HYDROGENATION OF AMIDES TO AMINES

Sir:

A useful process for the reduction of amides to amines has apparently not been described. Guerbet [*Chem. Zentr.*, II, 623 (1899)] reported the formation of ethylamine from acetamide (Na + ROH), but Bouveault and Blanc [*Compt. rend.*, **138,** 148 (1904)] obtained alcohols as the chief product from amides under similar conditions. Mailhe [*Bull. soc. chim.*, [3] **35,** 614 (1906)] reported the formation of ethyl and dimethyl amines from acetamide and of propyl and dipropylamines from propionamide in the vapor phase (Ni + H_2), but no details as to yields or purity of products were given.

The transformation $RCONH_2 + H_2 \longrightarrow RCH_2NH_2 + H_2O$ does not take place readily and is likely to go incompletely because the water formed in the reaction hydrolyzes unchanged amide with the formation of acid and ammonia, which may deactivate a catalyst. It has now been found possible to bring about this reaction over copper-chromium oxide under 100 to 300 atm. of hydrogen at 175 to 250°. It has been found advantageous to use dioxane as a reaction medium since thereby the water formed in the reaction is diluted and the hydrolysis of the amide is negligible. (Raney nickel should *not* be used with dioxane at 250°.)

Lauramide, heptamide, α-phenylbutyramide, furoamide and tetrahydrofuroamide have given yields of from 40 to 70% of the corresponding primary amines. The chief side reaction is the formation of secondary amines, which were isolated in yields of 25 to 50%. For example, 54 g. of α-phenylbutyramide in 125 ml. of dioxane with 10 g. of copper-chromium oxide under 250 atm. of hydrogen was hydrogenated in two hours at 250°, and 36 g. of 2-phenylbutylamine and 13 g. of di-2-phenylbutylamine obtained. The method has also been applied to the hydrogenation of substituted amides, *e. g.*, N-laurylpiperidine, N-sebacylpiperidine, mono- and di-N-β-phenylethyl lauramide, mono- and di-N-amyl lauramide, N-cyclohexyl lauramide, N-β-phenylethyl heptamide and N-phenyl lauramide. The yields of secondary or tertiary amines were from 70 to 95% except from the last mentioned compound [*cf.* Folkers and Adkins, THIS JOURNAL, **54,** 1152 (1932)]. The amides referred to above were prepared by the reaction of anhydrous ammonia or amines with an ester at 250°. The amide has also been prepared in place; *e. g.*, high yields of amines were obtained by the hydrogenation of ammonium laurate.

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POSSIBILITY OF INTERCHANGE BETWEEN DEUTERIUM GAS AND HYDROGEN IN COMPOUNDS

Sir:

In some studies on the reaction between deuterium and hydrogen, it was necessary to determine if interchange took place between the deuterium in the gas phase and the hydrogen atoms in ordinary water when deuterium-hydrogen mixtures were stored over water and also if the concentration of deuterium in the gas phase was affected by the stopcock grease which was present in our apparatus. A 425-cc. Pyrex bulb was fitted with a three-way stopcock at the top and a stopcock at the bottom connecting with a leveling bulb. The bulb was filled with distilled water and then all but 35 cc. of the water displaced by adding, through one arm of the upper stopcock, a deuterium-hydrogen mixture obtained by electrolysis of heavy water. Both stopcocks were closed and the apparatus shaken for several minutes to saturate the water in the bulb with gas. The pressure in the bulb was about 1.1 atm. A sample of gas was then removed through the second arm of the upper stopcock leaving the gas in the bulb at atmospheric pressure. The bulb was kept at room temperature and shaken occasionally for nineteen days. At the end of this time, a second sample of gas was removed by displacement with water. Mass spectrographic analysis of the samples showed the first to contain 2.29% deuterium and the second 2.30%.

This result shows that the concentration of deuterium-hydrogen mixtures in contact with water in clean glass vessels remains constant if precautions are taken to avoid preferential solubility, diffusion and the presence of metallic surfaces [Horiuti and Polanyi, *Nature*, **132,** 819 (1933)], and that the result reported by Oliphant [*Nature*, **132,** 675 (1933)] cannot be interpreted as being an interchange between the deuterium in the gas phase and the hydrogen atoms in the water without the aid of a catalytic surface other than the glass wall of the containing vessel.

Two Pyrex tubes were evacuated and filled simultaneously from a reservoir containing a deuterium-hydrogen mixture. The first tube was fitted with a magnetic break at the lower end and, after filling, was sealed off at the upper end. The second tube was equipped with a stopcock and was coated on the inside with a layer of "Lubriseal." At the end of twenty-two days mass spectrographic analysis showed the gas in the first tube to contain 2.07% deuterium and that in the second 2.09%. It is evident, therefore, that an apparatus containing stopcocks may be used in the study of deuterium-hydrogen mixtures without fear of interchange between deuterium and hydrogen from the stopcock grease.

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THE SYNTHESIS OF POLYNUCLEAR HYDROCARBONS BY THE CYCLODEHYDRATION OF AROMATIC ALCOHOLS

Sir:

Since our preliminary publications in this field,[1] a number of articles have been published abroad[2] which show that these communications of ours have escaped notice there and which make it seem desirable to us to report the following additional results which have been obtained in our laboratories. This is done in the hope that it will save our fellow investigators the time and money which might otherwise be spent in the duplication of experiments.

Our studies in the tetralin field, for example, already have shown that 1-methyltetralin can be obtained by the action of sulfuric acid upon any one of the following: $PhCH_2CH_2CH_2CH(OH)Me$, $PhCH_2CH_2CH_2CH{=}CH_2$, $PhCH_2CH_2CH(OH)CH_2Me$, or $PhCH_2CH{=}CHCH_2Me$.

1-Ethyltetralin has been prepared similarly from both $Ph(CH_2)_4CH(OH)Me$ and $Ph(CH_2)_4CH{=}CH_2$.

In two of the above compounds, a shift in the location of the double bond is indicated in connection with the cyclization.

In the case of $Ph(CH_2)_2CMe(OH)CH_2Me$, both 1,2-dimethyltetralin and 1-methyl-1-ethylindane appear to be formed.

As stated in our initial announcements,[1] these studies are being pursued in various directions, especially with the object in view of preparing synthetically compounds of biological interest.

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[1] (a) Bogert, *Science*, [N. S.] **76**, 475 (1932); (b) **77**, 197 (1933); (c) **77**, 289 (1933).

[2] (a) Schlenk and Bergmann, *Chemistry & Industry*, **52**, 207 (1933); (b) Cook, Hewett, Haslewood, *et al.*, *ibid.*, **52**, 949 (1933); (c) Ruzicka, Ehmann, Goldberg and Hösli, *Helv. Chim. Acta*, **16**, 833 (1933); (d) Kon, *J. Chem. Soc.*, 1081 (1933); (e) Cook and Hewett, *ibid.*, 1098 (1933); (f) Fulton and Robinson, *ibid.*, 1463 (1933).

FREEZING POINTS OF MIXTURES OF THE WATERS, $H^1{}_2O$ AND $H^2{}_2O$

Sir:

We have determined the freezing points and specific gravities at 25° on 15-cc. portions of mixtures of $H^2{}_2O$ and $H^1{}_2O$ using a Beckmann thermometer calibrated by the Bureau of Standards, and standard technique. The samples were prepared by electrolysis of potash solutions using nickel electrodes, followed by repeated distillations from alkaline permanganate to remove carbon dioxide and other impurities which would lower the freezing point. The freezing points were independent of the supercooling (1 to 2.8°) and were constant to within 0.001° for periods of at least ten minutes. The zero point of the thermometer was determined repeatedly against the freezing point of ordinary distilled water using precisely the same technique. Slow freezing of the 39.9% sample over a period of three hours with continuous stirring, until one-third had separated as ice, produced no change in equilibrium temperature greater than the experimental error of 0.002°. The specific gravities of the melted ice and unfrozen liquid, using a 1.3-cc. pycnometer, checked to 0.02%.

These observations indicate that the solid

Approx. % heavy component 100% = sp. g. 1.11165	F. p., °C.	Sp. gr. 25/25°	$\frac{\text{F. P.}}{(\text{sp. g.} - 1)}$	Observer
1.23	0.053	1.001376	38.5	Washburn, Smith and Frandsen, *B. S. J. Res.*, **11**, 453 (1933)
14.7	.632	1.01644	38.5	This investigation
19.1	.824	1.02135	38.6	This investigation
39.9	1.679	1.04456	37.7	This investigation
39.5	1.670	1.04411	37.9	This investigation; redistilled *in vacuo*
94.6?	3.8	1.1056[a]	36.	Lewis and Macdonald

[a] The terms specific gravity and density are used interchangeably for this value [Lewis and Macdonald, THIS JOURNAL, **55**, 3058 (1933)].