

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

BENZOIN REDUCTION. I. THE MECHANISM OF KETONE FORMATION. THE CASE OF BENZANISOIN

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It is generally known that symmetrical benzoinis when treated with certain metals and acids under suitable conditions produce desoxybenzoinis² and the reaction is usually explained by assuming a simple reduction of the alcoholic group —CHOH— of the keto-alcohol to the methylene group —CH₂—³ according to the reaction
$$\text{RCHOHCOR} \xrightarrow[\text{[M Acid]}]{\text{H}_2} \text{RCH}_2\text{COR.}$$
 Recently, however, the reduction of two unsymmetrical benzoinis has been described^{4a,b} and in each case *two isomeric* ketones were obtained. Since these benzoinis are known to be definite compounds,^{4b,5} the presence of isomeric desoxy derivatives cannot be accounted for on the usual assumption.³

Although benzanisoin has been studied already from many viewpoints by a number of investigators,⁶ in the present work the reduction of this substance will be described and the results obtained along with those previously reported^{4a,b} will be used as the basis of a new conception of the mechanism of benzoine reduction.

The starting material was obtained by condensing benzaldehyde and anisaldehyde by means of potassium cyanide. The compound melted at 106° and was shown to be authentic by comparison with a sample made by condensing mandelamide with *p*-methoxyphenylmagnesium bromide, according to the reaction

¹ Grafflin Scholar, 1930–1931.

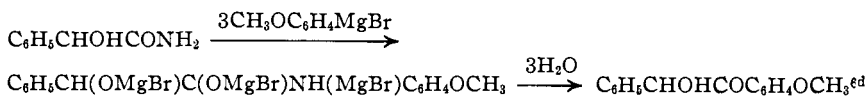
² Zinin, *Ann.*, **119**, 180 (1861); Meyer and Oelkers, *Ber.*, **21**, 1295 (1888); Juillard and Tissat, *Arch. sci. phys. nat. Genevé*, [3] **25**, 387; *Chem. Centr.*, II, 166 (1891); Wachter, *Ber.*, **25**, 1727 (1892); Bader, *Chem. Z.*, **19**, 1939 (1895); Sudborough, *J. Chem. Soc.*, **71**, 218 (1897); Stobbe, *Ber.*, **35**, 911 (1902); Apitzsch and Metzger, *ibid.*, **37**, 1676 (1904); Apitzsch, *ibid.*, **40**, 1803 (1907); Irvine and Moodie, *J. Chem. Soc.*, **91**, 543 (1907); Buck and Jenkins, *THIS JOURNAL*, **51**, 2163 (1929).

³ Gattermann, "Practical Methods of Organic Chemistry," The Macmillan Company, New York, 1928, p. 306.

⁴ (a) Jenkins, Buck and Bigelow, *THIS JOURNAL*, **52**, 4495 (1930); (b) Jenkins, *ibid.*, **53**, 3115 (1931).

⁵ Jenkins, Bigelow and Buck, *ibid.*, **52**, 5198 (1930).

⁶ Meisenheimer and Jochelson, *Ann.*, **355**, 292 (1907); (b) Ekecrantz and Ahlquist, *Ark. Kem. Min. Geol.*, **3**, No. 13, 1–26 (1908); *J. Chem. Soc. Abs.*, **94**, 991 (1908); (c) Asahina and Terasaka, *J. Pharm. Soc. Japan*, **494**, 219 (1923); (d) McKenzie, Louis, Tiffeneau and Weill, *Bull. soc. chim.*, [4] **45**, 414 (1929); (e) Kinney, *THIS JOURNAL*, **51**, 1592 (1929); (f) Buck and Ide, *ibid.*, **53**, 3510 (1931); (g) Tiffeneau and Levy, *Bull. soc. chim.*, [4] **49**, 725 (1931)



A number of derivatives was obtained. Thus when oxidized with Fehling's solution^{7a,b} or copper sulfate in pyridine,^{6e} the benzoin readily produced the benzil, which melted at 63°, and when reduced with sodium amalgam both hydro-^{7a} and iso-hydrobenzoinis^{7a} were obtained. These glycols readily lost water when heated with a mixture of glacial acetic and concentrated hydrochloric acids and formed *p*-methoxybenzyl phenyl ketone, which has been described by Tiffeneau and Orékhoff.^{7b} This ketone was reduced by means of sodium amalgam and produced *p*-methoxybenzylphenylcarbinol (not previously described) melting at 62°. This carbinol readily formed *p*-methoxystilbene^{7a} when dehydrated with the acetic-hydrochloric acid mixture.

In a recent article⁸ Buck and Ide have described the reduction of benzanisoin using tin and hydrochloric acid in alcoholic solution. They reported a yield of 87% of *p*-methoxybenzyl phenyl ketone and none of its isomer, benzyl *p*-methoxyphenyl ketone. The latter ketone certainly would be expected if the alcoholic group of the benzoin were attacked. Furthermore, it was stated that *p*-methoxybenzyl phenyl ketone formed both the *syn* and *anti* benzyl oximes when treated with hydroxylamine acetate in alcoholic solution.

In view of the unexpected results reported in the article just mentioned, a very careful reduction on a highly purified sample of benzanisoin was carried out, in the above manner, but *p*-methoxybenzyl phenyl ketone could not be obtained in a yield greater than 47%. The ketone was then treated with an excess of hydroxylamine acetate in alcoholic solution but, contrary to the statement of Buck and Ide, only the *anti* oxime was obtained and that in almost quantitative yield. There was not a trace of the *syn* oxime present.

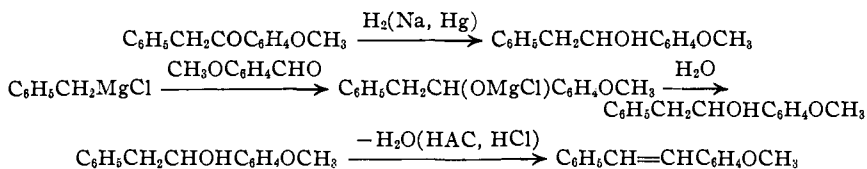
Other crystalline material was isolated from the reduction mixture. By careful fractional crystallization one portion, melting sharply at 77°, was obtained, in small amount, but the greater portion of the solid melted between 60 and 65° and appeared to be a mixture of *p*-methoxybenzyl phenyl ketone and the fraction melting at 77°, since the melting point was raised when mixed with either of the latter substances.

The fraction melting at 77° was found to be pure benzyl *p*-methoxyphenyl ketone in the following manner. It was readily reduced with sodium amalgam to a substance melting at 58°. Benzyl-*p*-methoxyphenylcarbinol, which also melts at 58°, was prepared according to the method

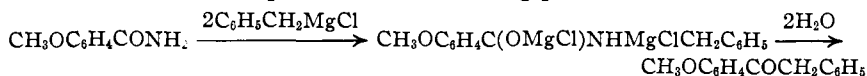
⁷ (a) Orékhoff and Tiffeneau, *Bull. soc. chim.*, [4] 37, 1410 (1925); (b) Tiffeneau and Orékhoff, *ibid.*, [4] 37, 430 (1925).

⁸ Buck and Ide, *THIS JOURNAL*, 53, 1536 (1931).

of Orékhoff and Tiffeneau^{7a} by condensing anisaldehyde with benzylmagnesium chloride. The two compounds were found to be identical. The carbinol as prepared by either method readily lost water when heated with the acetic-hydrochloric acid solution and produced *p*-methoxystilbene.^{7a} The reactions are

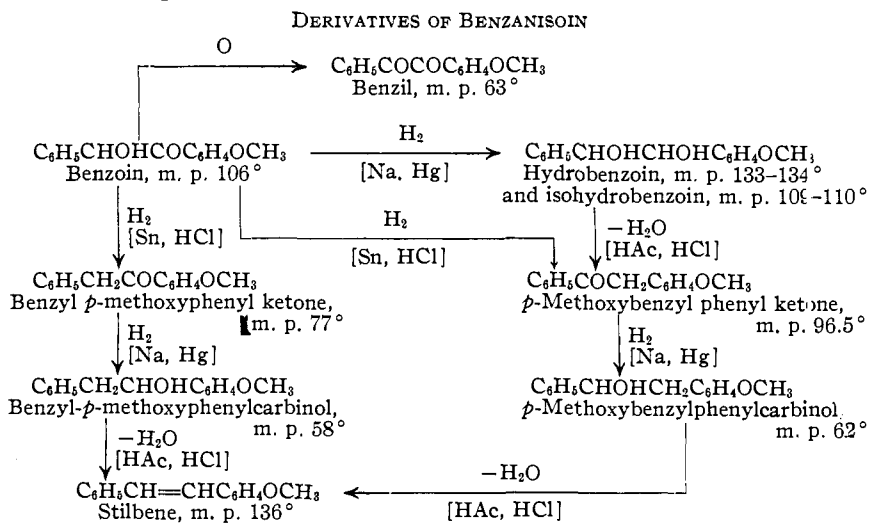


In order to prove the structure of the substance melting at 77° in a *direct* manner and beyond question, *p*-methoxybenzamide was condensed with benzylmagnesium chloride according to the general method of Béis⁹ and after hydrolysis of the complex benzyl *p*-methoxyphenyl ketone was obtained. This compound also melted at 77° and when mixed with the substance above there was no depression of the melting point. The reactions are



The ketone prepared in this manner was readily reduced with sodium amalgam and also produced the above carbinol. Thus it is seen that benzanisoin when reduced with tin and hydrochloric acid in alcohol solution yields both of the possible isomeric ketones as was to be expected.

The reactions which have been described above are represented in the following diagram.

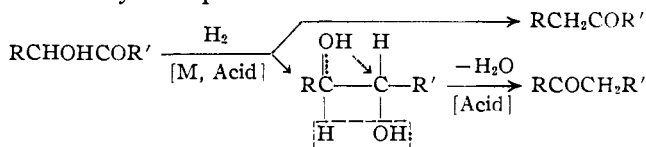


⁹ Béis, *Compt. rend.*, 137, 575 (1903).

Buck and Ide, in the paper mentioned above, prepared a substance which they thought was benzyl *p*-methoxyphenyl ketone by condensing phenylacetyl chloride and anisole in the presence of aluminum chloride. This reaction was first described by Ney¹⁰ in 1888. He obtained a substance which melted at 76° and gave an oxime fusing at 111° but did not assign a position to the methoxyl group. The writer also carried out the reactions but obtained very small yields which varied in composition with different runs (see experimental part for details). In one run the material obtained was identical with the ketone prepared by the method of Béis, in another, however, the substances were unlike, as was shown by the melting points and the mixed melting point. This reaction thus affords another instance of the unreliability of the Friedel and Crafts method when applied to work of structure. This reaction is being studied further.

In view of the facts which have come to light in this and in the previous work which has been reported,^{4a,b} it is certain that the usual conception of benzoin reduction with metals and acids is only partially true and that the reaction involves not only the alcoholic group of the keto-alcohol but the carbonyl group as well. Thus a certain amount of the glycol is produced which easily loses water in the acid medium to form the isomeric ketone.

The reactions may be represented as



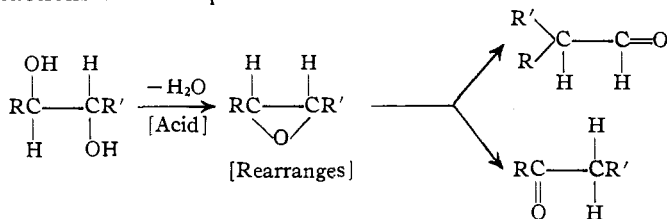
It is evident that glycols of this type might also lose water in such a way as to produce aldehydes or mixtures of these with the ketones and, indeed, this has been demonstrated in certain cases.¹¹ Orékhoff and Tiffeneau found that hydrobenzoin when dehydrated with sulfuric acid produced *p*-methoxydiphenylacetaldehyde^{7a} along with *p*-methoxybenzyl phenyl ketone. One may also assume the presence of ethylene oxides as intermediate products in the formation of either ketones or aldehydes when these glycols are dehydrated. Thus, according to the rule of Breuer and Zincke,¹² "On abstraction of water, which can be effected by means of various reagents, all diatomic alcohols, containing OH groups attached to two neighboring carbon atoms, give first oxides (anhydrides or ethers) without any intramolecular changes, and then by further action of the reagent, ketones or aldehydes, or both."

¹⁰ Ney, *Ber.*, **21**, 2450 (1888).

¹¹ Zincke, *ibid.*, **9**, 1769 (1876); Breuer and Zincke, *ibid.*, **11**, 72 (1878); Nevole *ibid.*, **9**, 448 (1876); Montagne, *Rec. trav. chim.*, **21**, 30 (1902); Tiffeneau and Orékhoff, *Bull. soc. chim.*, [4] **33**, 1832 (1923).

¹² Breuer and Zincke, *Ann.*, **198**, 141 (1879).

The reactions can be represented as



For the present purpose, however, these considerations are not pertinent. This work is being continued.

Experimental

Preparation of Benzanisoin

First Method.^{6a}—To a solution of 40 g. of benzaldehyde, 52 g. of anisaldehyde and 115 cc. of 95% alcohol was added 12 g. of potassium cyanide dissolved in 80 cc. of water. The mixture was refluxed for one and one-half hours and allowed to stand in a cool place overnight. The crystalline material was filtered and washed twice with water and then with a small portion of cold alcohol. After three crystallizations from alcohol it weighed 29 g., which was 31% of the theoretical and melted at 106° (corr.).

Second Method.^{6d}—In a 500-cc. round-bottomed flask were placed 3.0 g. of thin, bright, magnesium turnings, 22.4 g. of *p*-bromoanisole and 50 cc. of anhydrous ether. The reaction was started with a small crystal of iodine and after adding 50 cc. more of ether was allowed to proceed spontaneously for an hour. The flask was then heated for another hour over a 25-watt light. Mechanical stirring was employed throughout. To the solution 3.0 g. of finely powdered mandelamide in small portions was then added over a period of twenty minutes and the heating and stirring continued for eight hours. At the expiration of this time the reaction mixture was poured into 200 g. of a slush of ice and water containing 20 g. of concentrated sulfuric acid and thoroughly stirred. The ether layer was separated and the water layer extracted again with 100 cc. of ether. The combined extracts were washed with 100 cc. of 1% sodium carbonate solution and then with water. The ether was evaporated and the remaining yellow oil steam distilled. The residue was then dissolved in a small amount of alcohol and filtered hot. After standing in a cool place overnight the solution deposited 1.50 g. of snow-white needles melting at 102–104°. After two further crystallizations from alcohol the product melted at 106° (corr.). When this was mixed with the substance obtained by the *first method* there was no depression of the melting point.

***p*-Methoxybenzil.**^{6e}—This diketone was readily prepared by oxidizing the keto-alcohol either with concentrated Fehling's solution^{4a, b} or copper sulfate-pyridine solution, according to the method of Kinney.^{6e} The first method, in which Fehling's solution was used, was found to be satisfactory. The benzoïn dissolved in alcohol was heated on the water-bath with a small excess of reagent for thirty minutes, after which the solution was diluted with an equal volume of water and extracted twice with small portions of ether. After distilling the ether and crystallizing twice from 80% alcohol, the substance was obtained in a yield of 75–85% as yellow needles and melted at 63° (corr.).

Hydro- and Isohydrobenzanisoin.^{7a}—These glycols were prepared by reducing the benzoïn with sodium amalgam. Satisfactory yields were obtained by means of the following method. In a 125-cc. Erlenmeyer flask, in the lower edge of which a small bulb had been blown, was placed 0.01 mole (2.42 g.) of the benzoïn and 40 cc. of 95%

alcohol. Solution was effected by warming and 15 g. (30% excess) of 4% sodium amalgam was then added. The mixture was mechanically shaken in an atmosphere of coal gas for five hours. By trapping the mercury in the bulb of the flask the solution was easily decanted and washed out with small portions of solvent. The alcohol was evaporated under reduced pressure and the substance dried. After recrystallizing twice from benzene the *hydrobenzoin* was obtained in a yield of 61% (1.50 g.), melting at 133–134°, as snow-white leaflets.

The mother liquors were evaporated to half-volume and allowed to stand in a cool place for several hours. About 0.2 g. of substance melting at 96–99° was obtained. The filtrate was then diluted with an equal volume of ligroin (Skelly solve "C") and placed in a cool place overnight. The solution deposited 0.40 g. of fine colorless needles which, after two further crystallizations from the benzene–ligroin solution, melted at 109–110° and was evidently impure *isohydrobenzanisoin*,^{7a} as will be shown below.

p-Methoxybenzyl Phenyl Ketone^{7a,b}

First Method.—This ketone was produced in about 50% yield when either hydro- or isohydrobenzanisoin, as prepared above, was heated for twenty to thirty minutes with a mixture of 80% glacial acetic and 20% concentrated hydrochloric acids in the proportion of one part of glycol to 20–30 parts of the acid mixture. To obtain the ketone the solution was diluted with three volumes of water, neutralized with sodium carbonate, cooled and the solid filtered. After two crystallizations from alcohol it melted at 96.5° (corr.). On extracting the water mother liquors with ether and evaporating the latter, a colorless oil remained which was probably the *p*-methoxydiphenylacetaldehyde of Orekhoff and Tiffeneau^{7a} but was not further investigated in the present work.

Second Method.—A mixture of 25 g. of benzanisoin (m. p. 106° corr.), 20 g. of mossy tin, 0.50 g. of hydrated copper sulfate, 100 cc. of alcohol and 70 cc. of concentrated hydrochloric acid was refluxed for six hours and filtered hot. After standing for some time in a cool place the crystalline material was filtered, washed twice with small portions of alcohol and dried *in vacuo*. It weighed 14.5 g. and melted at 86–92°. After two further crystallizations from alcohol, the substance was obtained as colorless plates which weighed 9.30 g. and melted at 96.5° (corr.). The filtrates from which the crystals were obtained were combined, diluted with an equal volume of water and most of the alcohol distilled. The solution was then made slightly alkaline with sodium carbonate, cooled and filtered. The precipitate was washed with water, sucked dry and extracted three times with 50-cc. portions of boiling alcohol. The solution was then evaporated to a volume of about 100 cc. and filtered hot. On standing the solution deposited 1.80 g. more of the ketone which after a further crystallization melted at 95–96°. The total yield of substance amounted to about 47%.

Benzyl *p*-Methoxyphenyl Ketone

First Method.—The filtrate above was evaporated to a volume of about 50 cc. On cooling 9.10 g. of material, melting at 55–60°, was obtained. After evaporating to a volume of about 20 cc., the filtrate deposited a further 0.50 g. of material which melted at 52–61°. The mother liquors were then evaporated *in vacuo* and an oily residue remained which smelled strongly of benzaldehyde but was not further studied. The two crops of crystals were combined and recrystallized from ligroin–benzene (5:1) solution. On standing the solution deposited two types of crystals; one portion consisted of flakes, the other was made up of clusters of thick prisms radiating from a common center. The latter were mechanically separated and recrystallized from a small portion of the ligroin–benzene mixture and 0.50 g. of material melting at 76–77°

was obtained which after another crystallization melted at 77°. The other portion (flakes) melted at 61–65°. When this was mixed with either *p*-methoxybenzyl phenyl ketone or the substance melting at 77° the melting point was raised. As will be shown below, the substance melting at 77° proved to be benzyl *p*-methoxyphenyl ketone; that which melted at 61–65° was a mixture of the two ketones which was not further studied.

Second Method.—In order to prove the structure of the substance melting at 77°, obtained above, the general method of Béis⁹ was employed. In a 500-cc. three-necked round-bottomed flask was placed 7.5 g. of magnesium turnings and a small crystal of iodine. The flask was fitted with a dropping funnel containing 38 g. of benzyl chloride dissolved in 100 cc. of anhydrous ether. A few cc. of this solution was added to the magnesium and after the reaction had started 50 cc. more of ether was added. The benzyl chloride–ether solution was then slowly added during the course of thirty minutes, after which the solution was heated over a twenty-five watt light for an additional hour. To the mixture 10 g. of finely powdered *p*-methoxybenzamide was added in small portions during twenty minutes and the whole refluxed for eight hours. The mixture was then poured into 200 g. of a slush of ice and water containing 20 g. of concentrated sulfuric acid. After thorough stirring the ether was separated and the water again extracted with 100 cc. of ether. The combined extracts were steam distilled and the residue dissolved in ether and dried over anhydrous sodium sulfate. After distilling the ether the residue was dissolved in ligroin and filtered hot. On standing 3.0 g. of material melting at 69–74° was obtained. After two further crystallizations from ligroin it melted at 77° (corr.). When this was mixed with the substance obtained in the *first method*, there was no depression of the melting point.

Anal. Calcd. for C₁₈H₁₄O₂: C, 79.60; H, 6.24. Found: C, 79.40; H, 6.41.

***p*-Methoxybenzylphenylcarbinol.**—To a solution of 2.26 g. (0.01 mole) of the ketone in 40 cc. of warm alcohol was added 15 g. of 4% sodium amalgam (about 30% excess). The mixture was shaken in an atmosphere of coal gas (apparatus and technique described above) for five hours. The mercury was separated, the alcohol evaporated under reduced pressure and 100 cc. of water added. The product was extracted with ether and the solution dried over anhydrous sodium sulfate. After evaporating the ether the carbinol was recrystallized from ligroin. It weighed 1.85 g., which was 81% of the theoretical, and melted at 56–59°. The substance was moderately soluble in hot water, from which it separated on cooling as long needles, and was quite soluble in ether and alcohol. From ligroin it crystallized as thick colorless prisms and when pure melted at 62° (corr.).

Anal. Calcd. for C₁₈H₁₆O₂: C, 78.90; H, 7.06. Found: C, 78.76; H, 6.98.

Benzyl-*p*-methoxyphenylcarbinol^{7a}

First Method.—This carbinol was obtained by reducing *p*-methoxybenzyl phenyl ketone with sodium amalgam according to the method already described. The substance was obtained in a yield of 80–85% and when purified by crystallization from ligroin it melted at 58° (corr.).

Second Method.—Anisaldehyde was condensed with benzylmagnesium chloride according to the directions of Orékhoff and Tiffeneau.^{7a} The substance thus obtained, after several crystallizations from ligroin, melted at 58° (corr.) and when mixed with that obtained by the *first method* there was no depression of the melting point.

***p*-Methoxystilbene.**—This compound was obtained in 80–85% yield by heating for twenty to twenty-five minutes either *p*-methoxybenzylphenylcarbinol or benzyl-*p*-methoxyphenylcarbinol with 20 parts of the acetic–hydrochloric acid mixture mentioned above. Recrystallized from alcohol it melted at 135° (corr.).

***p*-Methoxybenzyl Phenyl Ketone Oxime.**^{7a,8}—In a small Erlenmeyer flask (125-cc.) was placed 2.00 g. of *p*-methoxybenzylphenyl ketone, 2.00 g. of hydroxylamine hydrochloride, 3.00 g. of potassium acetate and 50 cc. of alcohol. The flask was corked and left overnight. The following morning the mixture was heated on the water-bath for three hours and then diluted with 100 cc. of water. After cooling, filtering and washing with water, a mass of colorless needles was obtained which on drying *in vacuo* weighed 2.075 g. and melted at 132–133.5° (corr.). To the mother liquors 100 cc. more of water was added and another crop of crystals was obtained which weighed 0.049 g. and melted at 129–132° (corr.). When the two substances were mixed there was no depression of the melting point. The combined yield obtained was over 99%. Recrystallized from ligroin the compound melted sharply at 134° (corr.).

***p*-Methoxyphenylacetanilide.**⁸—To 0.50 g. of the above oxime was added 30 cc. of anhydrous ether and 1.2 g. of phosphorus pentachloride. The mixture was shaken for twenty minutes and poured into 50 cc. of water. After evaporating the ether and cooling, the crude anilide was filtered and recrystallized from a small amount of 75% alcohol. It weighed 0.30 g. and melted at 115.8° (corr.).

The anilide was hydrolyzed by heating for thirty minutes with 20 cc. of concentrated hydrochloric acid. The solution was made alkaline with sodium carbonate and extracted with ether. From the ether solution aniline was obtained and was identified by its odor and conversion into acetanilide. The water solution was acidified and the *p*-methoxyphenylacetic acid separated and identified by its melting point and crystalline structure.¹³

Benzyl *p*-Methoxyphenyl Ketone Oxime.—This oxime was prepared from the corresponding ketone in a manner similar to that above and was obtained in a yield of 95%. When crystallized from ligroin it melted at 114° (corr.).

Anal. Calcd. for C₁₆H₁₅NO₂: N, 5.80. Found: N, 5.67.

Friedel and Crafts Reaction.¹⁰ **Examples.**—To a solution of 20 g. of phenylacetyl chloride, 16 g. of anisole and 80 g. of carbon disulfide, 20 g. of aluminum chloride (anhydrous, Baker's c. p.) was added in small portions during the course of thirty minutes. The solution was then heated on the water-bath for three hours and after treatment with ice water was steam distilled. The yellow oil remaining was washed with 5% sodium hydroxide solution and then with water. Two methods were employed for purifying the substance.

(1) The oil was dissolved in alcohol and allowed to stand in a cool place overnight. From the solution four grams of material was obtained which after two further crystallizations from alcohol melted at 73–74° (corr.).

(2) The oil was fractionated *in vacuo*. The greater portion failed to distil at 200° under a pressure of 3–5 mm. A fraction of about two grams which distilled between 120–140° at 3–5 mm. was obtained and when twice crystallized from alcohol melted at 75–76° (corr.). This substance was different from that obtained by *Method 1* as was shown by a mixed melting point determination, but was identical with benzyl *p*-methoxyphenyl ketone obtained in the Grignard reaction mentioned above.

The writer wishes to thank Professor E. Emmet Reid for his interest and help in this work.

Summary

1. A new conception of the mechanism of benzoin reduction is advanced.

¹³ Cain, Simonsen and Smith, *J. Chem. Soc.*, 103, 1035 (1913)

2. It has been shown that benzanisoin when reduced under suitable conditions produces not only *p*-methoxybenzyl phenyl ketone but also its isomer, benzyl *p*-methoxyphenyl ketone. Only the *anti* benzyl oxime was obtained from *p*-methoxybenzyl phenyl ketone.

3. By means of the Grignard reaction the structure of benzyl *p*-methoxyphenyl ketone has been determined by two independent methods.

4. A number of derivatives of benzanisoin has been obtained. A new carbinol was prepared and characterized.

5. The reliability of the method of Friedel and Crafts in structural work of this nature is brought into question.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, THE GOODYEAR TIRE & RUBBER Co.]

THE REACTION OF DIAZONIUM SALTS ON SODIUM ALKYL DITHIOCARBAMATES

BY A. M. CLIFFORD AND J. G. LICHTY

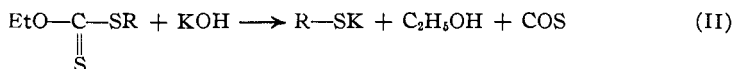
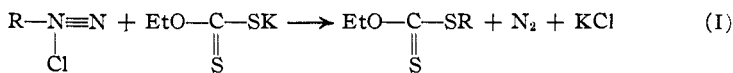
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Bernthsen and Friese¹ and also Billeter and Strohl² were apparently among the first to describe esters of disubstituted dithiocarbamic acids and reported the synthesis and properties of the ethyl and the phenyl esters of ethylphenyldithiocarbamic acid. Since these publications, little has appeared in the literature concerning this class of compounds. Certain nitro substituted aryl esters of dialkyl dithiocarbamic acids are claimed in patents issued to Cadwell,³ and obtained by reaction between dithiocarbamate and an aryl compound containing reactive halogen.

A reaction has been found in this Laboratory which is capable of yielding the unsubstituted, as well as the substituted, aryl esters of alkyl dithiocarbamic acids.

Leuckart's excellent reaction⁴ for the preparation of thiophenols sug-



gested that diazonium salts should react in a manner similar to Equation I with alkyl dithiocarbamates, to yield the aryl ester of the dithiocarbamate

¹ Bernthsen and Friese, *Ber.*, **15**, 568 (1882).

² Billeter and Strohl, *ibid.*, **21**, 102 (1888).

³ Cadwell, U. S. Patents, 1,726,646, 1,726,647, 1,726,648, Sept. 3, 1929; 1,736,429, Nov. 19, 1929.

⁴ Leuckart, *J. pract. Chem.*, [2] **41**, 179 (1890).