COMMUNICATIONS TO THE EDITOR

BENZANTHRONE AND 4-PHENYLBENZANTHRONE

Sir:

In a recent elaboration of their former work, Charrier and Ghigi [*Ber.*, **69,** 2211 (1936)] have suggested that in our study of Grignard addition to benzanthrone [THIS JOURNAL, **57,** 740 (1935)] we failed to concede priority to them. We regret that our mode of presentation failed to make clear that the Italian workers first proved two instances of 1,4-addition of the Grignard reagent to benzanthrone and predicted the structure of 4-phenylbenzanthrone.

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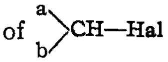
WALDEN INVERSION IN SUBSTITUTION REACTIONS ON INORGANIC COMPLEX COMPOUNDS

Sir:

Recently Bailar, Haslam and Jones [THIS JOURNAL, **58,** 2226 (1936)] have published an interesting paper on the steric course of the substitution reaction between *l*-dichloro-diethylenediamino-cobaltichloride and 2 moles of ammonia which leads to a *levo*-product at low, to a *dextro*-product at high, temperature. Since the theoretical considerations about Walden inversion on which the paper is based are likely to be misunderstood, I would like to draw attention to the following point. According to the authors, Bergmann, Polanyi and Szabo [*Z. physik. Chem.*, **20B,** 161 (1933); *Trans. Faraday Soc.*, **32,** 843 (1936)] in their theory of Walden inversion predict that each reaction involving a single step in substitution on the tetrahedral carbon atom will bring about inversion, an even number of substitutions therefore reproducing the original configuration. In the above case, this apparently is not always the fact. As a matter of fact, Bergmann, Polanyi and Szabo are concerned expressly with substitutions of polar bonds by ions;[1] they assert that substitution of such a polar bond by a negative ion is necessarily connected with configurational inversion, while substitution by a positive ion leads either to the initial configuration or to a racemic product. The reaction under discussion does not involve a substitution by ions, and especially not by negative ions; it reminds one of the well-known observation of Senter and co-workers [*J. Chem. Soc.*, **107,** 638 (1915); **109,** 1091 (1916); **117,** 140, 151 (1918)] that *l*-phenylchloroacetic acid by interaction with ammonia in water or alcohol gives *d*-, in acetonitrile or liquid ammonia *l*-phenylaminoacetic acid, or the experiments of Holmberg [*Ber.*, **60,** 2194, 2198 (1927)] on the relationship between the rotation of xanthogenosuccinic acid and the temperature at which it was prepared from active bromosuccinic acid. The theory of Bergmann, Polanyi and Szabo does not make any prediction for such cases.

It may be added that in the group of these octahedral complexes some substitutions by negative ions are already known to be accompanied by configurational inversion. Without discussing the whole existing material, reference may be made to the following two reactions: (*a*) *cis*-Chloro-isorhodanato-diethylenediamino-cobaltic ion is converted by means of rhodanide ions into *trans*-diisorhodanato-diethylenediamino-cobaltic ion [A. Werner, *Ann.*, **386,** 1 (1912)]. (*b*) *trans*-Chloro-isorhodanato-diethylenediamino-cobaltic salts are converted by hydroxide ions (aqueous ammonia solution) into *cis*-hydroxoisorhodanato-diethylenediamino-cobaltic salts. Likewise, the auto-racemization observed in some of the inorganic complex compounds may be due to the same mechanism as the racemization of  $\overset{a}{\underset{b}{>}}\text{CH—Hal}$ by halogenide ions, *e. g.*, the autoracemization of dichloro-diethylenediamino-cobaltic chloride to the substitution of the inner chloro atoms by negative chloride ions. [Werner, *Ber.*, **44,** 3279 (1911); **45,** 3294 (1912), suggested that the racemization is caused by aquation, but this has never been proved by isolation of a chloroaquo-diethylenediamino-cobaltic salt.] Of course, we cannot predict whether all the known cases fit into our simple scheme, but we hope to come to some definite conclusions in the course of our further investigations on Walden inversion.

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[1] It may be added that the afore-mentioned inorganic complex salt has an octahedral, not a tetrahedral, structure, but the theory should really be extendable to this case.