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).