of 3-hydroxy-5,6-diphenyl-1-pyrazolo[b]pyrazine (VI, R = $-H$, R' = $-C_6H_5$) with Raney nickel in boiling ethanol solution for three hours gave in 80% yield 2-amino-5,6-diphenylpyrazine-3-carboxamide (VII, R = $-H$, R' = $-C_6H_5$), m.p. 203–205°, identical in all respects with an authentic sample prepared previously.[13] Similar cleavage of VI (R = $-CH_3$, R' = $-H$) yielded 2-methylaminopyrazine-3-carboxamide[7] (VII, R = $-CH_3$, R' = $-H$, m.p. 200–201°. *Anal.* Calcd. for $C_6H_8ON_4$: C, 47.4; H, 5.3; N, 36.8. Found: C, 47.5; H, 5.3; N, 36.6). In a trial experiment, this reaction sequence leading to the pyrazine intermediates was shortened by several steps by direct condensation of 3-hydroxy-4-nitroso-5-aminopyrazole (V, R = $-H$) with biacetyl in ethanol solution in the presence of Raney nickel to give 2-amino-5,6-dimethylpyrazine-3-carboxamide (VII, R = $-H$, R' = $-CH_3$, m.p. 255°. *Anal.* Calcd. for $C_7H_{10}ON_4$: C, 50.6; H, 6.1; N, 33.7. Found: C, 50.6; H, 6.1; N, 33.2) directly, the Raney nickel effecting both the reduction of the nitroso group and the ring cleavage of the subsequently formed pyrazolo[b]-pyrazine.

Since pteridines may be prepared directly from these intermediates by known methods,[1–5,7] the reactions outlined above constitute a new total synthetic approach to these important heterocycles.

[13] E. C. Taylor, THIS JOURNAL, **74**, 1651 (1952).

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RECEIVED AUGUST 31, 1956

AN EXPLOSION DURING THE PREPARATION OF DIAZOACETONITRILE

Sir:

The preparation of diazoacetonitrile has recently been described[1] and we have repeated the procedure on several occasions without incident. However, a violent explosion occurred during one preparation and the operator was seriously injured as a result.

A concentrated solution of approximately 15 g. of diazoacetonitrile in methylene chloride was under water-pump vacuum in a four liter suction flask. The temperature was approximately 10° when the operator allowed air to enter the system. When the rubber stopper bearing the capillary was removed, the explosion resulted.

It is probable that some pure diazoacetonitrile was between the rubber stopper and the neck of the flask and the friction generated by removing the stopper was sufficient to initiate the explosion. *It is important that the nitrile be used only in dilute solution because it is highly explosive in concentrated form.*

A similar incident has been reported[1,2] during the attempted distillation of diazoacetonitrile but its highly explosive nature even in the presence of solvent has not been stressed adequately.

[1] S. H. Harper and K. C. Sleep, *J. Sci. Food Agr.*, **6**, 116 (1955).
[2] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2026 (1956).

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RECEIVED SEPTEMBER 17, 1956

THE PREPARATION OF THE NEW COMPOUND CALCIUM COBALTATE(III)

Sir:

Although compounds of BaO and MgO with Co_2O_3 have been prepared as summarized by Mellor,[1] an attempt to prepare the compound $CaO \cdot Co_2O_3$ under similar conditions was not successful.

Difficulty in obtaining exact stoichiometry with cobalt compounds and the desirability of obtaining intimate mixture of reactants led to the following preparative procedure. Exactly one mole of cobaltous oxide which had been calcined at 950° under vacuum to insure absence of higher oxides was dissolved in hydrochloric acid and cobaltous hydroxide was precipitated with base. The precipitate was washed by decantation without loss until analysis showed absence of chloride ion in the wash water. Precipitated calcium carbonate (1.00 mole) was stirred into the cobaltous hydroxide, and the mixture was filtered. After drying at 110°, the mixture was calcined at 1100° for several hours in air. Analysis of the product corresponded to the formula $CaO \cdot Co_2O_{2.57}$.

A sample of 10.00 g. of $CaO \cdot Co_2O_{2.57}$ was put in a porcelain boat in a vacuum system at 525° in an atmosphere of oxygen. Reaction at this temperature was extremely slow, taking about three days to absorb sufficient oxygen to form a compound of formula $CaO \cdot Co_2O_3$.

A second 10.00-g. sample of the same material was allowed to react with oxygen at 660°. After 52 hours the pressure would decrease no further. Analysis agreed with the formula $CaO \cdot Co_2O_3$.

Analysis of Co(III) content of all samples was carried out by solution in hydroiodic acid and titration of the liberated iodine with thiosulfate.

Evidence of a probable chemical binding of calcium oxide in the compound is afforded by the observation that the calcium oxide in the compound could not be converted to soluble calcium hydroxide by placing in water at room temperature for 24 hours. The compound was slowly hydrolyzed by boiling 1 molar ammonium nitrate solution. Further, the compound would not absorb nitrogen dioxide from a dilute mixture with air in the temperature range 250 to 350° as does calcium oxide alone.

At room temperature the compound $CaO \cdot Co_2O_3$ has qualitatively the same magnetic properties as does Co_2O_3.

[1] J. W. Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, N. Y., 1935, vol. XIV, p. 594.

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RECEIVED AUGUST 22, 1956

L-RIBULOSE-5-PHOSPHATE: FORMATION BY PURIFIED KINASE FROM *AEROBACTER AEROGENES*

Sir:

Lampen[1] has reported the enzymatic interconversion of L-arabinose ⇆ L-ribulose by extracts of

[1] J. O. Lampen, *Abstr. Proc. Amer. Chem. Soc.*, Sept., 1954, 44c-45c.