dently limited to formula (II); the oxidation of alpha-methyl *d*-mannopyranoside (I) by hypobromite removes carbon atom 3 and oxidizes carbons 2 and 4 to carboxyl groups.

This unusual type of oxidation is that which has been postulated recently by Hérissey, Fleury and Joly [*J. pharm. chim.* [8] **20,** 149 (1934); *cf.* Malaprade, *Bull. soc. chim.* [4] **43,** 683 (1928); *ibid.* [5] **1,** 833 (1934); Karrer and Pfaehler, *Helv. Chim. Acta,* **17,** 766 (1934)] to account for the analytical data which they obtained in the oxidation of various methyl aldohexosides by periodic acid, with the difference that carbons 2 and 4 are oxidized by this reagent only to the aldehyde group (formula III). To test the matter we have oxidized alpha-methyl *d*-mannopyranoside with periodic acid, followed by an oxidation of the assumed dialdehyde (III) with bromine water in the presence of strontium carbonate; the above mentioned strontium salt (II) was obtained readily in a yield of about 65%. Inspection of the formulas shows that this strontium salt should be expected from all the alpha-methyl *d*-aldohexopyranosides; we have obtained it from alpha-methyl *d*-glucoside by oxidation with periodic acid, followed by bromine water, with the same yield as reported for the mannoside. The work is being extended.[2]

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(2) One of us (C. S. H.) has expressed the view [This Journal, **52,** 1680 (1930)] that alpha-methyl mannoside ($[\alpha]_D$ +79°) possesses a 1,4-ring. Subsequent criticisms of this view, especially by Haworth, Hirst and their collaborators [Haworth and Hirst, *J. Chem. Soc.,* 2615 (1930), *et seq.*] have shown that it is not tenable and that the 1,5-ring structure pertains to the substance. The properties of the strontium salt herewith reported (particularly the presence of *d*-glyceric acid in its structure) also show that the 1,4-ring cannot be present in the mannoside and limit the ring to position 1,5 or 1,6; well-known evidence, which need not here be discussed, excludes the 1,6 ring.

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RECEIVED JANUARY 20, 1936

A NEW SYNTHESIS OF N-PHENYLPIPERAZINO-N′-BETA-ETHANOL

Sir:

N-Phenylpiperazino-N′-beta-ethanol has been synthesized previously by two methods. Prelog and Blazek [*Coll. Czechoslov. Chem. Comm.,* **6,** 549 (1934)] prepared it by the action of ethylene oxide on N-monophenylpiperazine; while D. E. Adelson and C. B. Pollard [This Journal, **57,** 1430 (1935)] prepared it by the reduction of N-phenylpiperazino-N′-ethyl acetate. The former report a melting point of 91°; the latter, 83°.

The writer has now prepared this compound by the condensation of triethanolamine with aniline in the presence of concentrated sulfuric acid as dehydrating agent.

The amines are mixed in molecular proportions and the acid slowly added, the mixture being mechanically stirred and gently heated at the same time. With a charge of 80 g. of triethanolamine, 60 g. of acid was used. After addition of the acid is completed, the mixture is boiled gently under a reflux condenser for six to eight hours. On cooling, the mixture sets to a brown gummy mass. The free base is liberated by means of a concentrated sodium hydroxide solution and the dark brown viscous oil is fractionated under vacuum, b. p. 171–175° (uncorr.) at 1 mm. (uncorr.). The almost colorless oil solidifies to a white crystalline mass in the receiver. Recrystallizations from ethyl ether gave pure white needles, melting sharply at 84° (corr.). Analysis for nitrogen gave: calcd. N, 13.59; found, N, 13.46.

This work is being continued.

DEPARTMENT OF CHEMISTRY CHESTER B. KREMER
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RECEIVED DECEMBER 27, 1935

REVERSIBLE ADSORPTION IN THE SURFACE OF SOAP SOLUTIONS

Sir:

Many substances greatly lower the surface tension of water in dilute solution but the surface tension then passes through a minimum and rises again with increasing concentration. This appears almost inexplicable from the standpoint of the Gibbs adsorption theorem, $\Gamma = d\sigma/d\mu$ or $-\frac{a}{RT} \times \frac{d\sigma}{da}$ or, approximately, $-\frac{c}{RT} \times \frac{d\sigma}{dc}$, which predicts a large amount of adsorption in the free surface of the dilute solutions, followed by no adsorption at the minimum where the slope is horizontal, followed by negative adsorption for all the higher concentrations. In other words, where the surface tension is most greatly lowered there is no adsorption to cause the lowering, and where the surface tension is still low the surface-active material is supposed to be relatively absent from the surface. True, most authors have plotted surface tension against concentration, instead of using the accurate thermodynamic formula based upon chemical potential or activity. This, however, affords no relief from the dilemma because for any solution capable of stable existence, concentration and activity must be identical in sign. Furthermore, the activity is definitely