minutes, the suspended material had dissolved and the solution began turning yellow. The chlorination was stopped after one hour. A small amount of a yellow crystalline material was filtered. (The entire apparatus was kept at 0–5°.) It was apparently chlorine hydrate, m. p. 10°. The filtrate was refrigerated (10–15°) over the week-end. No oil was present, so the solution was chlorinated for fifteen minutes. Separation of a heavy yellow oil took place. Approximately 4 or 5 ml. of the oil were drained from a separatory funnel into a vial. The substance exploded immediately.

**S-Ethyl Isothiourea Sulfate.**—This was prepared by the method of Sprague and Johnson,[1] using 76 g. of thiourea and 85 g. of diethyl sulfate. The yield of S-ethyl isothiourea sulfate was 102 g.

**Reaction of Chlorine on S-Ethyl Isothiourea Sulfate.**—The S-ethyl isothiourea sulfate (102 g.) was suspended in 350 g. of ice and water and stirred mechanically. After cooling to 5°, chlorine was passed in until the mixture had become yellow-green and a heavy oil had separated, while the mixture was kept below 10°. This required about ten hours. Stirring was continued for half an hour after the chlorination was stopped. The flask was then removed from the cooling bath, approximately ten minutes previous to the explosion. The explosion occurred as the flask was grasped preparatory to removal from the clamp holding it.

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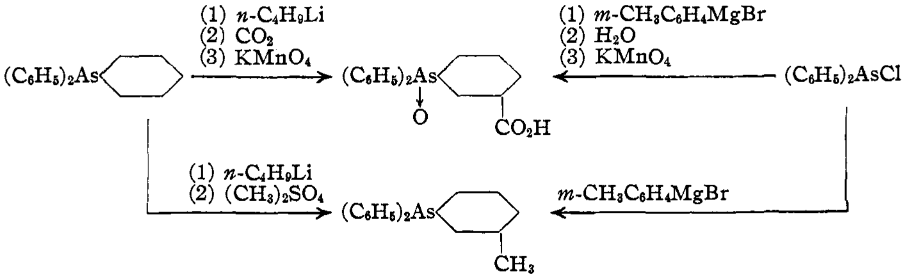
## Metalation of Triphenylarsine

BY HENRY GILMAN AND CLARENCE G. STUCKWISCH

The metalation of triphenylamine by *n*-butyllithium takes place in a meta position,[1a] and not ortho as might have been predicted on the basis of earlier general observations.[1b,c] This anomalous orientation suggested an examination of the metalation of the related triphenylarsine. Here, also, metalation occurred in a meta position, and the structures of the products were established by the reactions



By analogy with N-phenylcarbazole,[1c] it is to be expected that metalation of As-phenyldibenzarsenole will take place in an ortho position of the As-phenyl group.

### Experimental

**Triphenylarsine and *n*-Butyllithium.**—A solution of 20 g. (0.10 mole) of triphenylarsine and 0.25 mole of *n*-butyllithium in 500 ml. of ether was stirred and refluxed for forty-eight hours. The resulting solution was poured jetwise on solid, crushed carbon dioxide and the carbon dioxide allowed to evaporate. The ether solution was extracted with 10% potassium hydroxide. Acidification of the alkaline extract yielded 0.5 g. of a gummy, acidic material which could not be crystallized.

***m*-Carboxyphenyldiphenylarsine Oxide.**—The gummy material obtained from the metalation of triphenylarsine was dissolved in 10 ml. of acetone and refluxed for thirty minutes with 1 g. of potassium permanganate, in accordance with the directions of Blicke[2] for the conversion of arsines to arsine oxides. After cooling, the solution was diluted with water and acidified with hydrochloric acid. The solid which separated was filtered off and crystallized from dilute ethanol; m. p. 215°.

*Anal.* Calcd. for $C_{19}H_{15}O_3As$: neut. equiv., 266; As, 20.5. Found: neut. equiv., 262; As, 20.3.

***m*-Tolyldiphenylarsine.**—To the Grignard reagent from 17.7 g. (0.1 mole) of *m*-bromotoluene and 2.5 g. of magnesium in 60 ml. of ether was added dropwise 12 g. (0.05 mole) of diphenylchloroarsine in 50 ml. of ether. After addition was completed the solution was refluxed for one hour, cooled in an ice-bath, and hydrolyzed with dilute hydrochloric acid. The ether layer was dried and the ether was evaporated. The residue was distilled at 3 mm. The yield of *m*-tolyldiphenylarsine distilling at 170–173° (3 mm.) was 11.5 g. or 72%.

*Anal.* Calcd. for $C_{19}H_{17}As$: As, 20.8. Found: As, 20.6.

The mercuric chloride derivative crystallized in colorless plates from glacial acetic acid and melted at 201–202°.

**Oxidation of *m*-Tolyldiphenylarsine.**—A mixture of 6.4 g. (0.02 mole) of *m*-tolyldiphenylarsine and 250 ml. of water saturated with potassium permanganate was heated on an oil-bath at 60° for four weeks. The excess permanganate was removed with ethanol. The solution was then filtered and the filtrate acidified with hydrochloric acid. The solid which separated melted at 213–214° after crystallization from dilute ethanol. A mixed melting point with the product of the oxidation of the acidic material obtained from the metalation and subsequent carbonation of triphenylarsine gave no depression.

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(1) (a) Gilman and Brown, THIS JOURNAL, **62**, 3208 (1940); (b) Gilman and Bebb, *ibid.*, **61**, 109 (1939); (c) Gilman, Stuckwisch and Kendall, *ibid.*, **63**, 1758 (1941).

(2) Blicke and Safir, *ibid.*, **63**, 575 (1941).

**Methylation of Metalation Product.**—When the *n*-butyllithium metalation product of triphenylarsine was treated with methyl sulfate a 2.7% yield of *m*-tolyldiphenylarsine was obtained. Its mercuric chloride derivative, melting at 201°, was identical with that obtained from *m*-tolyldiphenylarsine described above.

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## Hydrated Lithium Aluminum Sulfate (Lithium Alum)

BY HAROLD A. HORAN AND JOHN J. DUANE

In the course of additional work on the ternary system $Li_2SO_4$–$Al_2(SO_4)_3$–$H_2O$ at 0° aimed at determining the degree of hydration of aluminum sulfate in equilibrium with saturated solutions, which will be reported later, an invariant point with solution composition differing from the previously reported one[1] has been found. Careful investigation of the region between these invariant points clearly shows the existence of a third phase in the system. Figure 1 is a photograph of this solid, its appearance being unlike that of either hydrated lithium or aluminum sulfates. The existence of lithium alum has been referred to before.[1,2,3] The present evidence clearly indicates the formation of a double salt of composition closely approximating $LiAl(SO_4)_2\cdot12H_2O$, which might be called lithium alum if the crystals are shown to have a structure similar to the other alums.

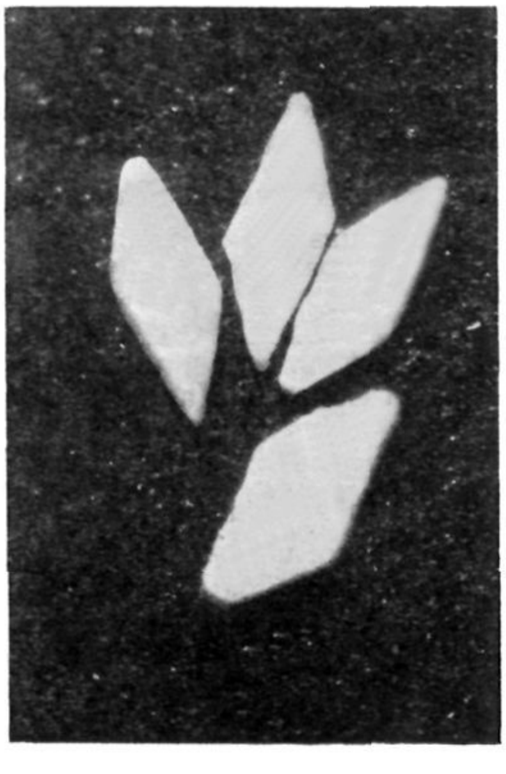

Fig. 1.—Hydrated lithium aluminum sulfate (×10).

Kralovansky, in 1828, may have found lithium alum, but many investigators since that time have been unable to repeat his work. The general opinion up to the present time is that lithium does not (and even cannot) form an alum.

### Experimental

The methods used are essentially those of the previous investigation,[1] the only difference being the use of an analyzed concentrated solution of purified aluminum sulfate in making up the complexes. This locates the original complex with greater certainty. The wet residues are the corresponding solids, quickly separated from the solutions and centrifuged. The experimental data are given in Table I and the values are represented graphically in Fig. 2. The latter is only part of the isotherm, for obvious reasons.

TABLE I

PARTIAL ISOTHERM AT 0° FOR $Li_2SO_4$–$Al_2(SO_4)_3$–$H_2O$

| Solution | | Original complex | | Wet residue | | |
|---|---|---|---|---|---|---|
| Wt. % $Al_2(SO_4)_3$ | Wt. % $Li_2SO_4$ | Wt. % $Al_2(SO_4)_3$ | Wt. % $Li_2SO_4$ | Wt. % $Al_2(SO_4)_3$ | Wt. % $Li_2SO_4$ | Solid phase |
| 16.66 | 14.65 | 17.96 | 18.98 | ... | ... | I |
| 16.63 | 14.59 | 20.06 | 17.01 | ... | ... | I |
| 17.23 | 14.11 | 22.45 | 13.68 | 34.75 | 12.60 | II |
| 17.31 | 13.94 | 23.38 | 13.59 | 33.82 | 12.66 | II |
| 17.85 | 13.28 | 23.96 | 13.10 | 37.65 | 12.47 | II |
| 18.05 | 13.02 | 22.11 | 12.52 | ... | ... | III |
| 18.07 | 13.07 | 22.62 | 12.16 | ... | ... | III |
| 18.05 | 13.08 | 23.91 | 11.18 | ... | ... | III |

The solid phases represented by the numerals I, II and III are respectively: $Li_2SO_4\cdot1H_2O + LiAl(SO_4)_2\cdot12H_2O$, $LiAl(SO_4)_2\cdot12H_2O$ and $LiAl(SO_4)_2\cdot12H_2O + Al_2(SO_4)_3\cdot nH_2O$ (*n* not determined in this study).

Algebraic extrapolations[4] of the tie lines through the compositions of the saturated solutions, the original complexes and the wet residues to the theoretical $Al_2(SO_4)_3$ value in $LiAl(SO_4)_2\cdot12H_2O$, give $Li_2SO_4$ values all within 0.2% absolute of the theoretical $Li_2SO_4$ value demanded by this formula (point A, Fig. 2).

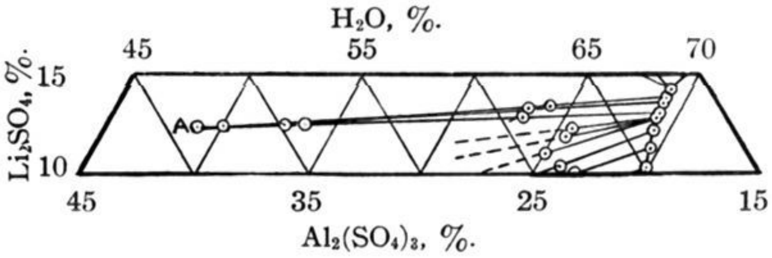

Fig. 2.—Partial isotherm 0°: $Li_2SO_4$-$Al_2(SO_4)_3$-$H_2O$.

Several samples of the unwashed solid, free from most of the adherent solution, were analyzed for

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(1) Horan and Skarulis, THIS JOURNAL, **61**, 2689 (1939).

(2) Kralovansky, *J. für. Chem. und Physik*, **54**, 347 (1828).

(3) Rammelsberg, *Sitzgber. preus. Akad. Wiss., Berlin*, 385 (1848).

(4) Hill and Ricci, THIS JOURNAL, **53**, 4306 (1931).