COMMUNICATIONS TO THE EDITOR

THE ACTION OF ARSINES WITH HALOARSINES

Sir:

In a recent publication by F. F. Blicke and L. D. Powers [This Journal, **54**, 3353 (1932)] on the interaction of phenylarsines with phenylhaloarsines, these workers have found that the data of Steinkopf and Smie [*Ber.*, **59**, 1459 (1926)] are not correct, but overlooks that I myself have rectified this mistake more than two years ago, when investigating in cooperation with H. Dudek [*Ber.*, **62**, 2494 (1929)] the action of diphenylarsine with phenyldichloroarsine and phenylarsine with diphenylchloroarsine. I obtained the same data as recently published by F. F. Blicke and L. D. Powers.

Furthermore, I stated that owing to these new facts I could not uphold any more the existence of all other compounds published with Smie in *Ber.*, **59**, 1459 (1926).

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THE ACTION OF ARSINES WITH HALOARSINES

Sir:

We wish to express our deep regret at our failure to read thoroughly the article of Steinkopf and Dudek, "Zur Kenntnis organischer Arsenverbindungen. XV. Ueber die Existenz der Arseno-azo-bindung und ueber das Phospho-arseno-benzol," *Ber.*, **62**, 2494 (1929). It should, however, be pointed out that while the alleged discovery of six new types of arsenicals was clearly stated in the title of the original article [Steinkopf and Smie, "Zur Kenntnis organischer Arsenverbindungen. IX. Darstellung neuer Typen organischer Arsenverbindungen," *Ber.*, **59**, 1453 (1926)], the correction of this work appeared in an article whose title—"Ueber die Existenz der Arseno-azo-bindung und ueber das Phospho-arseno-benzol"—gave no hint of this important matter.

In this connection it might also be mentioned that no reference to this correction occurs in *Chemical Abstracts* for 1930, although the material dealing with arseno-azo- and phospho-arseno compounds was abstracted.

The information in our articles [This Journal, **54**, 3353 (1932); **55**, 316 (1933)] does not duplicate that presented by Steinkopf in his retraction. We have investigated in detail each of the six reactions by means of which Steinkopf and Smie thought they had obtained six new types of arsenicals and have recorded experimental procedures by means of which the mixtures of previously known arsenicals—which are actually formed in place of Steinkopf's new types—can be separated. Steinkopf reinvestigated only two of the six reactions and merely waives his claim to the discovery of the new compounds which he originally thought had been formed in the four other reactions.

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THE CALCIUM CHLORIDE MODIFICATIONS OF MANNOSE AND GULOSE

Sir:

The writer previously reported [*J. Bur. Standards*, **8**, 615 (1932)] that α- and β-*d*-mannose, on oxidation with bromine in the presence of barium carbonate yield δ-lactones, which indicates that these sugars have 1,5 ring structures. Application by the writer of the same method to the labile calcium chloride compound of mannose reported by Dale [THIS JOURNAL, **51**, 2225 (1929)] shows that this substance gives largely mannonic γ-lactone. This is evidence that *d*-mannose·$CaCl_2 \cdot 4H_2O$ has a 1,4 ring structure rather than a normal 1,5 ring.

A quantitative oxidation of the labile mannose compound is not possible because, in solution with water, it is converted rapidly into normal α-*d*-mannose. If the oxidation period is short the oxidation product is largely γ-lactone, but with longer periods considerable δ-lactone is formed. Presumably the γ-lactone is derived from the original product, while the δ-lactone arises from normal α-*d*-mannose, formed by the mutarotation reaction.

A 0.025-mole sample of crystalline mannose·$CaCl_2 \cdot 4H_2O$ was added to 100 cc. of ice water containing 5 cc. of bromine and 15 g. of barium carbonate. After five minutes the reaction was stopped by shaking with olive oil. The aqueous solution contained 0.0127 mole of unoxidized sugar and 0.0123 equivalent of lactone (estimated by titration). Hence the oxidation was 49% complete. The specific rotation of the product based on the above analysis, after eighteen minutes, was +42.6°; (60 min.), +37.9°; (180 min.), +35.2°; (48 hrs.), +26.7°. Since the rotation of the δ-lactone is +111°, the γ-lactone +52°, and that of the unoxidized sugar about +20°, changing to +14.7°, it is estimated that the oxidation product contained 76% γ-lactone and 24% δ-lactone.

The writer is applying his Barium Carbonate Oxidation Method to the sugars and their solutions to obtain data as to the isomeric changes accompanying mutarotation and the effect of salts on the equilibrium existing in solutions. It was previously shown [*Bur. Standards Jour. Res.*, **5**, 748 (1930)] that the equilibrium between the various forms of gulose in solution may be altered by the addition of calcium chloride. The experiments