

The 2,4-dinitrophenylhydrazone⁴ 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.

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(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

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Received August 16, 1957

Yanovskaya^{1,2} 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.

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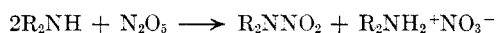
Nitration of Amines with Dinitrogen Pentoxide¹

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Received August 16, 1957

In spite of the fact that dinitrogen pentoxide, N₂O₅, 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^{4,5} but other than a report that triethylamine and dinitrogen pentoxide form an unstable explosive complex,⁶ 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.

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(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).