I. The yields of nitramines obtained in this way are excellent testimony to the effectiveness of dinitrogen pentoxide for the preparation of secondary nitramines. This is particularly true for the branched secondary amines which gave essentially quantitative conversions to the nitramines; it will be recalled that acetone cyanohydrin nitrate was virtually ineffective with those

(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) Present address: Rohm & Haas Co., Philadelphia, Pa.

(3) To whom inquiries should be addressed.

(4) E. Bamberger, *Ber.*, **27**, 584 (1894); **28**, 397 (1895).

(5) E. Hoff, *Ann.*, **311**, 91 (1900).

(6) L. B. Haines and H. Adkins, *J. Am. Chem. Soc.*, **47**, 1419 (1925).

amines having high steric requirements such as diisopropylamine.<sup>7</sup>

TABLE I

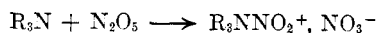
NITRATION OF SECONDARY AMINES WITH DINITROGEN PENTOXIDE

Nitramine	Yield, %	B.P., °C.	$n_D^{20}$
Nitropiperidine <sup>a</sup>	64	120 (20 mm.)	1.4960
Diisopropyl <sup>b</sup>	91	M.p. 105–106°	
Di- <i>n</i> -propyl <sup>c</sup>	84	106–108 (9 mm.)	1.4540
Diisobutyl <sup>d</sup>	97	M.p. 80–82°	
Nitromorpholine <sup>e</sup>	91	M.p. 50–52°	
Diethyl <sup>f</sup>	81	38° (0.05 mm.)	1.4523
Nitropyrrolidine <sup>g</sup>	91	M.p. 58–59°	

<sup>a</sup> Lit. b.p. 62–64° (0.2 mm.),  $n_D^{20}$  1.4968 (ref. 7). <sup>b</sup> G. F. Wright, *et al.*, *Can. J. Research*, 26B, 114 (1948) report m.p. 108–108.5°. <sup>c</sup> Lit. b.p. 90–92° (8 mm.),  $n_D^{20}$  1.4558 (ref. 7). <sup>d</sup> Lit. m.p. 79–80° (ref. 7). <sup>e</sup> Lit. m.p. 51–53° (ref. 7). <sup>f</sup> Lit. b.p. 50–52° (0.2 mm.),  $n_D^{20}$  1.4525. <sup>g</sup> Lit. m.p. 55–57° (ref. 7).

The nitration of primary amines took a somewhat different course. *n*-Octylamine yielded octyl nitrate as the major product isolated. Only a trace of nitramine was formed. No appreciable nitramine was produced from cyclohexylamine or hexylamine and dinitrogen pentoxide. In order to investigate the possibility that primary nitramines are destroyed by dinitrogen pentoxide under these relatively mild reaction conditions (the acid-catalyzed decomposition of primary nitramines is well known),<sup>8</sup> *n*-octylnitramine was allowed to react with dinitrogen pentoxide in carbon tetrachloride at –25° both in the presence and absence of excess *n*-octylamine. In both cases about 55% of the *n*-octylnitramine was recovered. Octyl nitrate and smaller amounts of unidentified products, including a solid material, were obtained. These results suggest that N<sub>2</sub>O<sub>5</sub> will cause the acid-catalyzed decomposition of primary nitramines; however, from the limited amount of experimental data available it cannot be ascertained whether or not the nitramine is a primary product of the reaction.

The reaction of dinitrogen pentoxide with tertiary amines was examined briefly. It was hoped that the reported insoluble complexes formed from a tertiary amine and dinitrogen pentoxide,<sup>6</sup> presumably the nitronium nitrate salt of the amine, would be good alkaline nitration reagents.



It was found, however, that the complexes formed by pyridine, 2-chloropyridine or triethylamine and dinitrogen pentoxide would not nitrate secondary amines.

(7) W. D. Emmons and J. P. Freeman, *J. Am. Chem. Soc.*, 77, 4387 (1955).

(8) J. Barrett, I. N. Denton, and A. H. Lamberton, *J. Chem. Soc.*, 1798 (1953).

## EXPERIMENTAL

*Dinitrogen pentoxide.* For most of the experiments reported here dinitrogen pentoxide was prepared from trifluoroacetic anhydride and absolute nitric acid.<sup>9</sup> The material was recrystallized from carbon tetrachloride–methylene chloride at –50° and dried in a stream of dry nitrogen. The sample was then dissolved in carbon tetrachloride at –10° to 0°, and an aliquot hydrolyzed and titrated with standard base to determine the dinitrogen pentoxide concentration. A more satisfactory procedure for the preparation of larger quantities of dinitrogen pentoxide free of trifluoroacetic anhydride is that given in *Inorganic Syntheses*.<sup>10,11</sup> This method has been outlined elsewhere.<sup>12</sup>

*Nitration of secondary amines.* The yields of secondary nitramines obtained from dinitrogen pentoxide and a secondary amine by the procedure given below for diisopropylnitramine are shown in Table I. A solution of 0.069 mole of dinitrogen pentoxide in 200 ml. of carbon tetrachloride was added over 15 min. to 20 g. (0.2 mole) of diisopropylamine in 150 ml. of carbon tetrachloride cooled to –30°. The reaction was maintained between –30° and –20° throughout the addition by means of a Dry Ice–acetone bath. The solution was allowed to warm to 0°, and the organic layer was then washed with 10% hydrochloric acid solution and water. The organic layer was dried over magnesium sulfate and then evaporated to give 9.2 g. (91%) of diisopropylnitramine, m.p. 100–105°. After recrystallization from aqueous ethanol the sample melted at 105–106°.

*Dinitrogen pentoxide and n-octylamine.* A solution of 38 g. (0.3 mole) of *n*-octylamine in 150 ml. of carbon tetrachloride was cooled to –30°, and 0.070 mole of dinitrogen pentoxide in 200 ml. of carbon tetrachloride was added over 15 min. while the temperature of the reaction mixture was maintained between –20 and –30°. The reaction mixture was allowed to come to room temperature, and then 250 ml. of 10% potassium hydroxide was added and the mixture stirred for 30 min. The aqueous layer was separated, acidified at 0° with 10% sulfuric acid, and extracted with ether. The ether extract was washed with water and dried over magnesium sulfate. Evaporation of the ether left 0.9 g. of a red oil whose infrared spectrum indicated it was mainly *n*-octylnitramine. The carbon tetrachloride solution was washed with 10% hydrochloric acid and water and dried over magnesium sulfate. Evaporation of the carbon tetrachloride left a red oil containing some solid material. After addition of 30 ml. of petroleum ether, the solution was filtered to give 1.5 g. of a white solid, m.p. 89–91°. After recrystallization from ethanol the solid, whose identity has not been established, melted at 90–91°.

*Anal.* Found: C, 72.37, 72.48; H, 12.75, 13.24; N, 8.96, 8.87.

The petroleum ether was removed from the filtrate, and the red oil remaining was distilled through a Holzman column to give forerun, b.p. 82–95° (20 mm.), 1.5 g., and *n*-octyl nitrate, b.p. 96–106° (20 mm.), 4.5 g. (37%),  $n_D^{20}$  1.4284.

*Dinitrogen pentoxide and n-octylnitramine.* A solution of 6.5 g. (0.037 mole) of *n*-octylnitramine in 100 ml. of carbon tetrachloride was treated with 0.040 mole of dinitrogen pentoxide in the manner described above for *n*-octylamine.

(9) J. H. Robson, *J. Am. Chem. Soc.*, 77, 107 (1955).

(10) L. F. Audrieth, *Inorganic Syntheses*, Vol. III, McGraw-Hill Book Company, New York (1950), p. 78.

(11) Although many experiments were carried out using carbon tetrachloride as the solvent for dinitrogen pentoxide, methylene chloride appeared to be the solvent of choice.<sup>12</sup> The greater solubility of dinitrogen pentoxide in the latter solvent allowed one molar solutions to be handled readily.

(12) T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, 79, 6008 (1957).

From the potassium hydroxide extract was recovered 3.5 g. (54%) of *n*-octylnitramine. From the carbon tetrachloride solution was obtained 1.7 g. of liquid whose infrared spectrum showed nitrate ester absorption.

When dinitrogen pentoxide (0.065 mole) was added to a mixture of *n*-octylamine (17.0 g., 0.13 mole) and *n*-octylnitramine (11.5 g., 0.066 mole) in the above manner, there was obtained 6.5 g. of *n*-octylnitramine, 2.2 g. of the unidentified solid, and 7.0 g. of residue whose infrared spectrum indicated it was mainly *n*-octyl nitrate.

**Dinitrogen pentoxide, triethylamine and diisopropylamine.** A solution of 0.070 mole of dinitrogen pentoxide in 200 ml. of carbon tetrachloride was added to 20.2 g. (0.20 mole) of triethylamine in 150 ml. of carbon tetrachloride at  $-30^{\circ}$ . The solution turned red. After complete addition of the dinitrogen pentoxide, 20.2 g. (0.20 mole) of diisopropylamine was added dropwise. The solution was allowed to warm to room temperature and then washed with water, 10% hydrochloric acid, and again with water. After drying over magnesium sulfate, the carbon tetrachloride was removed to leave only 0.2 g. of residue. Similar results were obtained when the dinitrogen pentoxide-triethylamine solution was allowed to warm to  $20^{\circ}$  before addition of the diisopropylamine, and when the dinitrogen pentoxide was added to a triethylamine-diisopropylamine mixture.

**Dinitrogen pentoxide, pyridine and diisopropylamine.** A solution of 3.3 ml. (0.041 mole) of pyridine in 50 ml. of methylene chloride was cooled to  $-20^{\circ}$  and 0.037 mole of dinitrogen pentoxide in 30 ml. of methylene chloride was added dropwise. A white solid precipitated. The mixture was stirred 5 min. at  $-20^{\circ}$  after addition of the dinitrogen pentoxide, and then 11.2 ml. (0.08 mole) of diisopropylamine was added dropwise. The reaction mixture slowly turned a deep red. When the reaction mixture had warmed to  $0^{\circ}$ , 10% hydrochloric acid was added and the organic layer was then separated and washed with water. Evaporation of the methylene chloride left 1.5 g. of a dark residue, the infrared spectrum of which indicated no secondary nitramine was present.

**Dinitrogen pentoxide, 2-chloropyridine and diisopropylamine.** When dinitrogen pentoxide (0.045 mole) in methylene chloride (30 ml.) was added to 2-chloropyridine (0.10 mole) in 60 ml. of methylene chloride at  $-20^{\circ}$  there was a yellowing of the solution but no solid precipitated. Diisopropylamine (0.10 mole) was then added, and the reaction worked up as in the case of pyridine. There was no evidence for the formation of diisopropyl nitramine.

ROHM & HAAS COMPANY  
REDSTONE ARSENAL RESEARCH DIVISION  
HUNTSVILLE, ALA.

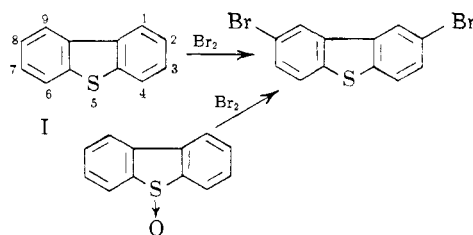
## Bromination in the Thianthrene System

HENRY GILMAN AND DHAIRYASHEEL R. SWAYAMPATI

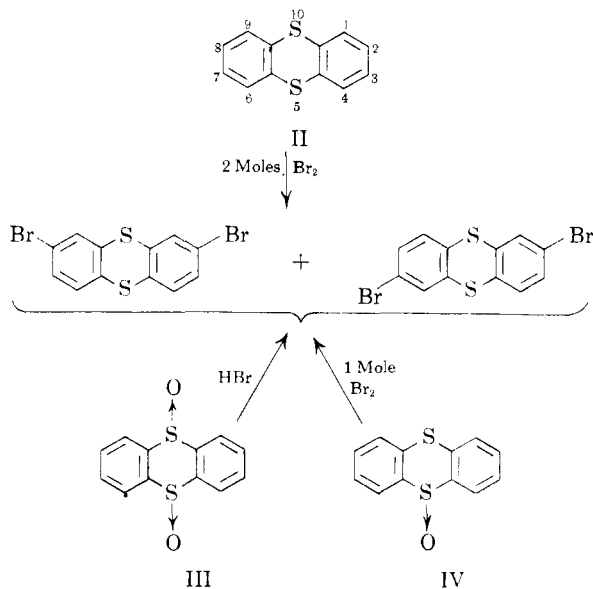
Received August 21, 1957

Successful bromination of heterocycles is of significance in synthetic organic chemistry since the bromo derivatives can be converted to the corresponding carboxylic acids, boronic acids, silanes, amines, and phenols through a halogen-metal interconversion reaction followed by treatment with carbon dioxide, tri-*n*-butyl borate, chlorotriphenylsilane, methoxylamine, and oxygen, respectively. Dibenzothiophene (I) brominates in the 2,8-posi-

tions.<sup>1</sup> The 2,8-dibromodibenzothiophene is also obtained by the action of bromine on dibenzothiophene-5-oxide,<sup>2</sup> a reaction in which the sulfoxide undergoes bromination accompanied by reduction.



Thianthrene (II) reacts<sup>3</sup> with a molar equivalent of bromine to give a fair yield of 2-bromothianthrene, and with two molar equivalents of bromine to give a high yield of a mixture of 2,7- and 2,8-dibromothianthrene. The isomeric mixture was also obtained in high yields by the action of hydrobromic acid on thianthrene-5,10-dioxide (III) and of bromine on thianthrene-5-oxide (IV).<sup>3</sup> The product could not be separated into the two isomers probably due to the very similar physical properties of the two dibromothianthrenes. Oxidation of the mixture with hydrogen peroxide yielded another product which also melted over a wide range after several recrystallizations but gave an analysis corresponding to a dibromothianthrene-5,5,10,10-tetroxide.<sup>3</sup>



In the present investigation we found additional support for considering the dibromothianthrene as a mixture of 2,7- and 2,8-dibromothianthrene. The thianthrene molecule has the 2-, 3-, 7-, and 8-posi-

(1) C. R. Neumoyer and E. D. Amstutz, *J. Am. Chem. Soc.*, **69**, 1920 (1947).

(2) H. Gilman and R. K. Ingham, *J. Am. Chem. Soc.*, **73**, 4982 (1951).

(3) H. Gilman and D. R. Swayampati, *J. Am. Chem. Soc.*, **77**, 5944 (1955).