

**BRYN MAWR COLLEGE
MONOGRAPHS.
MONOGRAPH
SERIES, VOL. I, NO. 1-3**

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649378722

Bryn Mawr College Monographs. Monograph series, Vol. I, No. 1-3 by Various

Except for use in any review, the reproduction or utilisation of this work in whole or in part in any form by any electronic, mechanical or other means, now known or hereafter invented, including xerography, photocopying and recording, or in any information storage or retrieval system, is forbidden without the permission of the publisher, Trieste Publishing Pty Ltd, PO Box 1576 Collingwood, Victoria 3066 Australia.

All rights reserved.

Edited by Trieste Publishing Pty Ltd.
Cover @ 2017

This book is sold subject to the condition that it shall not, by way of trade or otherwise, be lent, re-sold, hired out, or otherwise circulated without the publisher's prior consent in any form or binding or cover other than that in which it is published and without a similar condition including this condition being imposed on the subsequent purchaser.

www.triestepublishing.com

VARIOUS

**BRYN MAWR COLLEGE
MONOGRAPHS.
MONOGRAPH
SERIES, VOL. I, NO. 1-3**

U.P.
Unit
B

*Monograph Series, vol I. comp
The Gen. I.P. & Index was for*

BRYN MAWR COLLEGE

MONOGRAPHS



MONOGRAPH SERIES, Vol. 1, Nos. 1-3.

BRYN MAWR, PENNA., U. S. A., JUNE, 1901

The Ford Baltimore Press
THE FRIEDENWALD COMPANY
BALTIMORE, MD., U. S. A.
1901

*106-68
20/11/10*

ANNOUNCEMENT.

The Bryn Mawr College Monographs will be issued in two series: the first, the **Monograph Series**, containing articles that appear here for the first time; the second, the **Reprint Series**, containing reprints of articles that have appeared in other journals.

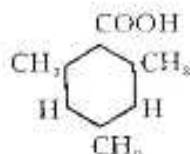
It is proposed to publish these monographs in separate numbers at irregular intervals as material is accumulated. The numbers will be combined into volumes of about 500 pages.

The monographs are edited by a committee of the Faculty of Bryn Mawr College, consisting at present of President M. Carey Thomas, *ex-officio*, Professor Thomas Hunt Morgan (chairman), Professor Charlotte Argas Scott, and Professor Herbert Weir Smyth.

THE POLYBASIC ACIDS OF MESITYLENE

The polybasic acids of the higher homologues of benzene form a field to a great extent unexplored. Of the acids theoretically possible, the most interesting are those derived from mesitylene and the durenes by the introduction of carboxyl groups in place of the hydrogen of the nucleus. In the case of these hydrocarbons, however, only one carboxyl group has so far been introduced. Of the sixteen possible acids derived from mesitylene by successively replacing ring hydrogen atoms with carboxyl groups and subsequently oxidizing the various methyl groups, only five are known.

The object of the following investigation was to prepare and study the three acids derived from mesitylene by replacing the hydrogen atoms of the nucleus with one, two, and three carboxyl groups. The simplest of these acids, mesitylene carbonic acid,



has already been described. It was first prepared in pure condition by Jacobsen,¹ who oxidized isodurene with dilute nitric acid and got a mixture of acids. One of these, "3-isodurylic acid," with a melting point of 151°, is identical with mesitylene carbonic acid. Claus² prepared it later from acetylmesitylene,



which he oxidized with dilute alkaline permanganate to the cor-

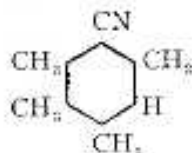
¹ Berichte, 15, 1255.

² Journ. f. prak. Chem. [2], 41, 506.

responding glyoxylic acid, $C_6H_2(CH_3)_2COCOOH$, and then oxidized this further to the mesitylene carbonic acid. Feith,² by heating mesitylene glyoxylic acid in a stream of carbon dioxide, obtained among other substances the same mesitylene carbonic acid. Its acid amide was prepared by Gattermann³ by treating mesitylene with chlor carbonic amide, $ClCONH_2$, and aluminium chloride.

Historically, mesitylene carbonic acid is interesting as the substance whose failure to give an ester when treated with alcohol and hydrochloric acid, first led to a systematic study of di-ortho-substituted compounds and their peculiarities. Victor Meyer,⁴ wishing to make its ester, tried the above-mentioned process, but got so poor a yield that he investigated the cause of the difficulty. After examining a large number of similarly substituted acids, he was led to enunciate his "Ester Law"—that those aromatic acids in which the two positions ortho to the carboxyl group are occupied by substituents other than hydrogen, when treated with alcohol and hydrochloric acid in the cold, give esters in very small quantity or not at all. Conversely, he found⁵ that the esters of such acids, when made by the action of an alkyl halide on their silver salts, are saponified with great difficulty.

Several instances of abnormal behavior in di-ortho-substituted compounds had been recorded before this work of Meyer's, but he first pointed out the cause, and laid down the general principle that di-ortho-substitution profoundly affects the reactivity of any group. For example, A. W. Hofmann⁶ had found that he could not saponify a nitrile of isodurene,



² Berichte, 24, 3544.

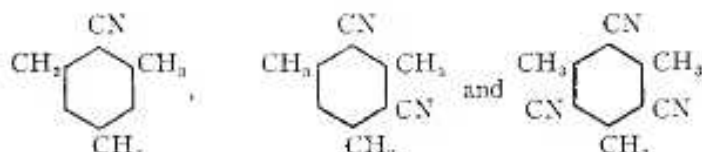
⁴ Liebig's Ann., 244, 55.

³ Berichte, 27, 510. Cf. also, Berichte, 27, 158; and 3146; Berichte, 28, 182, 1197.

⁵ Berichte, 28, 1252.

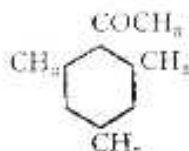
⁶ Berichte, 17, 1914.

Küster and Stallberg,⁸ also, had made the nitriles of mesitylene mono-, di-, and tri-carbonic acids.



but could not convert any of them into the acids by saponification. Di-ortho-substituted nitriles are, in general, very difficult to saponify. The process is not impossible, however, as is shown by the fact that the nitrile of mesitylene carbonic acid has been converted into the acid⁹ by boiling for 72 hours with concentrated alcoholic caustic potash, and diazotizing the resulting acid amide by Bouveault's method.¹⁰ Acid anides and also acid chlorides, when di-ortho-substituted, were found by Meyer and his pupils to be surprisingly stable. For example,¹¹ *o, o*, di-iodo-benzoyl chloride can be boiled with sodium hydroxide solution without much decomposition.

Many other carboxyl compounds, such as mixed ketones, when di-ortho-substituted, exhibit an inertness similar to the acids and nitriles. Substances of the type of acetyl mesitylene,



give no oximes or hydrazones.¹² Klages¹³ also has shown that such di-ortho-substituted ketones give no addition product in the normal way with phosphoric acid. Instead, the ketone group is split off, leaving a hydrocarbon.

⁸ Liebig's Ann., 278, 219.

⁹ Berichte, 29, 834, footnote.

¹⁰ Bull. Soc. Chim. [2], 9, 368.

¹¹ Lützens, Berichte, 29, 2838. Cf. V. Meyer, Berichte, 27, 3153; Sudborough, Journ. Chem. Soc., 71, 229.

¹² Berichte, 28, 3207; 29, 830.

¹³ Berichte, 32, 1549.

These phenomena V. Meyer explained as a result of the space arrangement of the molecule. Heavy or complicated groups on each side of a carboxyl group, for instance, diminish the latter's reactivity in a way that suggests the analogy of the "damping" of vibrating bodies. This inertness of the di-ortho-substituted group is evident not only in its indifference to reagents, of which cases have been cited above, but also in the comparatively small effect which the presence of such a group has on the molecule as a whole. Certain well-known peculiarities of mesitylene, for instance, can be explained as the effects of di-ortho-substitution, such as the ease with which two or three groups like the nitro group are introduced. One nitro group goes easily into benzene, but once there it makes the introduction of a second group more difficult; while in mesitylene the first nitro group has so little inhibiting effect that it is practically impossible to stop nitration at the point where only one group has entered.

A more remarkable example of this is that although only *one* acyl group can be introduced into benzene, toluene and other hydrocarbons, by the action of an acyl chloride and aluminium chloride, *two* such groups can be introduced into mesitylene, durene and isodurene by the same reaction.¹⁴ Ordinarily an acyl group "protects" the remaining hydrogen atoms from further action of the reagents; but the first acyl group to enter mesitylene or the durenes is necessarily di-ortho-substituted and consequently inert, and a second group can then be made to enter the molecule. In the case of mesitylene, it has been found that even a *third* group can be introduced by sufficiently energetic means. E. Louise¹⁵ succeeded in getting successively one, two and three benzoyl groups into mesitylene, the latter by using a large excess of benzoyl chloride and heating to 198° for several hours. But as yet no one has succeeded in introducing three aliphatic acyl groups into mesitylene.

This account of di-ortho-substitution effects shows that, if the three methods available for introducing carboxyl groups into

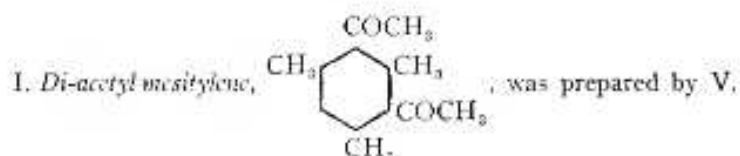
¹⁴ Baum and V. Meyer, *Berichte*, **28**, 3212; V. Meyer, *Berichte*, **29**, 846 and 1413.

¹⁵ *Ann. Chim. Phys.* [6], **6**, 236.

hydrocarbons—(1) the formation of the nitrile and its subsequent saponification, (2) the introduction of an acid amide or acid chloride group with the help of aluminium chloride, and (3) the introduction and oxidation of a ketone group—the first two can be applied only under very unfavorable conditions when the acid to be formed is di-ortho-substituted. Di-ortho-substitution is in these methods a hindrance, while in the third method it is a help. It favors the introduction of acyl groups to form the necessary ketones and does not interfere with oxidation of these ketones to the desired acids. This last method was, therefore, selected for preparing the acids of mesitylene.

In selecting the acid chlorides suitable for the purpose, benzoyl chloride could not be considered, as Louise¹⁶ showed that the oxidation of benzoyl mesitylene gave (o) and (p) benzoyl mesitylenic acids; and Mills and Easterfield¹⁷ on oxidizing di-benzoyl mesitylene got two dibenzoyl uvitic acids. An aliphatic acyl group was therefore necessary, and acetyl and chloroacetyl chlorides were used.

EXPERIMENTAL.



Meyer's¹⁸ method; but as this method was worked out originally only for small quantities of material, it was found necessary to modify it in some details when working on a larger scale. Meyer comments on the tendency of the diketone to remain oily (it melts at 46° and distils undecomposed at 310°), and it was found that,

¹⁶ *Loc. cit.*, p. 218.

¹⁷ *Proc. Chem. Soc.*, 15, 22; *Chem. Centralbl.*, 1899, 1, 679.

¹⁸ *Berichte*, 29, 1413.