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THE INTERACTION OF THE AZIDO GROUP
IN ORGANIC COMPOUNDS
WITH ADJACENT FUNCTIONAL GROUPS

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OBJECT

The objectives of this research are the preparation and study of tertiary alkyl azides and of aryl azides in which the azido group is adjacent to formal unsaturation.

SUMMARY

1. 8-Nitro-2-naphthylamine has been prepared and converted to 8-nitro-2-naphthyl azide. The thermal decomposition of this azide is now being investigated.
2. Hexahydrobenzyl and isobutyl azides have been characterized in the form of adducts with bicycloheptadiene or dicyclopentadiene. A by-product of the preparation of hexahydrobenzyl azide is bis(hexahydrobenzyl)urea.
3. Attempts to prepare N-amino derivatives from t-butylurea, cyclohexylurea, t-butylurethane, cyclohexylurethane and p-tolylurea have been successful only with the last compound. The N-amino derivatives were desired as intermediates for the preparation of the corresponding azides.
4. A compound believed to be 1-o-nitrophenyltetrazole has been prepared by the von Braum and Rudolf procedure from o-nitroformanilide. It is intended to convert it to 1-o-azidophenyltetrazole.

EXPERIMENTAL DESCRIPTION

8-NITRO-1-NAPHTHYLAMINE

Using essentially the method of Hodgson and Davey¹, 7 g (0.117 mole) of powdered urea and 14 g of powdered 8-nitro-1-naphthylamine (0.098 mole) were dissolved in that order in 100 ml of concentrated sulfuric acid, contained in an ice bath. A mechanical stirrer was started, and 11 g (0.109 mole) of finely powdered potassium nitrate was added gradually. The mixture was stirred for $1\frac{1}{4}$ hours, poured into 200 g of ice, and filtered. The filtrate was cooled and then neutralized with ice-cold aqueous ammonia. The resulting precipitate was boiled with several portions of 90-100° petroleum ether; the combined extracts were evaporated a little and then cooled to give 3.9 g (21%) of the crude 8-nitro isomer. Recovery of the other isomer from the original precipitate has not been attempted, but it is said by Hodgson and Davey¹ to amount to 8 g (43.3%).

1-AZIDO-8-NITRONAPHTHALENE

Following essentially the method of Forster and Fierz², 0.3 g (0.0016 mole) of 8-nitro-1-naphthylamine was dissolved in a mixture of 8 ml of glacial acetic acid, 2 ml of water, and 1 ml of sulfuric acid at 0°. A solution of 0.17 g (0.0025 mole) of sodium nitrite was added, and after ten minutes the excess HNO₂ was destroyed with sulfamic acid. A solution of 0.17 g (0.0025 mole) of sodium azide was then added. Nitrogen was evolved, and a creamy yellow precipitate appeared. The precipitate was recrystallized from dilute acetone and then from dilute methanol to give 0.25 g (85%) of very pale yellow needles with a melting point of 129-31° dec. They rapidly darkened in diffuse daylight.

DECOMPOSITION OF 8-NITRO-1-NAPHTHYLAZIDE

The azide (0.25 g, 0.0013 mole) was dissolved in about 100 times its weight of resorcinol dimethyl ether, and the solution was heated on a hot plate. When the temperature reached ca. 190°, the yellow solution suddenly turned deep red. After another minute of heating the ether was evap-

¹ H. H. Hodgson and W. Davey, J. Chem. Soc., 348 (1939).

² M. O. Forster and H. E. Fierz, J. Chem. Soc., 91, 1942 (1907).

orated and the residue crystallized from dilute methanol to give a very small amount of black powder, mp 132-137°. Further characterization is being attempted.

1-o-NITROPHENYLTETRAZOLE

Phosphorus pentachloride (7.7 g, 0.037 mole) and 5.3 g (0.032 mole) o-nitroformanilide were heated in 35 ml of benzene for 45 minutes. The benzene solution was decanted, and a small amount was decomposed with water, and evaporated to crystallization. The crystals obtained were starting material.

To the remainder of the benzene solution was added a dry benzene solution of slightly more than the theoretical amount of hydrogen azide. There was a rather vigorous evolution of gas (HCl?), and an immediate precipitate which soon gave way to a small amount of a phase denser than benzene. After standing overnight, the heavy phase was separated and the benzene layer was washed with sodium carbonate solution and then with water. The benzene was evaporated and the residue crystallized three times from dilute methanol to give 0.1 g of stocky yellow needles, with a melting point of 81.5-82.5°. Elementary analysis is pending. If the analysis is correct it is proposed to increase the yield greatly by reacting the PCl₅ and o-nitroformanilide in the dry state, a method which preliminary experiments have shown to be successful.

ISOBUTYL AZIDE-BICYCLOHEPTADIENE ADDUCT

A mixture of 1.50 g (0.015 mole) of isobutyl azide and 0.70 g (0.0076 mole) of bicycloheptadiene was allowed to stand at room temperature for several days. A small amount of methylene chloride was added and sufficient 40-60° petroleum ether to cause precipitation. A yield of 0.16 g (7.3%), mp 186-188°, was obtained; presumably, more could have been obtained from the mother liquors.

This material was recrystallized from the same solvents to give an analytical sample, mp 188-191°.

Analysis Calculated for C₁₅H₂₆N₆: C, 62.02; H, 9.02.

Found^{ML}: C, 62.05, H, 9.18.

HEXAHYDROBENZYL AZIDE

In a 300-ml, three-necked flask, 34.2 g (0.2 mole) of 2-hexahydrobenzylsemicarbazide was triturated with 50 ml of concentrated hydrochloric acid and heated on a steam bath. To the hot suspension was added 50 ml of water, and the flask was cooled to 0°. The solution was stirred mechanically, and a solution of 20.7 g (0.3 mole) of sodium nitrite in 35 ml of water was added dropwise. Stirring was continued for an additional hour, and the solution was made basic and then filtered, to remove a small amount of solid material.

The filtrate was placed in a 1-l. three-necked flask and steam-distilled. The distillate was extracted with ether, and the extracts were dried over calcium chloride. The ether was removed on the aspirator and the residue distilled under vacuum. The entire amount of material distilled at 30-34°/0.15 mm, yielding 14.5 g (48.6%). The distillate gave a very vigorous reaction with concentrated sulfuric acid.

Analysis Calculated for $C_7H_{13}N_3$: C, 60.40; H, 9.41.
 Found^{ML}: C, 60.58; H, 9.64.

The solid material which was filtered from the basic solution was dried, giving 2.62 g of material which began to melt at about 100° over a range of 20°. It was recrystallized from absolute alcohol, giving a sample which was again recrystallized from ethanol before analysis: mp 144-147°.

Analysis Calculated for $C_{15}H_{28}ON_2$: C, 71.38; H, 11.18
 Found^{ML}: C, 71.21; H, 11.41.

This material was sym-dihexahydrobenzylurea and weighed 1.08 g (4.3%).

Upon the addition of water to the mother liquors, a second solid was obtained. This material was recrystallized from ethanol-water to give a yellowish sample, mp 97-98.5°, weighing 1.41 g (3.5%). This material gave a Liebermann nitroso test, and an analysis is pending.

HEXAHYDROBENZYL AZIDE-BICYCLOHEPTADIENE ADDUCT

This material was prepared in 53% yield in the same manner as the isobutyl azide bicycloheptadiene adduct, mp 208-212°.

Analysis Calculated for $C_{21}H_{34}N_6$: C, 68.07; H, 9.37.
 Found^{ML}: C, 68.15; H, 9.37.

HEXAHYDROBENZYL AZIDE-DICYCLOPENTADIENE ADDUCT

In a 50-ml Erlenmeyer flask were placed 5.0 g (0.036 mole) of hexahydrobenzyl azide and 2.38 g (0.018 mole) of dicyclopentadiene with 10 ml of ether. The flask was allowed to stand for several days, after which time the ether was evaporated, and the solid residue was filtered off, washed with petroleum ether, (bp 40-60°), and dried. The white solid weighed 2.30 g (31.2%), mp 108-114°. This material will be submitted for analysis.

sym-DIHEXAHYDROBENZYLUREA

To a stirred suspension of 33.9 g (0.3 mole) of hexahydrobenzylamine and 16.8 g (0.3 mole) of potassium hydroxide in 100 ml of water, was slowly added 17 g (0.15 mole) of phosgene in 100 ml of reagent benzene. A white solid was formed, which was filtered off. The benzene layer was evaporated and a small additional amount of product was obtained.

The yield of white sym-dihexahydrobenzylurea was 21.2 g, (56.2%), mp 117-124°. The product was recrystallized from ethanol-water to obtain fine white platelets, mp 148-150°. A mixed melting point with the sym-dihexahydrobenzylurea obtained from the hexahydrobenzyl azide preparation showed no depression.

p-TOLYLUREA

To 2-l. of water in a 3-l. beaker was added 107 g (1 mole) of p-toluidine dissolved in 100 ml of glacial acetic acid. While the mixture was stirred rapidly, a solution of 81 g (1 mole) of potassium cyanate in 200 ml of water was added. A thick white paste was immediately formed. The beaker was allowed to cool in the refrigerator, and the solid material was filtered off, washed with water, and dried.

The yield of crude p-tolylurea, mp 159-170°, was 135.3 g (90.3%) and the product was not further purified. Reported values of the melting point are 172° (Bougault and Leboucq)³, and 181-182° (Walther and Wlodkowski⁴, and Boivin and Boivin⁵).

³ J. Bougault and J. Leboucq, Bull. Soc. Chim., (4) 47, 602 (1930).

⁴ R. Walther and St. Wlodkowski, J. prakt. Chem., (2) 59, 266 (1899).

⁵ J. L. Boivin and P. A. Boivin, Can. J. Chem., 29, 479 (1951).

N-NITROSO-N-p-TOLYLUREA AND 2-p-TOLYLSEMICARBAZIDE

A modification of the method given by Walther and Wlodkowski⁴ for the preparation of N-nitroso-N-p-tolylurea was employed.

To a solution of 73.5 g (0.49 mole) of p-tolylurea in 100 ml of glacial acetic acid, heated on a steam bath and then cooled to 0°, was added 101 g (1.47 mole) of sodium nitrite, while the mixture was stirred at a rate so that the temperature remained constant. The resulting mixture was filtered, the filtrate poured into water, and the solid material filtered off.

The solid material was taken up in 150 ml of acetic acid and added dropwise to a stirred suspension of 150 g of zinc dust in 500 ml of 50% acetic acid at a rate so that the temperature remained below 20°. After the solution was complete, the solution was heated to 40-50° for one hour, and the excess zinc was filtered from the hot solution.

The clear solution was neutralized to the point where the zinc hydroxide had not yet precipitated, and the solid material was filtered off. The solid was washed with water and dried, yielding 12.5 g of starting material.

The filtrate was made basic and filtered. The solid material was filtered off, washed and dried, yielding 28.5 g (43.5% after correcting for recovered starting material), mp 140-152°.

This material was recrystallized twice from ethanol-water to give the product, mp 147-148.5.

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