of the cystine; otherwise too high values are obtained] and the Mirsky and Anson modification of the Folin method) [A. E. Mirsky and M. L. Anson, *J. Gen. Physiol.*, **18**, 307 (1934). Correct values for cystine by this method are obtained only after removal of the hydrogen cyanide. This was achieved by evacuation with oxygen-free nitrogen passing through the capillary].

At 35° a slow formation of cysteine was noted in a 0.1 *M* citrate buffer solution (*p*H 5.0) containing 0.0025 mole of cystine and 0.0625 mole of potassium cyanide and hydrogen chloride per liter; 5% of the cystine was found to be reduced after twenty-four hours, 11% after seventy-two hours, 18% after six days. At 95° with 0.005 *M* cystine and 0.125 *M* hydrogen cyanide the reaction proceeded quite rapidly, the amount of cysteine formed within one hour corresponding to 49% of the cystine used. Further heating up to six hours caused a slow decrease in the yield of cysteine. When a cystine–hydrogen cyanide reaction mixture, after heating to 95° for one hour, was treated with sulfite to reduce any unchanged cystine, no significant increase in color intensity was found (beyond that due to the cysteine already formed), indicating the absence of any unreacted cystine. This, together with the fact that the yield in cysteine never exceeded 50%, is regarded as evidence that hydrogen cyanide, like potassium cyanide, does not cause reduction but "hydrocyanolysis" of the disulfide ($RS—SR + HCN \rightarrow RSH + RSCN$).

When a solution containing 0.01 mmole of (—S—S—) glutathione and 0.25 mmole of hydrogen cyanide was incubated at 35°, 22% of the glutathione was in the thiol form after three days. In the absence of the hydrogen cyanide no detectable amounts (<0.5%) of thiol were formed under the same conditions. Also in control experiments in which the cystine–hydrogen cyanide reaction mixtures were kept at low temperatures (3 and −10°) for as long as eight days, no formation of cysteine could be detected. When cystine was heated at 95° and *p*H 5 in the absence of hydrogen cyanide, only 1.5% of the cystine yielded cysteine in six hours (by hydrolysis).

From these experiments it is concluded that hydrogen cyanide at *p*H 5 attacks disulfides, forming thiol groups more slowly but probably by the same mechanism as does potassium cyanide in alkaline solution. It is impossible to decide whether the rate of this reaction at 40° is sufficient to explain the activating effect of hydrogen cyanide on papain, etc., in the presence of small amounts of disulfide–sulfhydryl systems.

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RECEIVED AUGUST 4, 1941

2-PHENYLTETRALONE-1. A CORRECTION

Sir:

In the recently published article, by Plentl and Bogert [THIS JOURNAL, **63**, 989 (1941)], on "The Synthesis of Tricyclic Hydrocarbons Related to Stilbestrol," 2-phenyltetralone-1 is described as though it were a new compound, whereas it has been reported previously both by Newman [*ibid.*, **60**, 2949 (1938); **62**, 872 (1940)], and by Miss Crawford [*ibid.*, **61**, 608 (1939)]. Newman designated his products as "1-keto-2-phenyl-1,2,3,4-tetrahydronaphthalene" in his first paper, and "1,2,3,4-tetrahydro-1-keto-2-phenylnaphthalene" in his second, while Miss Crawford used the name "1-oxo-2-phenyl-1,2,3,4-tetrahydronaphthalene" in hers. This variation in nomenclature accounts in part for our failure to catch these articles in reviewing the literature. Our apologies are extended to these fellow investigators for this oversight.

While we all used the same initial material, *viz.*, α,γ-diphenylbutyric acid, the methods for its conversion into the tetralone differed. Newman gave the m. p. as 76–77°, Miss Crawford as 79–80°, and our product melted at 79°.

Our statement on page 991 of that article that 2-phenyltetralone-1 "did not react with semicarbazide hydrochloride" should be corrected. We ran the reaction only once, in an alcoholic solution containing sodium acetate as buffer, and failed to insolate a semicarbazone. On repeating the reaction, however, with what little tetralone we had left (38 mg.), we have been more successful, and have obtained a semicarbazone, which proved rather difficult to purify, as it was already somewhat discolored, and then melted at 254° (Anschütz total immersion thermometer), with some prior gas evolution and sintering.

Anal. Calcd. for $C_{17}H_{17}ON_3$: C, 73.1; H, 6.1. Found: C, 73.4; H, 6.4.

Newman, who prepared the semicarbazone without difficulty, found that it melted with decomposition at 250–251.4°, after sintering at 245°.

Our somewhat higher m. p. need not be interpreted, however, as indicating any greater purity, for at high temperatures a difference of 3° is not serious, and our analytical results do not justify any such claim.

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RECEIVED JULY 18, 1941

ADDITION COMPOUNDS OF ZINC, CADMIUM, COBALT AND NICKEL HALIDES WITH 1,4-DIOXANE

Sir:

In a recent paper [THIS JOURNAL, **62,** 3522 (1940)] R. Juhasz and L. F. Yntema describe a series of "Addition Compounds of Zinc, Cadmium, Cobalt and Nickel Halides with 1,4-Dioxane." The great majority of these I prepared already some years ago (H. Rheinboldt, A. Luyken and H. Schmittmann, *J. prakt. Chem.*, **149,** 30–54 (1937); *C. A.*, **31,** 6615 (1937)), *i. e.*, the compounds: $ZnCl_2 \cdot 2(C_4H_8O_2)$, $ZnBr_2 \cdot 2(C_4H_8O_2)$, $ZnI_2 \cdot 2(C_4H_8O_2)$, $CdCl_2 \cdot (C_4H_8O_2)$, $CdBr_2 \cdot (C_4H_8O_2)$, $CdI_2 \cdot (C_4H_8O_2)$, $CoCl_2 \cdot (C_4H_8O_2)$, $CoBr_2 \cdot 2(C_4H_8O_2)$, $CoI_2 \cdot 2(C_4H_8O_2)$ and $NiI_2 \cdot 2(C_4H_8O_2)$.

Besides we described other compounds which belong to the same series: $CoI_2 \cdot 4(C_4H_8O_2)$, $NiCl_2 \cdot 2(C_4H_8O_2)$ and $NiBr_2 \cdot 2(C_4H_8O_2)$.

Further on we described addition compounds of dioxane with certain metal halides: $CaCl_2$, $CaBr_2$, CaI_2, $SrBr_2$, SrI_2, BaI_2, $MgCl_2$, $MgBr_2$, MgI_2, $HgCl_2$, $HgBr_2$, HgI_2, $Hg(CN)_2$, $Hg(CNS)_2$, $CuCl_2$, $CuBr_2$, $SnCl_2$, $SnBr_2$, $MnCl_2$, $MnBr_2$, MnI_2, $FeCl_2$, $FeBr_2$, FeI_2.

In a previous publication (*J. prakt. Chem.*, **148,** 81–87 (1937); *C. A.*, **31,** 4321 (1937)) we described dioxanates of LiCl, LiBr, LiI, NaI, KI and NH_4I.

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RECEIVED JULY 15, 1941

COMPOUNDS OF 1,4-DIOXANE WITH METAL HALIDES

Sir:

In a list of "New Compounds" of zinc, cadmium, cobalt and nickel halides with 1,4-dioxane (THIS JOURNAL, **62,** 3522 (1940)) that had been prepared in this Laboratory (Thesis, St. Louis University, (1934)), there were included a number described by Rheinboldt, Luyken and Schmittmann (*J. prakt. Chem.*, **149,** 30 (1937)). The compounds that should have been reported are as follows (R = 1,4-dioxane): $ZnCl_2 \cdot R$, $CdCl_2 \cdot {}^1/_2R$, $CoI_2 \cdot 3R$, $CoI_2 \cdot R \cdot 2H_2O$, $CoI_2 \cdot R \cdot 4H_2O$, $NiCl_2 \cdot R$ and $NiBr_2 \cdot R$.

The writer is glad to make this correction and assumes responsibility for the error.

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L. F. YNTEMA

RECEIVED JULY 28, 1941

THE THERMAL DECOMPOSITION OF ACETALDEHYDE

Sir:

It is known that reaction chains may be induced in the thermal decomposition of acetaldehyde by the addition of small amounts of oxygen or other materials, but whether pure acetaldehyde decomposes thermally by a chain mechanism is still a matter of controversy. Recently, Burton, Ricci and Davis [THIS JOURNAL, **62,** 265 (1940)], employing the Paneth technique with radioactive lead, have obtained some positive evidence for radical chains in the thermal reaction. Their work is open to two objections. (1) Even the slightest trace of impurity, for example 0.001% oxygen [Letort, *J. chim. phys.*, **34,** 428 (1937)] would have initiated reaction chains and thus led to a positive result for their experiments. (2) The experiments could not determine what fraction of the acetaldehyde was decomposing by way of the chains.

A method which seemed to offer better possibilities for deciding this question was to decompose mixtures of acetaldehyde and acetaldehyde-d_4. If a chain reaction occurred, such processes as the following would take place

$$\begin{aligned} CH_3CHO &\longrightarrow CH_3 + CHO \\ CD_3CDO &\longrightarrow CD_3 + CDO \\ CH_3 + CD_3CDO &\longrightarrow CH_3D + CD_3CO \\ CD_3 + CH_3CHO &\longrightarrow CD_3H + CH_3CO \end{aligned}$$

and the methanes produced in the reaction would be mixed as to deuterium content. On the other hand, if the reaction were intramolecular, only CH_4 and CD_4 would be formed. Since Benedict, Morikawa, Barnes and Taylor [*J. Chem. Physics*, **5,** 1 (1937)] have shown that methane and the deuteromethanes may be identified and determined by their infrared spectra, one should be able to evaluate these alternatives through an infrared examination of the products formed in the above experiment.