Summary

1. It has been shown that the method suggested by Gomberg and Bachmann can be applied to the preparation of many halogeno-benzopinacols, especially those from ketones containing bromine or chlorine atoms meta or para to the CO group. When the halogen atom is in the ortho position, however, the magnesium of the reducing mixture tends to remove the halogen atom from the ketone molecule and no pinacol is formed.

2. By a study of the iodomagnesium pinacolates from the point of view of Beer's law, the existence of the equilibrium pinacolate $\rightleftharpoons$ ketyl, has been demonstrated.

3. The relative migratory tendencies of the *p*-bromophenyl, *m*-bromophenyl and *p*-phenyl-phenyl groups have been determined by rearrangement of the appropriate pinacols to pinacolins. The results obtained are in good agreement with those obtained by previous investigators on different examples.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

REDUCTION OF AROMATIC 1,2-DIKETONES BY THE BINARY SYSTEM MAGNESIUM IODIDE (OR BROMIDE) + MAGNESIUM

BY M. GOMBERG AND F. J. VAN NATTA[1]

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Benzil is reduced by the binary system[2] to the unsaturated glycolate, iodomagnesium-stilbene-diolate, $C_6H_5(IMgO)C{=}C(OMgI)C_6H_5$, which when hydrolyzed gives benzoin. We have now extended this reaction to various benzils and find that it may be applied even to halogen-substituted diketones without danger of removing the halogen. Many of the reactions of the new unsaturated glycolates are analogous to those of the parent substance. More definite evidence, however, has now been obtained in regard to the reaction between the diketones and MgI_2 alone. It was reported that benzil liberates iodine from MgI_2, presumably in accordance with the reaction

$$RCOCOR + 2MgI_2 \rightleftharpoons R(IMgO)C{=}C(OMgI)R + I_2 \qquad (1)$$

About 5% of the calculated amount of iodine was found to be set free but most careful search failed to reveal benzoin in the hydrolyzed reaction product. Experience with substituted, more reactive, benzils here described has now definitely proved the correctness of that hypothesis.

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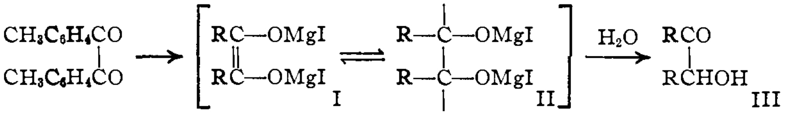
[1] The material here presented is part of a dissertation submitted by F. J. Van Natta to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928.

[2] Gomberg and Bachmann, THIS JOURNAL, 49, 2584 (1927).

When a diketone is added to the binary system, there is consequently liberation of some iodine from the magnesium iodide, with simultaneous formation of an equivalent amount of the unsaturated iodomagnesium glycolate. As reduction proceeds through the presence of the metallic magnesium, the red solution becomes still deeper in color, notwithstanding the fact that the iodine is being taken up by the metal. Later in the process the solution commences to lighten. While the reduction of benzil itself gave an almost colorless solution of the glycolate, the solutions which resulted on the reduction of substituted benzils are usually quite intensely colored. The loss in weight of metallic magnesium convinced us that all of the ketone had been reduced; quinhydrone formation between glycolate and unreduced ketone is, consequently, excluded. This persistence of color we are inclined to interpret by the supposition that we have here a partial opening of the double bond in the unsaturated glycolate, forming a single bond with the production of two trivalent carbon atoms. $\text{I} \rightleftharpoons \text{II}$.[3] Those glycolates especially which contain methoxyphenyl and biphenyl groups give deep colors—an indication of the extent to which C^{III} is produced. This behavior is in harmony with the extensive formation of free radicals from those hexa-arylethanes, tetra-arylhydrazines and tetra-aryldicyano-ethanes[4] which contain either anisyl or biphenyl groups.

Reduction of *p*-Tolil by the Binary System



$$\begin{matrix}CH_3C_6H_4CO\\ |\\ CH_3C_6H_4CO\end{matrix} \longrightarrow \left[\begin{matrix}RC{-}OMgI\\ \|\\ RC{-}OMgI\end{matrix}_{\text{I}} \rightleftharpoons \begin{matrix}|\\ R{-}C{-}OMgI\\ |\\ R{-}C{-}OMgI\\ |\end{matrix}_{\text{II}}\right] \xrightarrow{H_2O} \begin{matrix}RCO\\ |\\ RCHOH\end{matrix}_{\text{III}}$$

The solution of magnesium iodide was prepared from 2.5 g. (0.02 atom) of iodine and 0.5 g. of magnesium powder in a mixture of 25 cc. of ether and 20 cc. of benzene; it was filtered from the excess of magnesium into a 70-cc. test-tube. To this solution was added 1.19 g. (0.005 mole) of tolil, and a weighed magnesium rod was inserted, followed by the addition of 20 cc. of benzene. The tube was tightly corked and placed on the shaking machine. In the course of several days the solution underwent the color changes deep red, light red and light brown. The transparent brown solution at this stage is very sensitive toward oxygen, the surface becoming opaque when exposed to air for an instant. The magnesium rod was removed, washed with benzene and reweighed. The solution was quickly decomposed with water, the precipitated magnesium hydroxide dissolved in standard sulfuric acid and the excess of acid titrated with standard alkali.

Anal. Loss in wt. of Mg, calcd.: 0.1216. Found: 0.1268. $Mg(OH)_2$ (in equivalents), calcd.: 0.01 equiv. Found: 0.0101 equiv.

The ether–benzene solution, which contained the hydrolyzed reduction product,

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[3] Schlenk and Weickel, *Ber.*, **44,** 1189 (1911); Ingold and Marshall, *J. Chem. Soc.*, **129,** 3081 (1926).

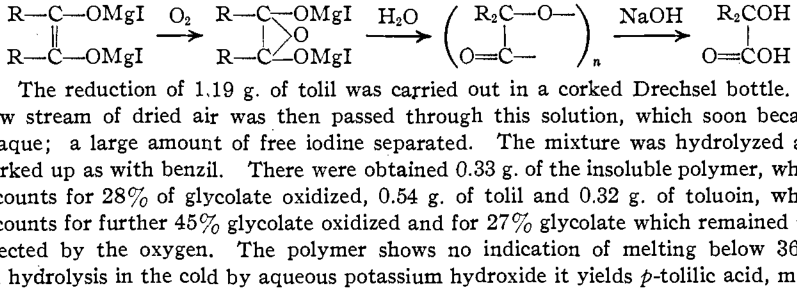
[4] Löwenbein and Gagarin, *Ber.*, **58,** 2643 (1925); Blicke, THIS JOURNAL, **47,** 1477 (1925).

was dried over sodium sulfate and evaporated spontaneously. The 1.15 g. of crystalline product consisted mainly of toluoin in admixture with a small amount of tolil. By fractional crystallization from hot alcohol the two products may be separated, but not quantitatively. For the estimation of the relative amounts of toluoin and tolil, the mixture in alcohol was boiled with excess of Fehling's solution and the amount of cuprous oxide, due to reduction by the toluoin, was determined. One mole of toluoin reduces two moles of cupric hydroxide. The reduction mixture from the 1.19 g. of tolil was in this manner found to consist of 77% of toluoin and 23% of tolil. In a separate experiment when hydrolysis was accomplished by means of boiled water and in a stream of nitrogen, the yield of toluoin was over 90%.

Reaction with Iodine and with Bromine.—The completely reduced solution of the glycolate, prepared as before from 1.19 g. of tolil, was treated with an equivalent amount of solid iodine and allowed to stand for two weeks. The reaction mixture was decomposed with dilute sulfuric acid and the free iodine titrated with sodium thiosulfate; about 52% of the iodine originally added was still present as such. Analysis by Fehling's solution showed the formation of an amount of tolil equivalent to the amount of iodine consumed. Evidently the reaction (Equation 1) reaches equilibrium when 48% of the glycolate has been oxidized.

With bromine the bromomagnesium glycolate reacted far more readily than with iodine, the end reaction being readily recognized and reached in a few minutes. The yield of tolil was over 90%.

Reaction with Dried Air



The reduction of 1.19 g. of tolil was carried out in a corked Drechsel bottle. A slow stream of dried air was then passed through this solution, which soon became opaque; a large amount of free iodine separated. The mixture was hydrolyzed and worked up as with benzil. There were obtained 0.33 g. of the insoluble polymer, which accounts for 28% of glycolate oxidized, 0.54 g. of tolil and 0.32 g. of toluoin, which accounts for further 45% glycolate oxidized and for 27% glycolate which remained unaffected by the oxygen. The polymer shows no indication of melting below 360°. On hydrolysis in the cold by aqueous potassium hydroxide it yields *p*-tolilic acid, m. p. 133–135°.[5]

***p,p'*-Dimethylstilbenediol-dibenzoate.**—To a solution of the glycolate, from 2.38 g. of tolil, there was added 6 g. of benzoyl chloride and the mixture was allowed to stand for a short time. It was then decomposed with water and the product isolated in the usual manner. Crystallization of the crude ester from hot alcohol produced colorless needles of the dibenzoate; m. p. 135°; yield, 59%.

Anal. Calcd. for $C_{30}H_{24}O_4$: C, 80.36; H, 5.36. Found: C, 80.14; H, 5.43. *Mol. wt.* in benzene, calcd.: 448. Found: 442.

Reaction of Tolil with Magnesium Iodide Alone (Equation 1).—To a filtered solution of 3.8 g. of magnesium iodide was added 1.19 g. of tolil. The resulting garnet-colored solution soon became turbid; within a half hour the tube was opaque. After standing in the dark for a month, the reaction mixture was decomposed with water. Titration with sodium thiosulfate showed the presence of 42% of the theoretical amount of iodine and analysis of the organic material showed that an equivalent amount of toluoin was produced.

Reduction by Magnesium Bromide and Magnesium.—To an ether solution of

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[5] Gattermann, *Ann.*, **347**, 364 (1906).

magnesium bromide[6] in a 70-cc. test-tube was added 4.76 g. of tolil and 20 cc. of benzene. A deep yellow solution resulted with no trace of insoluble double compound. No bromine is liberated, in contrast to the liberation of iodine from the reaction between magnesium iodide and tolil. A weighed magnesium rod was inserted and the tube was corked. Soon a deep brown coloration formed around the ends of the magnesium rod; after several hours the entire solution had become very deep brown. The reduction was apparently complete after twenty hours' shaking. The amount of magnesium used up in the reduction and that of the magnesium hydroxide formed on hydrolysis of the glycolate agreed satisfactorily with the calculated values. A yield of 82% of pure toluoin was obtained.

Reduction of *p*-Anisil

Anisil, 1.35 g., was added to a solution of magnesium iodide and immediately there formed, as an oil, an orange double compound. A weighed magnesium rod was then inserted and the tube stoppered. In the course of two days the solution became very deep red, and finally red in color, the double compound having disappeared. It was not possible to obtain a completely colorless solution even after three weeks, the final color being garnet-red.

The magnesium rod had lost 0.1249 g. (calcd. loss, 0.1216 g.) and the theoretical amount of magnesium hydroxide was formed on hydrolysis of the glycolate. By analysis with Fehling's solution, 62% of the theoretical amount of anisoin was shown to be present; the low yield is attributed to the fact that the reduction product, being extremely sensitive toward oxygen, is reoxidized in air to anisil.

With magnesium bromide solution, anisil forms a deep yellow insoluble addition compound; due presumably to the insolubility of this compound, it was not possible to reduce anisil in the cold by the system, $MgBr_2 + Mg$, even on prolonged contact of the reactants.

Reactions of the Glycolate.—After twelve days' reaction with the theoretical amount of iodine, equilibrium (Equation 1) was reached, and the reaction had proceeded to the extent of 63%. Also, when anisil was treated with magnesium iodide in ether solution, there was liberation of iodine with formation of glycolate to the extent of about 20%.

Air was passed into a solution of the glycolate for three days; much iodine was liberated. From the hydrolyzed reaction mixture there was isolated the polymerized acid anhydride, 31%, a cream-colored insoluble substance, infusible below 360°. Hydrolysis of this material by alkalies produced anisilic acid; m. p. 175°.

Reduction of *p,p'*-Dichlorobenzil

The crude benzoin, prepared by the condensation of *p*-chlorobenzaldehyde by means of potassium cyanide, showed no tendency toward crystallization even after extraction of the benzene solution with sodium bisulfite and subsequent evaporation of the benzene. Consequently, the mixture was oxidized directly by means of nitric acid diluted with acetic acid. After purification and recrystallization of the crude benzil from glacial acetic acid, pure *p,p'*-dichlorobenzil was obtained; m. p. 195–196°.

Reduction by Magnesium Iodide and Magnesium.—To a solution of magnesium iodide was added 1.40 g. of the benzil and a weighed magnesium rod. Iodine was liberated and during the course of two days' shaking the color of the solution changed from deep brown to light cherry-red; the magnesium rod had lost in weight the theoretical amount. The mixture was hydrolyzed, the organic solvent was evaporated, and the dichlorobenzoin and benzil were separated from each other by means of cold

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[6] Gomberg and Bachmann, THIS JOURNAL, 49, 245 (1927).

alcohol, the former being very much more soluble than the latter; in this way 9% of the benzil and 91% of the benzoin were isolated. After recrystallization from dilute alcohol, the dichlorobenzoin melted at 85–87°. Hantzsch[7] reports the m. p., 88°.

Careful tests of the original aqueous washings from the reaction mixture failed to show the presence of any chloride ion. The nuclear chlorine atoms in the para position to the C=O group do not, then, react with metallic magnesium under the conditions of this experiment.

Attempts were made to reduce this benzil at room temperature by means of the system, $MgBr_2 + Mg$, but owing to the slight solubility of the benzil + $MgBr_2$ double compound, there was no reduction, and over 90% of the benzil originally taken was recovered unchanged.

Reactions of the Glycolate.—With the theoretical amount of iodine after two weeks' shaking in the cold, the mixture was found to consist of equal parts of dichlorobenzil and of benzoin.

After two days' passage of air through a solution of it, the glycolate yielded 52% of the white, insoluble anhydride of dichlorobenzilic acid polymer, 26% dichlorobenzoin and 22% of the benzil. The amorphous polymer decomposes at 320–340°; it gives a brilliant carmine color with concentrated sulfuric acid, identical with that shown by pure dichlorobenzilic acid.

***p,p'*-Dichlorostilbene-diol-dibenzoate.**—After two recrystallizations from a mixture of benzene and alcohol, the product melted at 200–202°.

Anal. Calcd. for $C_{28}H_{18}O_4Cl_2$: Cl, 14.52. Found: Cl, 14.63. *Mol. wt.*, calcd.: 489. Found: 499.

Reduction with Magnesium Iodide Alone.—The equilibrium: dichlorobenzil $+ MgI_2 \rightleftharpoons$ glycolate $+ I_2$, was attained when 62% of the benzil had reacted and formed the unsaturated glycolate.

Reduction of α-Naphthil

α-Naphthoin, $C_{10}H_7COCH(OH)C_{10}H_7$.—This product may be prepared by either of two methods: from α-naphthaldehyde, using potassium cyanide as a catalyst; or from α-naphthoic acid by reduction with magnesium iodide and magnesium powder in ether–benzene solution.[8] The solution, composed of 26.5 g. of α-naphthaldehyde, 10 g. of potassium cyanide, 100 cc. of alcohol and 50 cc. of water, was refluxed on the steam-bath for three hours; 5 g. more of potassium cyanide was added and the heating continued for eight hours. The solution was diluted with water and the organic material extracted with benzene. The benzene was evaporated and the residue, an oil, was redissolved in ether; on slow evaporation of the solvent, 3.4 g. of crystalline α-naphthoin was deposited. After recrystallization from hot alcohol, it melted at 138–139°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.62; H, 5.13. Found: C, 84.51; H, 5.14.

The oil obtained on evaporation of the ether washings was oxidized to naphthil by copper sulfate in pyridine,[9] and 3.4 g. of naphthil was obtained as yellow prisms; m. p. 188–189°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.16; H, 4.52. Found: C, 84.87; H, 4.55. *Mol. wt.*, calcd.: 310. Found: 329.

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[7] Hantzsch and Glower, *Ber.*, **40**, 1519 (1907); Kenner and Witham, *J. Chem. Soc.*, **97**, 1967 (1910).

[8] Gomberg and Bachmann, THIS JOURNAL, **50**, 2767 (1928).

[9] Clarke and Dreger, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1926**, Vol. VI, p. 6.

The combined amount of naphthoin and naphthil obtained represented a yield of 26%, calculated on the amount of aldehyde taken.

The preparation of naphthoin from the acid is preferable to that from the aldehyde, as the acid is more accessible and the yield of naphthoin is somewhat larger.

The α-naphthil has previously been described by Stolle[10] who obtained it by the thermal decomposition of azo-dinaphthoyl, but in poor yield, owing to numerous side reactions. Quite recently Schlenk[11] described another method for the preparation of this substance. Our product agrees in its properties with those reported by these investigators.

The quinoxaline of α-naphthil, prepared by heating the diketone with *o*-phenylenediamine hydrochloride in pyridine, melts at 203–204°; color reaction with sulfuric acid, deep indigo-blue.

α-Naphthilic Acid $(C_{10}H_7)_2C(OH)CO_2H$.—This acid was prepared in good yield from α-naphthil by means of cold alcoholic potash in absolute ether solution.[12] It was recrystallized from benzene and petroleum ether; needle-like prisms, m. p., 137–138°, with decomposition. With concentrated sulfuric acid, naphthylic acid gives only a very slight brown color, while other benzilic acids produce brilliant colors.

Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80.49; H, 4.88. Found: C, 80.76; H, 4.95. *Mol. wt.*, calcd.: 328. Found: by the ebullioscopic method, 330: by ignition of the Ag salt, 328.

Reduction of α-Naphthil by Magnesium Iodide and Magnesium.—The reduction was completed within three days. During this time, the mixture, originally deep red, became opaque, but the color finally lightened to a yellow. The magnesium rod had lost 97.6% of the theoretical amount. In order to minimize oxidation, the benzene solution was decomposed with boiled water in a stream of carbon dioxide and then the yield of pure α-naphthoin was 91%.

When dried air was allowed to pass for some time through a solution of the glycolate and the solution hydrolyzed, there was complete absence of the usual formation of the polymer-anhydride. Instead, there was formed naphthilic acid to the extent of 40%.

Reduction of *p,p'*-Diphenylbenzil

***p,p'*-Diphenylbenzoin,** $(C_6H_5C_6H_4)(HO)HCCO(C_6H_4C_6H_5)$.—A solution of 8 g. of *p*-phenylbenzaldehyde and 3 g. of potassium cyanide in 80 cc. of alcohol and 40 cc. of water was refluxed for two hours. A thick precipitate of the benzoin formed within fifteen minutes. The yield of the purified product was 95%. The diphenylbenzoin is soluble, 1 g. in about 115 cc. of cold benzene or ethyl acetate; it is quite soluble in hot pyridine, glacial acetic acid and xylene, and from these it may be obtained as a white powder; m. p. 168–170°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.71; H, 5.50. Found: C, 85.42; H, 5.50. *Mol. wt.*, calcd.: 364. Found: 375.

***p,p'*-Diphenylbenzil,** $(C_6H_5C_6H_4)COCO(C_6H_4C_6H_5)$.—This was obtained by oxidizing the benzoin by means of copper sulfate in dilute pyridine. The yield of the diketone was 95%. The diphenylbenzil is very soluble in hot benzene and glacial acetic acid, but only slightly soluble in the cold solvents; light yellow needles, m. p. 141–142°. The quinoxaline, cream-colored iridescent needles, melts at 209–210°.

Anal. (of the benzil). Calcd. for $C_{26}H_{18}O_2$: C, 86.19; H, 4.97. Found: C, 86.03; H, 5.04. *Mol. wt.*, calcd.: 362. Found: 374.

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[10] Stolle, *Ber.*, **45**, 281 (1912).

[11] Schlenk and Bergmann, *Ann.*, **463**, 20 (1928).

[12] *Cf.* Schonberg and Keller, *Ber.*, **56**, 1638 (1923).

In order to verify further the structure of our benzil, the latter was allowed to react with an excess of phenylmagnesium bromide, and *p,p'*-diphenylbenzopinacol was obtained; m. p., 197–199°.[13]

Reduction by Magnesium Iodide and Magnesium.—The loss in weight of magnesium was 99.2% of the theoretical. On hydrolysis of the glycolate, the corresponding benzoin was obtained in a yield of 88%, and was identical with the product obtained from *p*-phenylbenzaldehyde by means of the benzoin condensation.

The reaction between the iodomagnesium glycolate and iodine attained equilibrium when 47% of the theoretical amount of the halogen had reacted. By the action of dried air on a solution of the glycolate, the polymer of the diphenylbenzilic acid anhydride was formed to the extent of 35%. This polymer, decomposition point 250°, was hydrolyzed with difficulty by hot aqueous potassium hydroxide, ultimately yielding the corresponding *p,p'*-diphenylbenzilic acid, m. p., 185–188°; Schlenk reports 178–181°.[14] The polymer, like the acid, produces a brilliant green color with concentrated sulfuric acid.

***p,p'*-Diphenylstilbene-diol-dibenzoate.**—Benzoyl chloride reacts vigorously with glycolate. The dibenzoate so formed behaves as though it were composed of a mixture of the two possible stereoisomers, *cis* and *trans;* when heated it passes through two points of fusion, 180 and 203°, with intermediate solidification. If this mixture of the isomers is fused by heating to 210° and then recrystallized from benzene, the colorless needles obtained melt sharply at 200–203°, indicating the presence of the more stable isomer alone. The lower-melting isomer could not be isolated in the pure state.

Reduction with Magnesium Iodide Alone.—In the case of this benzil, also, we obtained free iodine from the reaction between the benzil and magnesium iodide. Equilibrium was reached when about one-third of the benzil had been transformed to the glycolate.

Reduction of *p*-Phenylbenzil

p-Phenylbenzil, $(C_6H_5C_6H_4)COCO(C_6H_5)$.—This unsymmetrical benzil was prepared by the oxidation of benzyl-*p*-biphenyl ketone[15] in the cold with potassium permanganate in aqueous pyridine solution, with a yield of 64%. After recrystallization from hot alcohol the light yellow plates melted at 105°.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.92; H, 4.90. Found: C, 84.17; H, 5.05. *Mol. wt.*, calcd.: 286. Found: 293.

The structure of this benzil was further verified by its rearrangement to *p*-phenylbenzilic acid, which Schlenk[14] had prepared in another manner.

Reduction by the Binary Systems.—In the reduction by $MgI_2 + Mg$, practically the theoretical amount of magnesium was used up, and an equivalent amount of magnesium hydroxide was formed on hydrolysis. From the benzene solution there was obtained a good yield of the *p*-phenylbenzoin, but with a rather low melting point. A more easily purified product was obtained on reduction by the system $MgBr_2 + Mg$; the originally transparent yellow solution became deep brown, then finally orange. The crude benzoin, recrystallized from hot alcohol, was obtained as a pure white powder; m. p. 148–151°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.33; H, 5.56. Found: C, 83.39; H, 5.61. *Mol. wt.*, calcd.: 288. Found: 297.

It has not been established which isomer of the two possible benzoins this compound actually is.

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[13] Ref. 6, p. 251.

[14] Schlenk and co-workers, *Ber.*, **47**, 489 (1914).

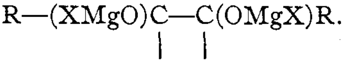
[15] Ferriss and Turner, *J. Chem. Soc.*, **117**, 1148 (1920).

Summary

The unsaturated halogeno-magnesium glycolates obtained by reduction of various aromatic diketones have been prepared and their reactions studied. Several new benzils and benzoins necessary for this work have been prepared and described.

It has been found that magnesium iodide alone, even in the absence of metallic magnesium, has a decided reducing action on the diketone; the amount of glycolate formed is dependent upon the equilibrium: diketone + $MgI_2 \rightleftharpoons$ glycolate + I_2. The amount of iodine thus set free is from 16 to 50% of the theoretical.

The characteristic color changes during and at the end of the reduction process suggest the probability of the existence in the unsaturated glycolates of molecules containing each two trivalent carbon atoms



$R{-}(XMgO)\underset{|}{C}{-}\underset{|}{C}(OMgX)R.$

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE SYNTHESIS OF SOME ALKYLXANTHINES[1,2]

BY D. W. MACCORQUODALE

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In view of the valuable therapeutic properties of the naturally occurring xanthine bases theophylline, theobromine and caffeine, it seems desirable that a study be made of the relation between the pharmacological action and the nature of the alkyl groups attached to the xanthine nucleus. This work was undertaken at the suggestion of the late Dr. A. S. Loevenhart in order to make available some of the homologs of these alkaloids for such a study.

A consideration of the various syntheses devised for the preparation of compounds of this type finally led to the selection of a series of reactions worked out by Emil Fischer during his researches on the purines and used by him for the preparation of caffeine.

Potassium urate when heated with phosphorus oxychloride yields 8-hydroxy-2,6-dichloropurine (I) which in turn is converted into trichloropurine when heated with a large excess of the same reagent.

The chlorine atom at position eight being much more firmly attached than those in the other positions, does not react with sodium ethoxide,

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[1] This paper is constructed from a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Read before the Regional Meeting of the American Chemical Society at Minneapolis on June 19, 1928.