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## COMMUNICATIONS TO THE EDITOR

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### PIPERAZINE DERIVATIVES FROM AMINO ALCOHOLS

Sir:

We have found that certain piperazine derivatives are conveniently prepared from  $\beta$ -hydroxyalkylamines by the catalytic alkylation method of Adkins [Paden and Adkins, *THIS JOURNAL*, **58**, 2487 (1936); Hill and Adkins, *ibid.*, **60**, 1033 (1938)].

Isopropanolamine in dioxane over copper chromite at 250–275° yields *trans*-2,5-dimethylpiperazine. It was identified as the 1,4-dinitroso derivative, m. p. 174° [Feist, *Ber.*, **30**, 1983 (1897)] and as the 1,4-dibenzoyl derivative, m. p. 228–229° [Bamberger and Einhorn, *ibid.*, **30**, 226 (1897)]. Similarly, diethanolamine yields piperazyl-1,4-*bis*- $\beta$ -ethanol, m. p. 134–135°. This was identified as the dibenzoate, m. p. 104.5–105° [Pyman, *J. Chem. Soc.*, **93**, 1802 (1908)]. Good yields of diphenylpiperazine, m. p. 163.5–164.5°, were obtained from phenylethanolamine. When mixed with an authentic specimen of diphenylpiperazine the melting point was not changed.

The copper chromite catalyst was partially reduced in most runs. The yields ranged from 20 to 50%. This work is being continued.

CONTRIBUTION FROM THE  
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RECEIVED JANUARY 16, 1939

### ULTRAVIOLET ABSORPTION SPECTRUM OF ANHYDROSARSASAPOGENOIC ACID

Sir:

Dr. F. S. Spring has kindly pointed out in a letter to one of us that the ultraviolet absorption curve for anhydrosarsasapogenoic acid reported in a recent paper with Jacobsen [Fieser and Jacobsen, *THIS JOURNAL*, **60**, 2753 (1938)] is not, as was stated, indicative of the presence of an  $\alpha,\beta$ -unsaturated ketonic group because, according to the graph, the intensity of the band at 243  $m\mu$  is much too low for such a compound ( $\log \epsilon = 0.98$ ). This inconsistency is due to an unfortunate error in reproducing Dr. Webb's curve. The figures for the intensity of absorption inadvertently were reported as  $\log \epsilon$  values, whereas they actually are values of  $\epsilon \times 10^{-4}$ . The ab-

sorption band thus has both the location and the high intensity characteristic of an  $\alpha,\beta$ -unsaturated ketone. The evidence on this point has been confirmed and extended by an examination of the absorption spectrum of anhydrosarsasapogenoic acid methyl ether acetate in absolute ethyl alcohol. This shows an intense band at 243  $m\mu$  ( $\log \epsilon = 4.13$ ) and a secondary band with a maximum at 303  $m\mu$  ( $\log \epsilon = 1.86$ ).

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RECEIVED JANUARY 21, 1939

### THE USE OF PHOSPHOTUNGSTIC ACID IN THE PRELIMINARY REFINING OF EXTRACTS CONTAINING VITAMIN K

Sir:

In this Laboratory, one of the most successful preliminary treatments of hexane extracts of dried alfalfa for the preparation of vitamin K concentrates has been the removal of the green pigments by adsorption on activated magnesium oxide. This procedure, however, is laborious and time consuming, and involves some loss of the vitamin.

It has been found that removal of the green pigments can be accomplished more conveniently by the use of phosphotungstic acid. To one volume of alfalfa hexane extract representing about 5 g. of dried alfalfa per cc., is added one-half volume of redistilled ethyl ether and phosphotungstic acid as a fine powder in the proportion of 0.03 g. per gram of dried alfalfa. The mixture is shaken vigorously until two phases form on standing: an upper, light green layer containing hexane, ether, about one-half of the total solids of the extract, and all of the vitamin K; and a lower, dark, viscous layer of ether, phosphotungstic acid, and the remainder of the solids of the extract. The lower layer is discarded.

The upper layer is washed repeatedly with approximately 50% ethanol and then with water. The ethyl ether is removed by distilling under reduced pressure and the remaining solution chilled at 0° for at least twenty-four hours. Solids which precipitate out are removed by filtering at 0° and discarded. From this point, the