

nitric acid and the lead was determined. The analytical data for the two experiments are given in Table III.

TABLE III  
LEAD ANALYSIS

Input	Pb found, g.	
	Test 1	Test 2
R <sub>4</sub> Pb (Hexane solution)	57.8640	60.7935
Recovery		
R <sub>4</sub> Pb, R <sub>3</sub> PbCl (Hexane solution)	55.5530	58.8735
R <sub>4</sub> Pb, R <sub>3</sub> PbCl (Hexane washings)	1.4430	1.5290
R <sub>3</sub> PbCl (NH <sub>3</sub> extraction)	0.2133	0.3691
R <sub>3</sub> PbCl (Benzene washings)	.5670	.5362
PbCl <sub>2</sub>	.0440	.0639
Residue (HNO <sub>3</sub> washings)	.0030	.0015

**Determination of Lead Chlorides Formed with Different Catalysts.**—The determination of the amount of tetraalkyllead compounds converted to alkyllead chlorides and lead chloride using different aluminum catalysts was carried out in the following manner.

To a weighed amount of the catalyst, contained in a 500-ml. 3-necked flask equipped with vapor-proof mechanical stirrer, thermometer, and reflux condenser, the tetraethyllead followed by the tetramethyllead was added slowly from a dropping funnel in the top of the condenser. The flask was cooled in an ice-bath and an atmosphere of nitrogen was maintained within the flask during the addition of the alkyllead compounds. Failure to follow the experimental procedure and precautions outlined above may result in violent decomposition of the tetraalkyllead, especially of the tetramethyllead. The ice-bath was then removed and replaced by an oil-bath; the mixture was stirred and maintained at 80° in an atmosphere of nitrogen for two hours.

The reaction flask was then cooled and the catalyst decomposed by shaking with 100 ml. of distilled water. The aqueous layer, containing alkyllead chlorides and lead

chloride, was separated, filtered through a wet filter paper and analyzed for lead. The alkyllead layer was extracted with four 25-ml. portions of concentrated ammonia solution, to remove trialkyllead chlorides. The extracts were combined, filtered through a wet filter paper, and analyzed for lead. The filter papers were finally washed with nitric acid to dissolve any lead residue, and the washings were analyzed for lead.

The alkyllead layers were finally distilled to ascertain the extent of redistribution. The reaction was complete in every case. Table IV gives the analyses of products for lead chlorides.

TABLE IV  
LEAD ANALYSIS

Products	Catalyst		
	Me <sub>3</sub> AlCl	MeAlCl <sub>2</sub>	AlCl <sub>3</sub>
Pb in Aq. layer, g.	0.1296	0.3150	0.9220
Pb in NH <sub>3</sub> , g.	.0000	.0926	.0193
Pb in residue, g.	.0000	.0000	.0000
Pb (total), g.	.1296	.4076	.9413

### Summary

By determination of an accurate material balance, the redistribution of a mixture of tetramethyl- and tetraethyllead in hexane solution is shown to be quantitative. When aluminum chloride is used as the catalyst, it is found to react irreversibly with the alkyllead compounds, as expected, forming alkyllead chlorides in very small quantities, equivalent to about 1.5 moles per mole of catalyst. When methylaluminum chlorides are used as catalysts, this amount becomes negligible.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Reaction of the Grignard Reagent with Homophthalic Anhydride

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The reaction of methylmagnesium iodide with homophthalic anhydride has been investigated as a possible method for the preparation of the unreported keto acid, *o*-acetylphenylacetic acid (I), which was desired in connection with another investigation.

Bauer and Wolz,<sup>1</sup> in determining the products from the action of an excess of several Grignard reagents on homophthalic anhydride, obtained only the various homophthalides. Since Simonis and Arand and Weizmann, Bergmann and Bergmann<sup>2</sup> have reported keto acids as well as phthal-

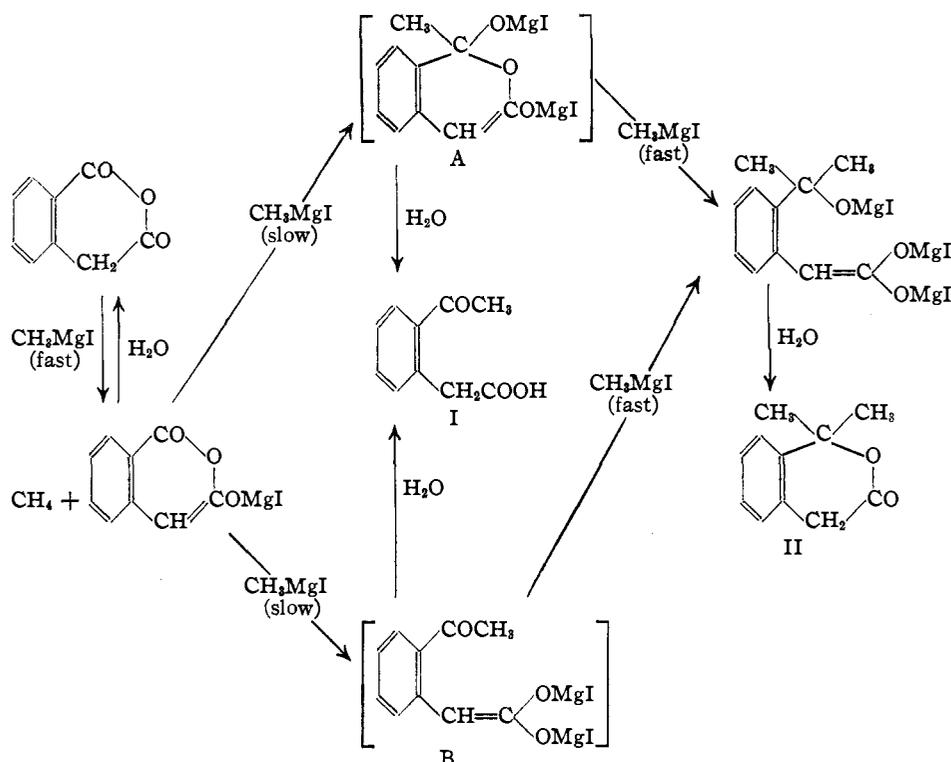
ides from phthalic anhydride, the reaction with homophthalic anhydride has been studied under conditions more favorable for the formation of the desired keto acid. However, in spite of using the inverse procedure, *i. e.*, adding the Grignard reagent to a solution of the anhydride, and using just the calculated amount of reagent, one-half of the starting material was converted to dimethylhomophthalide (II), the remainder was recovered unchanged. No *o*-acetylphenylacetic acid was obtained, although in a few cases the recovered homophthalic acid had a low melting point and gave an iodoform test, indicating the possible presence of small amounts of this substance.

(1) Bauer and Wolz, *Arch. Pharm.*, **249**, 454 (1911).

(2) (a) Simonis and Arand, *Ber.*, **42**, 3721 (1909); (b) Weizmann, Bergmann and Bergmann, *J. Chem. Soc.*, 1369 (1935).

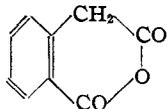
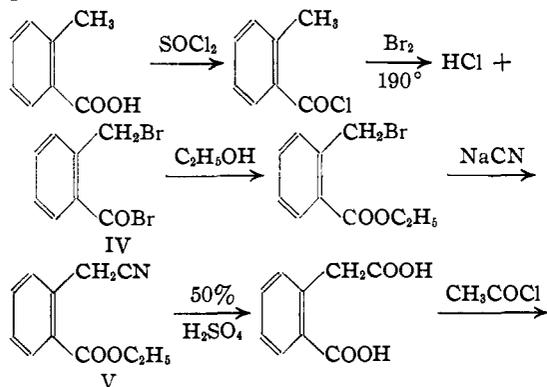
Since the anhydride enolizes readily, the first mole of Grignard reagent is converted to methane. The theoretical amount of reagent for the formation of the keto acid is, therefore, two moles. The non-formation of the keto acid by the second mole of reagent under these conditions indicates that the reaction must follow either of the two courses outlined below.

The latter acid is converted to its acid chloride and brominated according to the directions of Davies and Perkin.<sup>3</sup> Treatment with alcohol and sodium cyanide converted the bromo acid bromide (IV) to the nitrile ester (V) of homophthalic acid. Hydrolysis to the acid was accomplished by warming with 50% sulfuric acid. The preparation is relatively simple since the first product



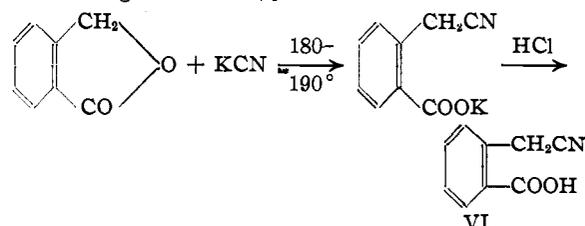
It is the opinion of the authors that the reaction through intermediate A is the more likely.

A procedure for the preparation of homophthalic acid from *o*-toluic acid has been de-



isolated is the nitrile-ester and the over-all yield from *o*-toluic acid to homophthalic anhydride is 70-75% of the theoretical.

Another simple preparation, which apparently has been neglected, is that reported by Wislicenus<sup>4</sup> starting from phthalide. The yield of acid nitrile obtained in this Laboratory by this method was as high as 80-85%.



### Experimental

*o*-Carbethoxyphenylacetonitrile (V).—*o*-Toluic acid (100 g.) was refluxed for two hours with twice the theoretical

(3) Davies and Perkin, *J. Chem. Soc.*, 121, 2202 (1922).

(4) Wislicenus, *Ber.*, 17, 2178 (1884).

quantity of thionyl chloride. After the excess thionyl chloride had been removed by distillation, the acid chloride was heated to 185–195° in an oil-bath and 135 g. of bromine was added slowly (one to two hours) through a separatory funnel the tip of which was below the surface of the reaction mixture. After cooling in an ice-bath, 200–250 cc. of absolute alcohol was added. The alcoholic solution of the bromoester was then poured into a solution of 40 g. of sodium cyanide in 30 cc. of warm water, the mixture refluxed for five hours and then half the alcohol removed by evaporation or distillation.

The ester was extracted with several portions of ether, the ethereal solution washed three times each with water, with sodium bicarbonate and again with water and then dried over sodium sulfate. Evaporation of the ether left a dark brown oil from which 85–90 g. (71–76%) of colorless material was obtained by distillation (16 mm.), b. p. 170–170.5°. This compound had the following properties:  $d_{20}^{20}$  1.1246;  $n_D^{20}$  1.5172;  $M_D$  calcd., 51.2;  $M_D$  found, 50.8. *Anal.* Calcd.: N, 7.4. Found: N, 7.7.

**Homophthalic Anhydride.**—The hydrolysis of the nitrile and ester groups in the above compound was accomplished readily in over 90% yield by the action of an equal volume of 50% sulfuric acid at 100° for twelve hours. Longer reaction time or higher or lower acid concentration decreased the yield. The reaction mixture was poured over an equal weight of ice and the precipitated acid collected and dried. Conversion to the anhydride was accomplished readily by refluxing a solution of the acid in three times its weight of acetyl chloride for half an hour and precipitating the anhydride with petroleum ether (60–90°). The product was obtained in 90–95% yields and melted at 140–141°.

*o*-Carboxyphenylacetonitrile (VI)<sup>5</sup> was prepared according to the directions of Wislicenus.<sup>1</sup> A mixture of 40 g. of phthalide and 40 g. of potassium cyanide yielded 35 g. (82%) of crystalline acid nitrile, m. p. 114–115°. Seven grams of phthalide was recovered unchanged.

**Experimental Procedure.**—A solution of methylmagnesium iodide was prepared by treating 2 g. of magnesium turnings with 4.7 cc. of methyl iodide and 39 cc. of ether for one hour. The solution, under an atmosphere of

nitrogen at all times, was transferred to a separatory funnel and added to 5 g. of homophthalic anhydride dissolved in ether in a flask equipped with a mechanical stirrer and a reflux condenser. During the addition of the first half of the reagent, methane was evolved with the formation of a yellow precipitate. The time for the addition of the remaining reagent varied from one to six hours, that of subsequent refluxing from three to six hours, and that of standing at room temperature after refluxing from zero to fifteen hours with no appreciable difference in the products of the reaction.

At the end of the specified time, the reaction mixture was poured into ice and 35 cc. of hydrochloric acid. Unreacted homophthalic anhydride precipitated. It was collected, recrystallized from ether and weighed 1.3–1.8 g., m. p. 140–141°. The ether layer in the first filtrate was washed thoroughly with sodium bicarbonate solution. Addition of acid to this bicarbonate extract precipitated homophthalic acid which was dried and weighed 0.4–0.6 g., m. p. 173–175°. In a few cases the precipitated acid melted low and over a wider range and gave an iodoform test indicating the presence of at least a small amount of *o*-acetylphenylacetic acid. The pure keto acid could not be isolated, however.

The ether solution was next dried and evaporated, leaving a neutral yellow oil and white solid. The solid was collected by filtration, washed with a minimum amount of ether and then recrystallized from ether. The white needle-like crystals were weighed 1.9–2.3 g., m. p. 94–95°. The combined ethereal mother liquors were evaporated and the residual yellow oil weighed 0.6–0.8 g. No pure compound was isolated from this material.

### Summary

The addition of the calculated amount of methylmagnesium iodide to homophthalic anhydride does not lead to the formation of a keto acid. Instead one-half of the starting material is recovered unchanged; the other half is converted to dimethylhomophthalide.

(5) This compound was prepared by Richard G. Rogers.