amount of dilute sulfuric acid, the mixture filtered and the filtrate evaporated to dryness *in vacuo*. The resulting sirup crystallized when triturated with alcohol; m. p. 148–150° after drying *in vacuo* at 75°. The pH of a 1% solution was 3.5 and the pK'_2 value (calcd. from the titration curve) was 4.2.

Anal. Calcd. for $C_6H_{11}NO_4$: C, 44.71; H, 6.88; neut. eq., 161.2. Found: C, 44.58; H, 6.83; neut. eq., 161.5 (potentiometric titration).

Recrystallization from methanol raised the melting point to 151–151.5°.

Monoammonium Salt of β,β'-Iminobispropionic Acid.—This compound was prepared from the crude monobarium salt and ammonium sulfate as previously indicated.' It crystallized readily from concentrated aqueous solutions when diluted with methanol, but less satisfactorily when ethanol was used; m. p. 172–176°, after two recrystallizations from aqueous methanol.

Anal. Calcd. for $C_6H_{14}N_2O_4$: C, 40.44; H, 7.92; N, 15.72. Found: C, 40.22; H, 8.12; N, 15.45.

Acknowledgment.—The author wishes to thank Mr. Anthony Bucci for technical assistance and Messrs. Harold Emerson and William A. Struck for the microanalyses.

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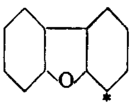
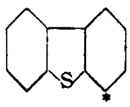
Competitive Metalations of Some Related Heterocycles[1]

BY HENRY GILMAN AND C. G. STUCKWISCH

In connection with the metalation of polynuclear systems having more than one hetero element it was desirable to have information on the rates of metalation of related heterocycles containing oxygen, sulfur and nitrogen, respectively. For this purpose, comparisons are best made with dibenzofuran (I), dibenzothiophene (II) and N-ethylcarbazole (III) inasmuch as each of these related heterocycles is known to undergo metalation by n-butyllithium in the 4-position (indicated by an asterisk).


(I)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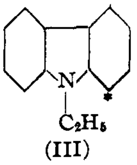
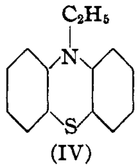

(III)

Three different procedures can be used to establish the relative effects of the hetero elements. First, the rates of metalation can be determined for each heterocycle. Second, competitive reactions can be run with two of the types, using an insufficient quantity of the metalating agent. Third, the preformed RLi compound from one of the heterocycles can be brought into reaction with another heterocycle which is not substituted to determine the extent of interchange. By these procedures, it has been shown[2] that I is metalated more readily than II. The least readily metalated type is III. For example, when a mixture of one equivalent of dibenzothiophene and one equivalent of N-ethylcarbazole was allowed to compete for but one equivalent of n-butyllithium, the only compound metalated after a six-hour period of reaction was dibenzothiophene. In support of this finding, other independent experiments showed that II was metalated by 4-N-ethylcarbazolyllithium, and that III was not metalated by 4-dibenzothienyllithium.

Accordingly, the order of decreasing ease of metalation by n-butyllithium of related heterocycles containing oxygen, sulfur, and nitrogen is: oxygen > sulfur > nitrogen. A striking illustration of the relative effects of oxygen and sulfur is found in dibenzo-p-dioxin and thianthrene: the di-oxygen heterocycle undergoing more rapid metalation by RLi compounds than its di-sulfur analog.[3] Also, phenoxathiin, which has a symmetrically disposed oxygen atom and sulfur atom, is metalated *ortho* to the oxygen.[2]

It was suggested recently,[4] in the absence of rigorous experimental evidence, that the metalation of N-ethylphenothiazine (IV) by n-butyllithium probably involves the position *ortho* to sulfur, most of the other positions having been eliminated by either synthesis or degradation. The present evidence of the greater influence of sulfur over nitrogen lends a high degree of plausibility to this assumption.


(IV)

The validity of the generalizations now reported is confined to comparisons of a selected metalating agent which metalates in corresponding positions. For example, N-ethylcarbazole is mercurated more readily than dibenzofuran, but mercuration of N-ethylcarbazole involves the 2-position and mercuration of dibenzofuran involves the 4-position.[5] Also, N-ethylphenothiazine is mercurated with great ease and metalated by n-butyllithium with difficulty; but in the former case the 3-position is involved, and in the latter case the position involved is definitely not 3 and is probably 4.

Experimental

Dibenzothiophene and N-Ethylcarbazole with n-Butyllithium.—A mixture of 0.051 mole of n-butyllithium in 200 cc. of ether was refluxed for six hours with an equivalent each of dibenzothiophene and N-ethylcarbazole. The acid isolated subsequent to carbonation was free of nitrogen, and the yield of pure 4-dibenzothiophenecarboxylic acid obtained after crystallization was 40%. Identification was established, as usual, by the method of mixed melting points with authentic acid and methyl ester.

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[1] Paper LIX in the series "Relative Reactivities of Organometallic Compounds": the preceding paper is Gilman, Haubein, O'Donnell and Woods, THIS JOURNAL, 67, (June) (1945).

[2] Gilman, Van Ess, Willis and Stuckwisch, THIS JOURNAL, 62, 2606 (1940).

[3] Gilman and Stuckwisch, *ibid.*, 65, 1461 (1943).

[4] Gilman, Van Ess and Shirley, *ibid.*, 66, 1214 (1944).

[5] Gilman and Kirby, *J. Org. Chem.*, 1, 146 (1936). In this paper is a report of the non-metalation of N-ethylcarbazole by 4-dibenzofurylpotassium. This is a reaction that fits in with the generalization that an oxygen-heterocycle is more readily metalated than a related nitrogen-heterocycle. See, also, Gilman and Lister, THIS JOURNAL, 67, (1945), for the different positions involved in the mercuration and metalation by n-butyllithium of N-phenylcarbazole.

Dibenzothiophene and 4-N-Ethylcarbazolyllithium; and 4-Dibenzothienyllithium and N-Ethylcarbazole.—The solution of 4-N-ethylcarbazolyllithium prepared by refluxing 0.045 mole of *n*-butyllithium in 200 cc. of ether for twenty hours with an equivalent of N-ethylcarbazole was shown to be free of *n*-butyllithium by two tests. The first of these established the absence of *n*-valeric acid when an aliquot was carbonated. The second was a negative color test II.[6] Then 0.045 mole of dibenzothiophene was added and refluxing was continued for six hours. Oxidation of the acid (which gave no nitrogen test) yielded 20% of 4-dibenzothiophenecarboxylic-5-dioxide acid, but no 4-N-ethylcarbazolecarboxylic acid.

From a corresponding reaction between 4-dibenzothienyllithium and N-ethylcarbazole, there was isolated 46% of 4-dibenzothiophenecarboxylic acid but no 4-N-ethylcarbazolecarboxylic acid.

Metalation of Dibenzofuran by Ethyllithium, *n*-Propyllithium and *n*-Butyllithium.—In order to determine the more effective metalating agent, a preliminary examination was made of the extent of metalation of dibenzofuran by these RLi compounds under corresponding conditions. It was found that the highest yield (63%) of 4-dibenzofurancarboxylic acid,[7] subsequent to carbonation, was obtained when *n*-butyllithium was used. With *n*-propyllithium the yield was 61%, and with ethyllithium the yield was 50%. This order is in general agreement with that noted earlier for the ethyl and *n*-butyl compounds in a study[8] concerned largely with branched-chain alkyllithium compounds.

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[6] Gilman and Swiss, THIS JOURNAL, **62**, 1847 (1940).

[7] A by-product of all the carbonations was bis-(4-dibenzofuryl) ketone, the yield of which reached 7.8% in some experiments.

[8] Gilman, Moore and Baine, THIS JOURNAL, **63**, 2479 (1941).

DEPARTMENT OF CHEMISTRY
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RECEIVED FEBRUARY 5, 1945

The Unit Cell and Space Group of Potassium Tetrachlorozincate

BY HAROLD P. KLUG AND GEORGE W. SEARS, JR.

In the studies of halogen complexes with certain elements under way in this Laboratory, potassium tetrachlorozincate, K_2ZnCl_4, was investigated with the hope that it might supply information concerning the coördination of chlorine around zinc, and the nature of the groups present in the crystalline tetrachlorozincates. Although the compound proved unsatisfactory for the complete study, certain results were obtained which are reported in this communication.

The salt was prepared by crystallization from aqueous solutions of mixtures of the component salts, KCl and $ZnCl_2$, as described by Marignac,[1] who made numerous angular measurements on the crystals. Steinmetz[2] made optical measurements on it and observed its cleavage parallel to (010). Groth[3] described the crystals as prismatic along the *c* axis, and belonging to the rhombic bipyramidal class. He reported the axial ratios $a:b:c = 0.7177:1:0.5836$, and the density to be 2.297. The identity of the prepared salt was verified by angular measurements in the [*hk*0] zone, and by chemical analysis for zinc and chlorine. *Anal.* Calcd. for K_2ZnCl_4: Zn, 22.91; Cl, 49.70. Found: Zn, 22.80, 22.77; Cl, 49.54, 49.55. A redetermination of the density was made by suspension in a liquid of equal density. Three separate determinations gave an average value of 2.364, which is somewhat higher than the value reported by Groth.

Preliminary layer line measurements on rotation photographs led to the cell edges a_0 = 8.90 Å., b_0 = 12.26 Å., c_0 = 7.28 Å., and a cell containing 4 K_2ZnCl_4. These values correspond to axial ratios $a:b:c = 0.726:1:0.5935$ in good agreement with Groth's values. However, closer inspection of the photographs about *a* revealed what appeared to be faint spots at distances of one-third and two-thirds that of the obvious layer lines. Much longer exposures definitely revealed fainter layer lines which necessitated the tripling of a_0 and the volume of the cell. The final values are a_0 = 26.70 Å., b_0 = 12.26 Å., c_0 = 7.28 Å., and 12 K_2ZnCl_4 per cell. The true axial ratios from these values are: $a:b:c = 2.178:1:0.5935$.

Laue photographs, analyzed by means of gnomonic projections, showed all types of pyramid planes to be present in the first order. The underlying lattice is thus simple primitive. The only first-order prism absence noted was (*h*0*l*) when *h* is odd. The space group symbol is thus *Pmam* if the crystal has a center of symmetry. A pyroelectric test by the method of Martin[4] revealed a decided positive pyroelectric effect with the *c* axis the polar axis. The true space group symbol then is *Pma*2 and the space group is $C_{2v}^4 - Pma$.[5]

With a non-centrosymmetrical space group and a twelve molecule cell it did not seem profitable to pursue the investigation further.

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[1] Marignac, *Ann. Min.*, [5] **12**, 15 (1857).

[2] Steinmetz, *Z. Krist.*, **56**, 166 (1921).

[3] Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1906, Vol. I, p. 342.

[4] Martin, *Min. Mag.*, **22**, 519 (1931).

[5] "International Tables," Vol. I, p. 105.

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RECEIVED FEBRUARY 13, 1945

Schiff Bases from Benzaldehyde and *o*-Aminophenols

BY L. CHAS. RAIFORD[1] AND JACOB LINSK[2]

Ehmke[3] condensed ortho-aminophenol with a number of substituted benzaldehydes and prepared derivatives. In the present work the condensation reaction was extended and eight Schiff bases were prepared from benzaldehyde and substituted *o*-aminophenols. In the preparation of derivatives some tendency to hydrolysis was noted. 2-Benzalamino-4-bromophenol and 6-ben-

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[1] Deceased Jan. 8, 1944.

[2] (a) Extracted from the Master's thesis of Jacob Linsk, August, 1941. (b) Present address: Research laboratory, George A. Breon and Co., Kansas City, Missouri.

[3] Ehmke, Master's thesis, State University of Iowa, 1940.