cellent paper on cocarboxylase has appeared. In that paper it was suggested that the use of silver might be avoided.

Acknowledgments.—I wish to express my appreciation to Dr. R. T. Major and Dr. J. R. Stevens for advice and interest; to Mr. Harold Levy for general assistance. The analytical work was carried out by Messrs. D. F. Hayman, W. Reiss and Harold Levy.

Summary

An improved process for the synthesis of cocarboxylase chloride has been presented as well as evidence indicating that cocarboxylase is stable under normal conditions except slight loss of water of crystallization.

RAHWAY, N. J. RECEIVED JANUARY 28, 1941

NOTES

Polymorphic Forms of Substituted Phenols

BY RICHARD T. ARNOLD, HAROLD KLUG, JOSEPH SPRUNG AND HAROLD ZAUGG

In connection with the research on another problem, we prepared 6-hydroxytetralin (β-tetralol) by fusion of the sodium sulfonate with alkali according to Schroeter.[1] This sample of tetralol melted at 53–54° in contrast to the reported value of 62°. It formed transparent, huskily built crystals when precipitated from low-boiling ligroin.

Another sample of β-tetralol from the decomposition of 6-tetralin diazonium chloride melted at 62° and formed opaque needles from low-boiling ligroin.

If a large crystal of the form melting at 54° was brought into contact with one fine needle of the 62° modification, it turned opaque at the point of contact and this opaque boundary passed across the crystal so that in about five minutes the transformation was complete. The resulting melting point of the big crystal was then 62°.

Using a Buerger[2] precision powder camera of 57.3 mm. radius, powder photographs were taken at room temperature using Fe K_α radiation. The powder samples were extruded rods of powder crystals prepared in the device described by Lukesh[3] using LePage's glue as a binder. The following photographs were taken: (a) 54° form, (b) 62°—from 54° by contact with 62° form, (c) 62° form. Both (b) and (c) were identical and different from (a).

In a similar manner 4-hydroxyhydrindene has been obtained in two crystalline forms. The first, m. p. 39.5–40°, was produced by alkali fusion of the sodium sulfonate and precipitated from ligroin in needles.

From the 4-hydrindenediazonium chloride we obtained 4-hydrindenol melting at 49–50° as described by Linder.[4]

Powder photographs of these two forms showed them to be entirely different. The melting point of the low-melting form (39.5–40°) was raised to 49–50° by contact with the 49–50° modification.

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(1) Schroeter, *Ann.*, **426**, 120 (1922).

(2) Buerger, *Am. Mineral.*, **21**, 11–17 (1936).

(3) Lukesh, *Rev. Sci. Instruments*, **11**, 200 (1940).

(4) Linder, *Monatsh.*, **72**, 219 (1939).

UNIVERSITY OF MINNESOTA
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p-(*p*-Aminophenyl)-benzenesulfonamide

BY CONARD K. DONNELL, JAMES H. DIETZ AND WILLIAM T. CALDWELL

Recently Van Meter, Bianculli and Lowy[1] reported the preparation of *p*-(*p*-aminophenyl)-benzenesulfonamide from *p*-aminobiphenyl. We, too, had prepared this compound in the same way with results essentially like theirs; however, we determined the orientation of the sulfonamide group differently by means of an independent synthesis from *p*-nitrobiphenyl, a synthesis which is, of course, equally applicable to the preparation of other N′-substituted sulfanilamides. The structure of the requisite intermediate *p*-(*p*-nitrophenyl)-benzenesulfonic acid was proved by Gabriel and Dambergis,[2] by showing that the same product is obtained upon sulfonation of *p*-nitrobiphenyl as upon nitration of *p*-phenyl-

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(1) Van Meter, Bianculli and Lowy, THIS JOURNAL, **62**, 3146 (1940).

(2) Gabriel and Dambergis, *Ber.*, **13**, 1410 (1880).

benzenesulfonic acid; accordingly, since the *p*-(*p*-aminophenyl)-benzenesulfonamide prepared from this was identical with that obtained from *p*-aminobiphenyl, the structure of the latter was established.

***p*-(*p*-Nitrophenyl)-benzenesulfonyl Chloride.**—This compound was prepared by the method of Gabriel and Dambergis[2] and also by adding, with good stirring, *p*-nitrobiphenyl to two and one-half moles of chlorosulfonic acid at a temperature below 15°, then allowing the temperature to rise to that of the room and finally to 60° for two hours. The dark, sirupy liquid was then poured, with vigorous stirring, into a slush of ice. After filtering, pressing out on a porous plate and recrystallizing from acetic acid, the yellow crystals melted at 178°, the melting point given by Gabriel and Dambergis,[2] yield 94%.

***p*-(*p*-Aminophenyl)-benzenesulfonamide.**—To 10 g. of *p*-(*p*-nitrophenyl)-benzenesulfonamide[2] dissolved in 200 cc. of ethanol, were added 8 g. of tin and 50 cc. of concd. hydrochloric acid. After heating for one and one-half hours, the material was neutralized with sodium hydroxide, diluted to a volume of 600 cc. and acidified with 15 cc. of concd. hydrochloric acid. The tin sulfide precipitated by hydrogen sulfide was removed by filtration, the filtrate made alkaline with ammonium hydroxide and the product so obtained was purified by recrystallization from ethanol; m. p. 263° (cor.), unchanged when mixed with product prepared from *p*-aminobiphenyl, yield, 3.1 g.

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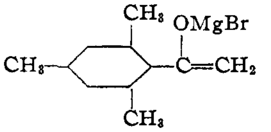
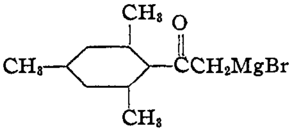
Metallic Derivatives of Acetomesitylene

BY HENRY GILMAN AND R. G. JONES

Bromomagnesium derivatives of sterically hindered ketones, like acetomesitylene, give enolates (A) which behave like true organomagnesium compounds (B)[1]


(A)


(B)

In view of the extensive studies by Fuson and co-workers and Kohler and co-workers[1b] on the reaction of these bromomagnesium types with the carbonyl group, one might have predicted a positive Michler ketone color test.[2a] We have found that the bromomagnesium derivative of acetomesitylene does give this color test. The bromomagnesium compound was prepared from phenylmagnesium bromide and an excess of acetomesitylene. Phenylmagnesium bromide was selected in preference to an alkylmagnesium halide because the recently described[2b] Color Test III differentiates between reactive *aryl*metallic compounds and *alkyl*metallic types. In this manner, any uncertainty concerning the influence of phenylmagnesium bromide is ruled out, for the negative test with triphenylbismuth dichloride (Color Test III) showed the absence of phenylmagnesium bromide in the bromomagnesium compound prepared from it and acetomesitylene.

Of greater interest are the metallic derivatives prepared from RLi and RNa compounds. If acetomesitylene is an equilibrium mixture of the keto and enol forms, the more reactive organolithium[2c] and organosodium[2d] compounds might be expected to add appreciably to the carbonyl group. The large quantities of acetomesitylene recovered subsequent to hydrolysis belied any significant addition.[3] Furthermore, acetomesitylene with excess methyllithium evolved essentially the theoretical volume of methane.

Both the lithium and sodium derivatives of acetomesitylene gave a positive Michler ketone test. Unlike the bromomagnesium salt, the lithium compound is completely soluble in ether.

If a formula like (B) is correct for the lithium and sodium derivatives of acetomesitylene, it is not novel to find within a molecule a carbonyl group and a reactive C-M linkage for C-Li linkages have been prepared recently in molecules containing reactive anil and carbonyl groups.[4a] It is improbable that coördinate compounds are formed in the Michler ketone color tests with the lithium and sodium derivatives.[4b]

Experimental Part

Phenylmagnesium Bromide.—A solution of 4.87 g. (0.030 mole) of acetomesitylene in 25 cc. of ether was added to 10 cc. of 2.40 molar phenylmagnesium bromide. After refluxing for one hour the mixture was allowed to cool. Both the white crystalline solid and the clear supernatant

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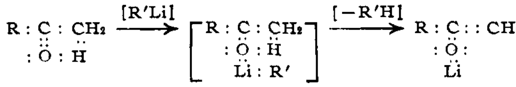
(1) (a) Malmgren, *Ber.*, **36**, 2608 (1903). (b) Fuson, Fugate and Fisher, THIS JOURNAL, **61**, 2362 (1939). This article contains references to earlier work, particularly by Kohler and co-workers and Fuson and co-workers.

(2) (a) Gilman and Schulze, *ibid.*, **47**, 2002 (1925). (b) Gilman and Yablunky, *ibid.*, **63**, 839 (1941). (c) Gilman and Kirby, *ibid.*, **55**, 1265 (1933). (d) Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).

(3) It is possible that the lithium and sodium atoms first added to the oxygen of the carbonyl form; then the enolate developed with the accompanying formation of R'H, the hydrogen coming from the methyl group and the R' from the initial R'Li or R'Na compound



(4) (a) Gilman and Spatz, THIS JOURNAL, **62**, 446 (1940). (b) Gilman and Jones, *ibid.*, **62**, 1243 (1940).