with lithium diethylamide might, like the corresponding reaction with *o*-bromodimethylaniline,[2] give some *m*-N,N-dimethyl-N',N'-diethylphenylenediamine.

Experimental

Reaction of *p*-Bromoanisole with Lithium Diethylamide.—The lithium diethylamide was prepared in ether by adding, in a nitrogen atmosphere, 0.2 mole of methyllithium to 0.23 mole of diethylamine. To the stirred, pale cream colored mixture which gave a negative color test I[3] was added 0.2 mole of *p*-bromoanisole in 50 cc. of ether. Reaction set in at once and the mixture gradually assumed a red color. After stirring and refluxing for twenty-four hours, the mixture was hydrolyzed by water. Fractionation of the dried ether extracts gave in addition to a recovery of 9.3 g. (25%) of *p*-bromoanisole, 12.2 g. of a mixture of *m*- and *p*-methoxydiethylanilines which is a 34% yield (or 45% based on the *p*-bromoanisole actually used up). The picrate, prepared in 95% ethanol, melted at 142.5–143.5°. An authentic specimen of the picrate of *m*-methoxydiethylaniline melted at 145–146°, and the mixed melting point was 143.5–144.5°.

Anal. Calcd. for $C_{17}H_{20}O_8N_4$: N, 13.7. Found: N, 13.7.

From a second experiment starting with 0.5 mole of *p*-bromoanisole, there were isolated as picrates both the *m*-methoxydiethylaniline, and a lesser amount of *p*-methoxydiethylaniline from the mother liquor of the picrate of *m*-methoxydiethylaniline. The *m*-isomer was again characterized by the picrate, the mixed melting point with an authentic specimen being 143.5–145°. The picrate of *p*-methoxydiethylaniline was obtained as yellow prisms melting at 122–123.5°. The picrate of an authentic specimen melted at 124–125°, and the mixed melting point was 123–124°. The *p*-methoxydiethylaniline[4] was prepared from *p*-anisidine, ethyl iodide and sodium hydroxide.

Anal. Calcd. for $C_{17}H_{20}O_8N_4$: N, 13.7. Found: N, 13.8.

In view of the fact that the critical *m*-methoxydiethylaniline might have formed from *o*- and *m*-bromoanisoles, a special examination of the *p*-bromoanisole was made and the compound was shown to be pure.

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[2] Gilman, Kyle and Benkeser, *ibid.*, **68**, 142 (1946).

[3] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[4] Davies, *Bull. soc. chim.*, [5] **2**, 295 (1935).

DEPARTMENT OF CHEMISTRY
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N-Phenacyltetrahydroisoquinoline

BY WILLIAM E. GOODE

During the course of an investigation of certain N-substituted tetrahydroisoquinolines, an apparent error in the melting point of N-phenacyltetrahydroisoquinoline, as reported by Wedekind and Oechslen,[1] was noted. They recorded a melting point of 100–101° for this compound as obtained from the reaction of phenacyl bromide with tetrahydroisoquinoline.

It now appears that when N-phenacylisoquinolinium bromide is reduced catalytically, N-phenacyltetrahydroisoquinoline, m. p. 75°, is obtained. In contrast, the melting point described by Wedekind and Oechslen is suggestive of the isomeric N-phenacyltetrahydroquinoline (needles, m. p. 101–103°,[2] 104°[3]). Indeed, when pure tetrahydroisoquinoline and phenacyl bromide were caused to react under conditions similar to those employed by Wedekind and Oechslen, the product melted at 75–76° and was identical with N-phenacyltetrahydroisoquinoline as obtained by the reduction procedure.

Experimental

N-Phenacylisoquinolinium Bromide.—To 20.0 g. (0.1 mole) of phenacyl bromide in 100 ml. of anhydrous ether was added a solution of 13.0 g. (0.1 mole) of isoquinoline in 50 ml. of anhydrous ether. The solution was allowed to stand at room temperature for twenty-four hours and then filtered. The product was recrystallized from an absolute ethanol–petroleum ether mixture; yield, 28.0 g. (85%); m. p. 201–203°.

Anal. Calcd. for $C_{17}H_{14}BrNO$: Br, 24.35. Found: Br, 24.28.

Reduction of N-Phenacylisoquinolinium Bromide.—Sixteen and four-tenths grams (0.05 mole) of N-phenacylisoquinolinium bromide was hydrogenated at 2 atm. and 60° over 0.2 g. of platinum oxide catalyst during one and one-half hours. After removal of the catalyst, the solution was evaporated to dryness. The residue was dissolved in water and 5% sodium bicarbonate solution was added. The yellow solid which separated was extracted with ether; the ether was evaporated, and the residue was recrystallized from 80% ethanol as faint yellow plates; yield, 7.8 g. (62%); m. p. 75°.

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.27; H, 6.77. Found: C, 81.30; H, 6.94.

N-Phenacyltetrahydroisoquinoline.—To 9.9 g. (0.05 mole) of phenacyl bromide was added 13.3 g. (0.1 mole) of tetrahydroisoquinoline. The mixture was cooled in running water to keep the temperature in the range 70–80°. The solid residue was extracted with two 100-ml. portions of boiling ether, and the ether was evaporated on the steam-cone. The product recrystallized from 80% ethanol as faint yellow plates; yield, 8.2 g. (66%); m. p. 73–74°. Further recrystallization raised the melting point to 75–76°. This product did not depress the melting point of the N-phenacyltetrahydroisoquinoline as obtained by the reduction procedure.

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[1] Wedekind and Oechslen, *Ber.*, **36**, 1161 (1903).

[2] Meisenheimer, Angerman, Finn and Vieweg, *ibid.*, **57**, 1744 (1924).

[3] Kunckell, *ibid.*, **30**, 576 (1897).

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Derivatives of Nitrodesoxyinositols

BY BEAT ISELIN AND HERMANN O. L. FISCHER

The synthesis of nitrodesoxyinositols by cyclization of 6-nitrodesoxyaldohexoses has been reported from this Laboratory.[1] Further attempts have been made since to convert these compounds to the corresponding inososes by means of the Nef reaction.[2] This method was used successfully for the removal of the nitro substituent in nitrodes-

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[1] J. M. Grosheintz and H. O. L. Fischer, THIS JOURNAL, **70**, 1479 (1948).

[2] J. U. Nef, *Ann.*, **280**, 263 (1894).

oxyhexoses,[3] but when applied to nitrodesoxyinositols no reaction occurred under varying experimental conditions, and the nitrodesoxyinositols could be recovered from the reaction mixture. Consequently, we attempted to desaminate substituted or unsubstituted aminodesoxyinositols to the corresponding hexahydroxycyclohexanes by means of nitrous acid or nitrous anhydride. The reaction products resulting from this treatment still contained 20–30% of the original nitrogen content, reduced Fehling solution in the cold and consisted of a variety of components which could not be separated.

We wish to report some new derivatives of nitrodesoxyinositols which were prepared in the course of these investigations. Nitrodesoxyinositol, I,[1] yielded, on acetylation, two pentaacetates, one of which was identical with that obtained from nitrodesoxyinositol, III.[1] Nitrodesoxyinositol I is thus a mixture of two isomers, as is to be expected from the mode of formation described in the original paper.[1] From nitrodesoxyinositol, II, only one acetate was obtained. Hydrogenation of the pentaacetyl-nitrodesoxyinositols to the corresponding amines could not be accomplished. In acid medium the hydrogenation was incomplete, whereas in neutral medium more than the calculated amount of hydrogen was consumed with simultaneous liberation of acetic acid. In contrast, hydrogenation of free nitrodesoxyinositol, II, yielded the pure amine hydrochloride.

Diacetone-nitrodesoxyinositol II[1] did not react with lead tetraacetate in glacial acetic acid. The position of the free hydroxyl in this compound is thus para to the nitro group.

Experimental

Acetylation of Nitrodesoxyinositol, I.—Ten grams of nitrodesoxyinositol, I, (m. p. 147–148°) was added to a mixture of 50 cc. of acetic anhydride and 2.5 cc. of concentrated sulfuric acid, with cooling. The nitrodesoxyinositol dissolved rapidly and after five minutes crystals appeared. After standing overnight at room temperature the crystals were filtered and washed with acetic anhydride; yield of 3.0 g. (18%) after one recrystallization from dioxane m. p. 258–259°. Admixture of pentaacetyl-nitrodesoxyinositol III[1] produced no depression of the melting point.

Anal. Calcd. for $C_{16}H_{21}O_{12}N$: C, 45.82; H, 5.04; N, 3.33. Found: C, 46.08; H, 4.97; N, 3.20.

The mother liquor was added gradually to two liters of ice-water with stirring. A sirup separated which solidified on standing. This was filtered after five hours and washed with water, 11.6 g. (70%) of product being obtained. Two recrystallizations from dry ethanol yielded 8.5 g. of fine needles melting at 186–188°.

Anal. Calcd. for $C_{16}H_{21}O_{12}N$: C, 45.82; H, 5.04; N, 3.33. Found: C, 46.03; H, 4.97; N, 3.16.

Nitrodesoxyinositol, I, after partial purification according to the method reported previously[1] (m. p. 172–173°), yielded, on acetylation, 56% of the higher melting pentaacetate and 25% of the lower melting one.

Pentaacetyl-nitrodesoxyinositol, II.—On acetylation of nitrodesoxyinositol II the pentaacetate crystallized directly in a 85% yield from the reaction mixture. A small portion of the same material (8%) was obtained from the mother liquor when added to ice-water. After one recrystallization from dioxane the pentaacetyl-nitrodesoxyinositol II melted at 207–209°.

Anal. Calcd. for $C_{16}H_{21}O_{12}N$: C, 45.82; H, 5.04; N, 3.33. Found: C, 46.01; H, 4.98; N, 3.13.

Aminodesoxyinositol (II) Hydrochloride.—An amount of 1.8 g. of nitrodesoxyinositol II was dissolved in 50 cc. of water and hydrogenated in presence of 500 mg. of platinum dioxide. Within three hours 95% of the calculated amount of hydrogen was absorbed. The catalyst was removed by filtration and the solution was neutralized with 1 *N* hydrochloric acid, filtered with some charcoal and concentrated under reduced pressure to 5 cc. On gradual addition of 20 cc. of acetone the amine hydrochloride crystallized with one mole of water in a yield of 64%. After recrystallization from water–acetone it sintered at 255° and melted under decomposition at 265–270° (evacuated capillary tube).

Anal. Calcd. for $C_6H_{14}O_5N \cdot HCl \cdot H_2O$: C, 30.84; H, 6.90; N, 5.99. Found: C, 30.90; H, 6.58; N, 5.72.

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[3] J. C. Sowden and H. O. L. Fischer, THIS JOURNAL, 69, 1963 (1947).

Concerning Anderson's Modifications of the B. E. T. Equation

BY A. G. KEENAN

In his recent statistical treatment of the sorption of vapors by solids, Dole[1] arrived at his equation 14 which he considered similar to Anderson's equation 6,[2] the two equations giving the same values for the constant N_s (or V_m) but different values for the constant *c*.

Although Anderson does not give an explicit derivation of his equation, it is clear from his statements that the following relations must exist between the various symbols, where the superscripts *D* and *A* refer to Dole's and Anderson's symbols respectively, *viz.*:

$$k^D = (a_2/a_1)^D = 1/c^A$$

and

$$c^D = (a_1/a_L)^D = c^A k^A$$

Substitution of these relations into either of the two equations under discussion shows that they are in fact equivalent.

Beebe and co-workers[3] have published heat of adsorption data for nitrogen and argon on carbon blacks, plotted in their figures 3 to 8. In three out of the four cases where the differential heats fall off sharply at about the monolayer volume, this drop occurs at an adsorption somewhat larger than the B.E.T. monolayer. Since Anderson's equation 6[2] predicts a monolayer volume some 8 to 15% higher than the B. E. T. monolayer, it appears that his modification corrects the B. E. T. equation, in three cases out of four, in the right direction by about the right amount, as judged by the above heat data. Actually it would be more

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[1] M. Dole, *J. Chem. Phys.*, 16, 25 (1948).

[2] R. B. Anderson, THIS JOURNAL, 68, 686 (1946).

[3] R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, THIS JOURNAL, 69, 95 (1947).