in vacuo[16] and a neutralization equivalent. Sufficient anhydrous acid was used to react with 0.2 mole of methylmagnesium iodide until no color test was obtained. From the iodomagnesium sulfonate obtained in this manner and 46 g. or 0.2 mole of *n*-butyl *p*-toluenesulfonate, there was obtained 12 g. or 33% of *n*-butyl iodide.

A part of the magnesium β-naphthalenesulfonate, which incidentally is less soluble in water than magnesium *p*-toluenesulfonate, was analyzed after drying to constant weight at 110°.

Anal. Calcd. for $(\beta\text{-}C_{10}H_7SO_3)_2Mg$: Mg, 5.99. Found: 6.09.

Phenyl *p*-Toluenesulfonate and Magnesium Bromide.—An ether–toluene solution containing 50 g. or 0.2 mole of phenyl *p*-toluenesulfonate and 0.25 mole of magnesium bromide etherate was refluxed for two hours at 100°. After hydrolysis, an ether extract of the steam distillate gave no test for halogen and there was no indication of the formation of magnesium *p*-toluenesulfonate. This experiment illustrates a difference between aryl and alkyl sulfonates (see Reactions 1 and 2).

Summary

Alkylation is not the only reaction that takes place when alkyl sulfonates are treated with organomagnesium halides. Alkyl halides are also formed. The reactions proposed to account for these products have a direct bearing on the formula for the Grignard reagent proposed some time ago by Jolibois.

Ames, Iowa

[Contribution from the Department of Chemistry, Washington Square College, New York University, New York, N. Y.]

NEW CONDENSATIONS OF KETONES WITH PHENOLS. THE PHORONE DI-META-CRESYL ETHER

By Joseph B. Niederl

Received March 28, 1928 Published August 4, 1928

Introduction

The importance of the condensations occurring between aldehydes and phenols gave the impulse to a number of investigations of the behavior of ketones toward phenols under the influence of dehydrating agents.

Previously the following four types of condensations of ketones with phenols had been established: (1) the formation of diphenylmethane derivatives,[1,2] (2) the formation of ketals,[2,3,4] (3) the formation of molecular addition compounds and (4) the formation of oxygen heterocyclics.[5]

It has now been found that diaryl derivatives of di-*iso*-butyl ketone

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[16] Witt, *Ber.*, **48**, 743 (1915).

[1] Dianin, *J. Russ. Phys.-Chem. Soc.*, **1**, 488–517 (1891).

[2] Mackenzie, *J. Chem. Soc.*, **121**, 1695 (1922).

[3] Claisen, *Ber.*, **29**, 1005 (1896); *Ber.*, **31**, 1010 (1898).

[4] Clough, *J. Chem. Soc.*, **89**, 771 (1906); *ibid.*, **26**, 170 (1910); Schmidlin and Lang, *Ber.*, **43**, 2806 (1910).

[5] Chem. Fabriken vorm. Weiler ter Mer, Ger. pat., 357,755.

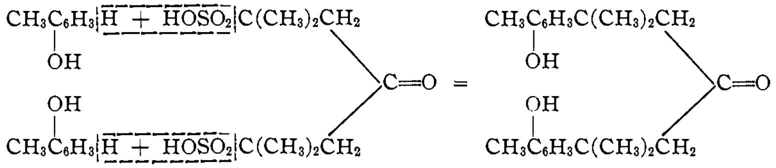
result on treatment of phenols with acteone in the presence of concentrated sulfuric acid.

The discussion of this condensation is the purpose of the present communication.

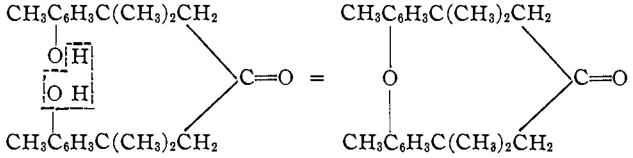
Discussion

The first condensation product of this type, phorone di-*m*-cresyl ether, was obtained by the author[6] by treating a mixture of *m*-cresol and acetone with concentrated sulfuric acid.

It apparently formed in four steps: (1) the formation of phorone from 3 molecules of acetone, with mesityl oxide as intermediate;[7,8] (2) the addition of 2 molecules of sulfuric acid, forming phorone di-sulfuric acid, analogous to the addition of halogen acids, which has already been observed;[9] (3) the re-elimination of 2 molecules of sulfuric acid and subsequent addition of 2 molecules of *m*-cresol.



(4) ether formation, yielding the final reaction product, the phorone di-*m*-cresyl ether.



$C_{23}H_{28}O_2$: Mol. wt., 336

The assigned structure is in harmony with the fact that the same product was also obtained when phorone was treated with 2 moles of *m*-cresol in the presence of concentrated sulfuric acid under the same reaction conditions.

Derivative.—The phorone di-*m*-cresyl ether very readily forms a bromine derivative, the phorone di-bromo-*m*-cresyl ether; it is also easily nitrated, whereby the phorone di-(di-nitro)-*m*-cresyl ether results.

Oxidation Products.—In order to substantiate more fully the assigned structure of the compound, its oxidation products were studied. On oxidation with chromic acid two simpler products were isolated. One of them was shown to be dimethyl malonic acid; the other appears to

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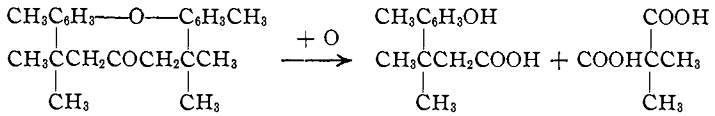
[6] Niederl, *Inaugural Dissertation*, University of Graz, Austria, April, 1925.

[7] Claisen, *Ann.*, **180**, 22 (1875).

[8] Orndorff and Young, This Journal, **15**, 255 (1893).

[9] Vorländer and Hayakawa, *Ber.*, **36**, 3536 (1903).

be *m*-cresyl *iso*valeric acid. Their formation may be represented as follows.



$$\begin{array}{c} CH_3C_6H_3-O-C_6H_3CH_3 \\ | \qquad\qquad | \\ CH_3CCH_2COCH_2CCH_3 \\ | \qquad\qquad | \\ CH_3 \qquad\quad CH_3 \end{array} \xrightarrow{+\,O} \begin{array}{c} CH_3C_6H_3OH \\ | \\ CH_3CCH_2COOH \\ | \\ CH_3 \end{array} + \begin{array}{c} COOH \\ | \\ COOHCCH_3 \\ | \\ CH_3 \end{array}$$

Dimethyl malonic acid is one of the oxidation products of phoronic acid;[10] its formation in the present case indicates that the compound under discussion is also a derivative of phorone.

Of the *m*-cresyl *iso*valeric acid, its di-bromo and mono-nitro derivative and di-sodium salt could be isolated and identified.

Experimental Part

Phorone Di-*m*-cresyl Ether, 2,6-Dimethyl-2,6-di-(4-oxy-2-methyl)-phenyl heptanone-(4) Ether, Di-(*m*-tolyl)-*iso*-butyl Ketone Ether, $C_{23}H_{28}O_2$.—For the preparation of this compound use was made at first of Baeyer's[11] aldehyde condensation process. Later the following procedure was adopted as being most effective.

Three moles of concentrated sulfuric acid was added to an ice-cold mixture of three moles of acetone and two moles of *m*-cresol, keeping the temperature at 0°.

This reaction mixture was allowed to stand at room temperature for forty-eight hours, precautions being taken to exclude all moisture, and was then heated on a water-bath for one hour.

On cooling a solid red mass was obtained. This was washed successively with cold and hot water, to remove the sulfuric acid, the *m*-cresol sulfonic acid-(4) and the *m*-cresol di-sulfonic acid, which formed in the reaction as by-products.

The remaining tar was then treated with hot potassium or sodium hydroxide in order to extract any unchanged *m*-cresol and again with water until free of alkali.

The tar was then dissolved in hot ethyl alcohol and on cooling the phorone di-*m*-cresyl ether crystallized out.

The tar, as obtained after purification with water and alkali, yielded on distillation a fraction boiling between 270 and 300°, from which the ether could be obtained on dilution with ethyl alcohol.

The treatment of either acetone or *m*-cresol separately with concentrated sulfuric acid under identical conditions yielded no new products.

However, when 1 mole of phorone was mixed with two moles of *m*-cresol and then subjected to the action of concentrated sulfuric acid, as before, the phorone di-*m*-cresyl ether also formed. The yields obtained by this method were as high as 80% of the theoretical, while in the previous experiment only about 15% could be isolated.

Phorone di-*m*-cresyl ether crystallizes in various forms, depending on the conditions and the solvents. Usually it is obtained in cubes, 2 to 3 mm. in diameter; on slow crystallization it forms prismatic aggregates or large hexagonal crystals; m. p. 127° (uncorr.); b. p. 270° (uncorr.) with partial decomposition.

It is insoluble in hot and cold water, dilute and concentrated alkalies and dilute acids. It is sparingly soluble in cold ethyl alcohol but dissolves easily on warming;

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[10] Pinner, *Ber.*, **14**, 1072, 1077 (1881); *Ber.*, **15**, 585 (1882).

[11] Baeyer, *Ber.*, **5**, 280, 1095 (1872).

it dissolves in hot concentrated sulfuric and nitric acids and is very soluble in ether, chloroform, carbon tetrachloride and glacial acetic acid.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.14; H, 8.33. Found: C, 81.92, 82.04; H, 8.26, 8.29.

Mol. wt. Calcd.: 336. Found (cryoscopic method): 325, 329; found (ebullioscopic method): 318, 322.

Qualitative tests show that the compound is saturated and that the two oxygen atoms in this compound are neither hydroxylic nor carboxylic in nature.

Dibromo Derivative, $C_{23}H_{26}O_2Br_2$.—Phorone di-*m*-cresyl ether was dissolved in carbon tetrachloride, an excess of bromine in carbon tetrachloride added and the mixture left standing in the dark at room temperature for twenty-four hours.

After this time the evolution of hydrogen bromide had completely ceased. The carbon tetrachloride was then distilled off, the residue dissolved in boiling glacial acetic acid and allowed to crystallize.

It crystallizes in large, colorless, prismatic rosets. It melts at 215° (uncorr.). It is insoluble in cold and hot water, cold and hot mineral acids and alkalies. It dissolves slightly in boiling alcohol and is freely soluble in ether, chloroform and carbon tetrachloride. It dissolves also in boiling glacial acetic acid and concentrated sulfuric acid.

Anal. Calcd. for $C_{23}H_{26}O_2Br_2$: C, 55.86; H, 5.26; Br, 32.39. Found: C, 55.61; H, 5.59; Br, 32.51.

Tetranitro Derivative, $C_{23}H_{24}O_{10}N_4$.—By treating the phorone di-*m*-cresyl ether with boiling concentrated nitric acid and diluting the resulting solution with cold water, a yellow, crystalline solid separated out. This substance was freed from adhering oxidation products formed simultaneously by repeated washings with alkalies and recrystallization from ethyl alcohol. Yellow crystals were obtained which melt at 243° (uncorr.).

The product is insoluble in cold and hot water and alkalies, but dissolves in ethyl alcohol, ether, chloroform, carbon tetrachloride and glacial acetic acid.

Anal. Calcd. for $C_{23}H_{24}O_{10}N_4$: C, 53.49; H, 4.65; N, 10.85. Found: C, 53.48; H, 4.44; N, 10.87.

Oxidation Products

***m*-Cresyl Isovaleric Acid,** $HO(CH_3)C_6H_3C(CH_3)_2CH_2COOH$.—The phorone di-*m*-cresyl ether was dissolved in hot glacial acetic acid and to this mixture an equal amount of chromic acid anhydride, dissolved in the same solvent, was added in small portions.

The mixture was refluxed for six hours and the solution then poured into cold water. A white precipitate consisting chiefly of the *m*-cresyl *iso*valeric acid separated. It was repeatedly dissolved in alkalies and reprecipitated with mineral acids. Finally it was crystallized from acetone.

It melts at 107° (uncorr.). It is soluble in alkalies, forming dark red solutions, and in organic solvents such as acetone, ethyl alcohol, ether, chloroform, carbon tetrachloride, etc.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69. Found: C, 68.94, 69.70; H, 7.24, 7.73.

Dibromo-*m*-cresyl Isovaleric Acid, $C_{12}H_{14}O_3Br_2$.—This substance was prepared by treating the solution of the *m*-cresyl *iso*valeric acid in glacial acetic acid with bromine water. The di-bromo-*m*-cresyl *iso*valeric acid precipitated out immediately.

It was purified by repeated precipitation from its solution in aqueous alkali (potassium or sodium hydroxide) and finally crystallized from ethyl alcohol; m. p. 140° (uncorr.).

Anal. Calcd. for $C_{12}H_{14}O_3Br_2$: C, 39.30; H, 3.82. Found: C, 39.67; H, 3.65.

Nitro-*m*-cresyl Isovaleric Acid, $HO(CH_3)C_6H_2(NO_2)C(CH_3)_2CH_2COOH$.—This acid was obtained as the oxidation by-product in the nitration of the phorone di-*m*-cresyl ether.

When the solution of the nitration and oxidation products in concentrated nitric acid was diluted with water, both the phorone di-(dinitro) *m*-cresyl ether and the nitro-*m*-cresyl *iso*valeric acid separated out. Subsequent treatment with aqueous alkalies dissolved the acid, which could be precipitated again easily from the colored alkaline solutions by mineral acids. It was finally crystallized from benzene; m. p. 108° (uncorr.). It is insoluble in water and dilute mineral acids but dissolves readily in alkalies and organic solvents.

Anal. Calcd. for $C_{12}H_{15}NO_5$: C, 56.92; H, 5.93; N, 5.53. Found: C, 57.13; H, 6.10; N, 5.44.

Its disodium salt could be obtained by neutralizing an alcoholic solution of the acid with sodium alcoholate. On standing a finely divided precipitate formed. It was isolated and finally crystallized from dilute methyl alcohol.

Anal. Calcd. for $C_{12}H_{13}O_5NNa_2$: Na, 15.48. Found: Na, 15.50, 15.35.

Dimethyl Malonic Acid.—This acid was obtained together with the *m*-cresyl *iso*valeric acid.

When the aqueous filtrate obtained after the removal of the *m*-cresyl *iso*valeric acid was treated with lead acetate, a heavy, white precipitate formed, which proved to be the insoluble lead salt of dimethyl malonic acid. It was purified by repeated precipitations and washings with water, alcohol and ether.

Anal. Calcd. for $C_5H_6O_4Pb$: C, 17.77; H, 1.78; Pb, 61.42. Found: C, 17.57; H, 1.51; Pb, 61.26, 61.32.

This lead salt was decomposed with hydrogen sulfide and the lead-free filtrate on evaporation left a residue which, when purified, corresponded for the tests (m. p., solubility) of dimethyl malonic acid as recorded in the literature.

All the quantitative determinations were carried out micro-analytically according to Pregl[12] and the author desires here to thank Miss Edith P. Silbert for her assistance in carrying out these analyses.

The author wishes to acknowledge here his appreciation for laboratory facilities placed at his disposal and repeated courtesies extended by Professors John A. Mandel of the University and Bellevue Hospital Medical College and William C. MacTavish of the Washington Square College, New York University.

Summary

(1) New condensations of ketones with phenols were investigated, resulting in the formation of aryl substituted ketones, the phorone di-*m*-cresyl ether being the first one isolated; (2) the mechanism of their formation is explained, and (3) the proof for their structure is given.

Further investigations of the condensation possibilities of phorone and

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[12] Pregl, "Die quantitative org. Mikro Elementar Analyse," Julius Springer, Berlin, 1923.

mesityl oxide with other phenolic compounds and of their oxidation products are being carried on.

New York City

[Communication from the Department of Industrial and Cellulose Chemistry, McGill University]

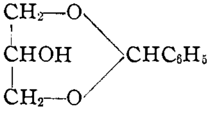
STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES.

XV. THE ISOMERIC BENZYLIDENE GLYCEROLS

By Harold S. Hill,[1] Myron S. Whelen[2] and Harold Hibbert[2a]

Received April 14, 1928 Published August 4, 1928

Fischer[3] was the first to describe a definite condensation product from the interaction of glycerol with benzaldehyde and the molecular structure of the cyclic acetal formed was represented as being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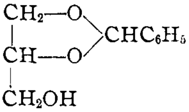
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The same reaction product was more thoroughly investigated by Irvine, Macdonald and Soutar[4] with a view to determining its structure, and by methods of direct synthesis the material in hand was shown to possess the five membered cyclic configuration (II). While these authors pointed out the possibility of the existence of the isomeric form (I), they were unable to detect its presence in their product. It is because of this fact, together with the generally accepted finished character of their research, that their results have been interpreted as indicating the absence of the six membered benzylidene derivative, and the conclusion that the condensation of benzaldehyde with a poly-alcohol takes place only through *adjacent* hydroxyl groups.

This is especially true since the formula for monobenzylidene α-methyl glucoside was given earlier as containing a five membered acetal ring[5] (A),

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[1] Research Fellow, Canadian Pulp and Paper Association.

[2] Holder of Bursary, Canadian National Research Council.

[2a] This work was carried out under the auspices of the coöperative research organization embracing the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada, and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their thanks for the generous support accorded them. One of them (M. S. W.) is also indebted to the Canadian National Research Council for the award of a Bursary for which he desires to express his thanks.

[3] Fischer, *Ber.*, **27**, 1536 (1894).

[4] Irvine, Macdonald and Soutar, *J. Chem. Soc.*, **107**, 337 (1915).

[5] Irvine and Scott, *ibid.*, **103**, 575 (1913).