[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTION OF CERTAIN ORGANIC COMPOUNDS WITH NITROGEN PENTOXIDE

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Apparently less attention has been paid to the behavior of nitrogen pentoxide with organic compounds than has been the case with the other oxides of nitrogen. Lothar Meyer,[1] Hoff,[2] Gibson[3] and Demjanow[4] have reported on the reactions of nitrogen pentoxide with various organic compounds. However, prior to 1913, nitrogen pentoxide was described as melting at 30° and boiling at 45–50°. Russ and Pokorny[5] showed that the pure compound had neither a melting point nor boiling point. Daniels[6] pointed out that the pure compound would have a vapor pressure of 760 mm. at 365°. The investigation described in this paper was inspired by Professor Daniels' interest in the reaction of nitrogen pentoxide.

Benzene and nitrogen pentoxide reacted almost instantaneously at 0°, one molecule of nitric acid being produced for every molecule of benzene nitrated. The reaction was almost quantitative, even in a very dilute carbon tetrachloride solution. When precautions were taken to prevent the rise of temperature of the reaction mixture no dinitrobenzene was formed. Apparently, a 0.1% solution of nitrogen pentoxide will not nitrate nitrobenzene even at room temperature. Equimolecular amounts of nitrobenzene and nitrogen pentoxide cooled to 0° reacted violently with the formation of *m*-dinitrobenzene and a considerable decomposition of the pentoxide due to the heat evolved in the reaction.

m-Dinitrobenzene could not be titrated to trinitrobenzene even at 76°. Lothar Meyer obtained trinitrobenzene at 160° by using sulfuric acid as a solvent. It is questionable whether under such conditions one is justified in assuming that the pentoxide accomplished the nitration without aid from the sulfuric acid.

Bromobenzene in a carbon tetrachloride solution was rapidly nitrated by a similar solution of nitrogen pentoxide at 0°. *p*-Bromonitrobenzene was apparently the only product. Nitric acid, of course, gives some of the *ortho* compound as well as the *para*.

Toluene upon nitration in a similar manner with nitrogen pentoxide

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[1] Meyer, *Ber.*, **22,** 23 (1889).

[2] Hoff, *Ann.*, **311,** 92 (1900).

[3] Gibson, *Proc. Roy. Soc. Edin.*, **28,** 96, 705 (1908).

[4] Demjanow, *Ann. l'Inst. Agronomique Moscow,* **4,** 155 (1898); *Chem. Centr.*, **70,** (1) 1064 (1899).

[5] Russ and Pokorny, *Monatsh.*, **34,** 1051 (1913).

[6] Daniels and Bright, THIS JOURNAL, **42,** 1131 (1920).

gave a mixture of nitrotoluenes, boiling at 228° (corr.). Benzoic acid could not be nitrated with nitrogen pentoxide. Phenol was readily nitrated to give picric acid. *n*-Heptane reacted rather rapidly with nitrogen pentoxide. The products of reaction after being freed of acids and dried, decomposed when an attempt was made to distil them at atmospheric pressure. A small amount of material boiling at 130–180° (25 mm.) was obtained, but most of the nitrated product could not be vaporized without decomposition.

Nitrogen pentoxide formed an addition compound with pyridine without the formation of any nitropyridines. The addition product was insoluble in carbon tetrachloride. When it was heated for a short time and the mixture poured into water, the pyridine could be recovered unchanged. Triethylamine was used with the pentoxide in attempting to obtain a more readily characterized addition product. The latter reaction was very violent, and even with the utmost precautions three small explosions took place. The only product of reaction was apparently triethylamine nitrate. Apparently, some of the amine had been oxidized with the formation of water which permitted the formation of the nitrate.

The results noted above are somewhat sketchy. The reason for this lies in the fact that on the night of December 8, 1922, the combustible equipment of the room in which this work was being carried out was destroyed by fire. The fire apparently originated in the desk in which the experimental materials were stored. In taking up the work again, attention was directed towards the behavior of the alkenes with nitrogen pentoxide. The fire hazard involved in this work is indicated by the fact that at a later time a reaction product of moist ethylene and nitrogen pentoxide burst into flame while partly covered with carbon tetrachloride. A mixture of pentenes reacted with solid nitrogen pentoxide with the production of a flame so hot that platinum was melted.

Ethylene.—Ethylene was prepared by the dehydration of ethanol over alumina.

In the earlier experiments the ethylene was passed from a storage bottle through a tube 25 mm. in diameter and 90 mm. in length, filled with calcium chloride. The nitrogen pentoxide was dissolved in carbon tetrachloride and the solution kept at 0°. The ethylene under a pressure of 750 mm. of water was kept over the pentoxide solution. The stopper was occasionally removed from the saturation flask in order to permit the escape of any gaseous products. The reaction was allowed to proceed for about 18 hours. Thirty g. of oil was obtained by combining the products of three experiments in which a total of 112 g. of nitrogen pentoxide had been used. The oil was fractionated under a pressure of 20 mm. according to Wieland's method. The bulk of the material boiled at 106–110° (20 mm.). It was insoluble in water and alkali and gave a nitrate test with diphenylamine acid reagent. These properties agree with those given by Wieland for the dinitrate.

Anal. Calcd. for $C_2H_4N_2O_6$: N_2, 18.4. Found (Dumas method): 17.85.

The preceding work was not entirely satisfactory and was repeated with great care and a more elaborate apparatus. The ethylene was prepared by passing alcohol vapor over an alumina catalyst heated to 450°. It was then thoroughly chilled at —10° in long, spiral condensers to remove all unchanged alcohol and other liquefiable impurities. The purification was completed in two tubes each 125 cm. long and 15 mm. in diameter. The first tube contained about 30 cm. of soda lime; the rest of the first tube and all of the second was filled with anhydrous calcium chloride. The ethylene was then cooled by passing it through a coil in an ice-salt mixture and bubbled into the reaction flask. Ethylene produced by this method was shown by analysis to be of a greater purity than 99% by volume. The impurities were nitrogen, hydrogen and methane, which should not seriously interfere in this case provided their volume is not too great.

Fifty g. of nitrogen pentoxide was placed in the holder and 150 cc. of carbon tetrachloride in the reaction tube. The cooling bath was prepared with calcium chloride hexahydrate and ice to give an effective temperature of —29° and the gas was bubbled through. Nitrogen pentoxide was occasionally added in small amounts but no apparent reaction occurred. The bath was, therefore, allowed to warm up to —4°, whereupon there seemed to be a slight liberation of heat. Mixing was continued at such a rate that the process was completed in about five hours. The waste gases at all times carried a considerable amount of nitrogen dioxide and possessed the characteristic odor of nitrogen pentoxide. When the brown color had disappeared from the issuing gas, the reaction was assumed to be complete.

The reaction mixture was treated with specially dried 100-mesh sodium bicarbonate until active effervescence ceased. The solid was then filtered off from the still ice-cold solution and washed several times with dry carbon tetrachloride. When the brown of the reaction mixture had all been removed the product was covered with a watch glass and left to drain. In a few minutes, this solid, still moist with carbon tetrachloride, suddenly ignited and burned like gunpowder, leaving a blackened mass of sodium carbonate. The solvent after this purification was distilled with the result that only about 2 cc. of oil was obtained. The possibility of a mixed distillate was considered, but 20% sodium hydroxide did not extract any material from the distillate. It is evident that very little reaction had taken place.

In another experiment the conditions were much the same as before, 30 g. of nitrogen pentoxide and 150 cc. of carbon tetrachloride being employed. The temperature was kept at 0° and a slow stream of ethylene passed in for six hours, at the end of which time the nitrogen pentoxide had disappeared. In order to avoid the use of basic substances and water, the solvent was distilled at about 30° under 20 mm., leaving about 1 cc. of oil.

The reaction was then tried without a solvent. Especially dry nitrogen pentoxide was dropped into the test-tube in small portions, while the temperature was maintained at about 10° and a continuous stream of ethylene was introduced. (An apparatus was devised that made it possible to drop in crystals of nitrogen pentoxide slowly so that they were never in contact with moist air.) The principal effect seemed to be a distillation of the nitrogen pentoxide since it could be detected in the issuing gases. From 20 g. of nitrogen pentoxide about 3 cc. of product was obtained, nearly all of which was soluble in dilute sodium hydroxide.

Demjanow believed that he obtained glycol dinitrate when he treated a cooled carbon tetrachloride solution of nitrogen pentoxide with ethylene. In our earlier experiments low yields of glycol dinitrate were also obtained, but later when the ethylene was more rigorously dried no such reaction was observed. It appears that the formation of glycol dinitrate in these experiments was due to reaction of water vapor on the pentoxide with the formation of nitric acid which then reacted with the ethylene to give the nitrate. This latter reaction has been demonstrated by Wieland to take place when ethylene, nitric acid and oleum are brought in contact.[7]

Stilbene reacted readily with nitrogen pentoxide, but the brown, sticky, plastic reaction products (which contained over 16% of nitrogen), could not be purified by use of solvents, crystallization or distillation.

The products obtained with the alkenes described below, are in general very difficult to handle. The vapors from these compounds, like those from other organic di- and trinitrates, exert a pronounced effect on the heart, was manifested by pounding at the temples, dizziness and finally severe headaches. This action was noted especially with glycol dinitrate but it was also apparent with the other products. The effect was felt by several in the Laboratory. The dinitrates are also very unstable so that distillation is impossible unless it can be accomplished at a fairly low temperature. This unstable character makes the compounds somewhat dangerous, since they are exploded by sudden heating. They are viscous oils from which crystals show little tendency to separate. Reduction experiments were singularly ineffective, due apparently to the presence of dinitrates.

Tetrachloro-ethylene.—In general two parts of nitrogen pentoxide were dissolved in three parts of the alkene. The nitrogen pentoxide first dissolved in the tetrachloro-ethylene, taking up so much heat that ice froze to the test-tube. No sign of reaction could be observed for an interval of as long as six hours provided the tube was kept cold. If at any time the tube was allowed to warm to approximately room temperature, a violent reaction began, resulting in the production of brown fumes and the liberation of a great deal of heat.

Two different methods of treatment were employed in working up the products of this reaction. The first three lots were washed several times with water to remove acid and then distilled. During the washing, the liquid took on a bright blue color and carbon dioxide was evolved. Frac-

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[7] Wieland, *Ber.*, **53B**, 201 (1920).

tional distillation of the remaining liquid after the gas reaction had ceased did not give any definite fractions.

The product from another experiment was distilled under about 20 mm. pressure and the portion coming over between 40° and 45° was considered to contain the compounds formed since the rest distilled at about 48°, which is the boiling point of tetrachloro-ethylene under this pressure. The higher-boiling portion was set aside, and employed for further work. It did not show much if any reaction with water while the lower fraction gave off gas vigorously and turned a bright blue, apparently containing oxalyl chloride. Five cc. of this lower fraction weighing 9.051 grams was hydrolyzed and produced 0.871 g. of carbon dioxide and 0.953 g. of hydrogen chloride. No nitrogenous compound was found in this mixture.

Two nitrations were carried out in carbon tetrachloride, and ammonia was later bubbled into saturation. Trichloro-acetamide, ammonium nitrate, ammonium chloride and oxamide were the only products. Besson[8] found that when tetrachloro-ethylene was treated with ozone, carbonyl chloride and trichloro-acetyl chloride were formed and Biltz[9] noted that a mixture of nitric and sulfuric acids produced the latter compound from tetrachloro-ethylene. It would appear, then, that nitrogen pentoxide did not form a stable addition product with tetrachloro-ethylene but oxidized it.

Cyclohexene.—The general procedure used with this compound was as follows. Forty g. of the cyclohexene was diluted with 150 cc. of anhydrous ether or carbon tetrachloride, and the solution stirred and cooled; 40 g. of solid nitrogen pentoxide was then slowly dropped into the solution by means of the device used for dropping the pentoxide into ethylene. The reaction did not proceed between —40° and —80°. It went rather smoothly at from —30° to 0°, when the pentoxide was dropped in very slowly. At higher temperatures the reaction went with almost explosive violence. These conditions were varied many times as to the proportion of reagents and solvents but the above represents a typical procedure. The product was treated in various ways to remove the acid, but usually by washing several times with water. No crystals could be induced to form from such a product within a day or two even by cooling with carbon dioxide snow. The viscous, red liquid was then distilled several times in an attempt to isolate constant-boiling portions. Distillation at ordinary pressures ended in a rapid decomposition at about 150°. Under a pressure of 9 mm. a crude separation into two portions could be effected. A new quantity of crude material was prepared and washed with alkali. It was then fractionally distilled under reduced pressure and gave two portions, one boiling at 89–92° (9 mm.) and the other at 140–144°. The residue in the flask decomposed at about 160° and, indeed, neither product was obtained in a

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[8] Besson, *Compt. rend.*, **118,** 1347 (1894).

[9] Biltz, *ibid.*, **118,** 1347 (1894).

very pure condition even after several distillations. The substance boiling at 89–92° amounted to about 7 cc. and had the following properties. It reacted with sodium ethoxide to form a brown solution and gave a positive nitrate test with diphenylamine reagent. It did not form hydroxylamine on hydrolysis with hydrochloric acid indicating that it was not an oxime. It was soluble in ether, alcohol, acetic acid and benzene, but not appreciably soluble in water or aqueous dilute alkali. It reacted with concd. alkali, giving off heat and turning brown. The nitrogen content could not be checked with a modified Kjeldahl analysis but gave the values: 9.43, 10.44, 9.11 and 9.85%. Neglecting the second value, the average would be 9.46%, which would most nearly check the formula for the nitro alcohol, $C_6H_{10}(NO_2)OH$, since from the formula this should contain 9.65%. Reduction with zinc and acetic acid did not yield a product that could be isolated. The fraction boiling at 140–144° had practically the same properties as the lower-boiling liquid, and by analysis contained 13.18, 13.17% of nitrogen. This would correspond to the dinitrate, which contains 13.6%. Reduction experiments were unsuccessful. The total yield of a nitration was next reduced with tin and concd. hydrochloric acid but no definite products were isolated. The work was repeated with the same lack of success using zinc and acetic acid, and later with iron and acetic acid.

Another nitration was carried out with extreme care. Instead of removing the acid by contact with water, 100-mesh, anhydrous sodium bicarbonate was stirred into the reaction mixture untill all effervescence ceased. It was then separated by filtration and thoroughly washed with carbon tetrachloride. The solid which supposedly was composed of sodium salts was extracted with alcohol but nothing dissolved. Most of the substance was then removed with water and a residue was obtained which was insoluble, or nearly so, in alcohol and ether.

The carbon tetrachloride solution containing the chief products was evaporated under reduced pressure at 40° to a red-brown oil from which 2 to 3 g. of crystals separated in the course of a week. Indeed, even after a month they were still forming very slowly. This compound was purified by washing with a large amount of cold, absolute alcohol and then crystallizing from acetone. An attempt was made to reduce it but no product was isolated. Analysis by Dumas' method showed a content of 15.1 and 15.2% of nitrogen. This value was nearest to that of the nitro-nitrate $C_6H_{10}N_2O_5$ which contains 14.7%. This structure is also indicated by the fact that the hydrolysis product of this ester was apparently previously isolated.

Tetramethyl-ethylene.—The alkene was made from pinacol as described by Thiele.[10] The yield of product boiling at 71–73° was 40% of that cal-

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[10] Thiele, *Ber.*, **27**, 455 (1894).

culated on the basis of the pinacol used. The procedure for the addition of the pentoxide was the same as in the case of cyclohexene.

The reaction took place with about the same visible results as with cyclohexene except that the solution became bright green. The acid formed was removed with dil. alkali and the solvent evaporated under reduced pressure. About 50 cc. of a bright green liquid was obtained. Two-fifths of this sirup was distilled in a small Claisen flask under a pressure of 24 mm. The green compound distilled at from 80–90° and the remaining liquid became orange. Further attempts to distil resulted in a sublimate forming when the oil-bath around the flask had reached 140°, and a sudden decomposition at about 160°.

The remaining three-fifths of the crude product was distilled in much the same manner but without raising the temperature above 120°. The distillate was combined with that obtained before and the whole thrice fractionally distilled. It then boiled at 80–90° (24 mm.) and had lost its green color. The substance that was non-volatile at 120° was sublimed under a pressure of 15 mm. at 120–150°. About a gram of a white solid was obtained. Three fractions were thus obtained; 7 g. of a slightly yellow liquid, one g. of a solid and the remaining brownish liquid.

The yellow liquid boiling at 80–90° was analyzed by the Dumas method and found to contain 13.4% of nitrogen. Among the probable products, the dinitrate most nearly checks this with a value of 13.6%. A reduction with zinc and acetic acid failed to produce pinacol; however, the sample available for this purpose was very small. The white solid was recrystallized several times from alcohol and its melting point taken as 210–211°. Analysis showed 16.55 and 16.64% of nitrogen, while the dinitro compound would have 16.1% of nitrogen. This compound has been prepared[11] by another method and has exactly the same melting point and solubility. The residue did not yield crystals by any of several methods of extraction. Finally, a reduction of the whole residue was attempted but without any success.[12]

Nitrogen Pentoxide.—This was prepared by a modification of Daniels' method.[13]

Nitric acid was first dried by distilling the ordinary "c. p. white fuming" acid from phosphorus pentoxide. About 200 g. of this acid was placed in a 2-liter Pyrex distilling flask, with side arm at right angles to the neck, and about 400 g. of phosphorus pentoxide slowly added, during cooling, until the mass had assumed a pasty consistency. The

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[11] Bewald, *Ber.*, **39**, 1231 (1906).

[12] Demjanow treated tetramethyl-ethylene with impure nitrogen pentoxide and thought that he obtained the nitroso nitrate and dinitrate and the nitro-nitrate. All of these compounds are questioned by the compilers of the 1918 edition of Beilstein. Our only knowledge of Demjanow's work is from the abstract, as the original article in Russian was not available.

[13] Ref. 6, p. 1133.

flask was attached with sealing wax to the first of a train of three wash-bottles sealed together. The first bottle was filled with glass wool sprinkled with phosphorus pentoxide, while the second and third were empty and held in an ice-salt mixture. A slow stream of air dried over sulfuric acid was drawn through the paste and condensing system. The water-bath around the flask was raised to 60–70° and the cooling bath held at from —15° to 0°. As soon as the distillation was completed, the nitrogen pentoxide was dug out of the wash bottle and immediately placed in a glass-stoppered bottle contained in a larger, cold, glass-stoppered bottle containing a shallow layer of sulfuric acid. The larger bottle was then kept in an ice box until the reagent was needed.

This procedure gave a heavy, brittle, slightly yellow solid. Except for traces of nitrogen tetra-oxide it was the same as that used by Daniels. The yield, when conditions were favorable, was about 50% of that calculated on basis of the acid used; 100 g. of the anhydride could be made in half a day provided the anhydrous acid was available.

Summary

Benzene, bromobenzene, toluene, phenol and heptane were rapidly and quantitatively nitrated by nitrogen pentoxide at 0°. Nitrobenzene was nitrated to dinitrobenzene. It was not found possible to nitrate benzoic acid or *m*-dinitrobenzene.

Pyridine formed an addition compound with nitrogen pentoxide, but it was not found possible to obtain a nitropyridine. Triethylamine reacted vigorously with the pentoxide but the only products isolated from the reaction were the result of the oxidation of the ethyl groups. Ethylene dried over soda lime and calcium chloride did not react with nitrogen pentoxide unless the conditions were such as to permit oxidation. Moist ethylene formed glycol dinitrate. Tetrachloro-ethylene did not react except through oxidation, trichloro-acetyl chloride and oxalyl chloride being produced but no organic nitrogen containing compounds.

Both tetramethyl-ethylene and cyclohexene readily added nitrogen pentoxide. The chief products of the reaction were apparently the dinitrates. A dinitro compound, a nitro alcohol and a nitro nitrate were apparently obtained. The limiting conditions for addition and oxidation by nitrogen pentoxide of these compounds have been pointed out, as has also the fact that stilbene adds nitrogen pentoxide. A flame hot enough to melt platinum is produced by the reaction of a mixture of pentenes with nitrogen pentoxide.

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