

pure form. A catalyst, double the regular size, was being used for the third time to reduce 65.2 g. of isonitrosopropiophenone; initial hydrogen absorption was 90 ml./min.; at the end of 220 minutes the rate was still 30 ml./min., but since 18,400 ml. of hydrogen had been taken up, that is, a slight excess over that calculated to give amino ketone, the reduction was purposely stopped at this point. The resulting product was purified by forcing it out of absolute alcoholic solution with ether and formed the characteristic red decomposing melt at 183.5° (corr.).¹¹

Summary

The effect of the presence of hydrogen chloride during the hydrogenation of α -oximino ketones, by means of palladium catalyst, has been described. The effect is manifested in three distinct ways. (1) It promotes the reduction of the oximino group. (2) It increases many fold the rate of hydrogenation. (3) It prevents the formation of contaminating secondary and tertiary bases.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

DERIVATIVES OF OPTICALLY ACTIVE TRIARYLCARBINOLS AND THEIR HALOCHROMIC SALTS¹

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Shortly after Gomberg's discovery of triphenylmethyl, Norris and Sanders² made the interesting observation that colorless triphenylchloromethane forms a dark brown crystalline salt with aluminum chloride of the formula $(C_6H_5)_3CCl \cdot AlCl_3$. Kehrman and Wentzel³ soon showed that this was a general property of triphenylchloromethane and they prepared double compounds with other metallic salts. Since then many investigators⁴ have studied these halochromic salts, and today we have a large number of colored double compounds of triarylmethyl halides with metallic salts, acids and halogens.

The question as to the constitution of these compounds and related substances such as the triarylmethyls and triphenylmethane dyes has long been debated. The problem has been approached both from the experimental and theoretical sides in the hope that a simple explanation for the color and salt-like nature of these compounds could be found. Following the observation that colorless triphenylchloromethane dis-

¹¹ Beilstein, 3d ed., Vol. III, supplement, p. 112.

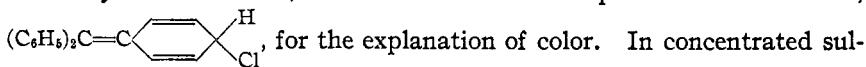
¹ Presented before the Organic Division of the American Chemical Society in Indianapolis, Indiana, April, 1931.

² Norris and Sanders, *Am. Chem. J.*, **25**, 54, 117 (1901).

³ Kehrman and Wentzel, *Ber.*, **34**, 3818 (1901).

⁴ Gomberg, *ibid.*, **35**, 1822 (1902); Baeyer, *ibid.*, **38**, 1162 (1905); Tschitschibabin, *ibid.*, **40**, 1817 (1907); Meyer, *ibid.*, **41**, 2576 (1908); Wieland, *ibid.*, **42**, 3024 (1909); Gomberg and Cone, *Ann.*, **370**, 142 (1909); Schlenk, *ibid.*, **372**, 9, 25 (1910).

solved in concentrated sulfuric acid, and in liquid sulfur dioxide to give intense yellow solutions, Kehrman⁵ assumed a quinonoid constitution,



for the explanation of color. In concentrated sulfuric acid and in liquid sulfur dioxide a tautomerism of the molecule occurred, and in the halochromic double salts of the triarylmethyl compounds with metallic halides the presence of color was also due to this quinonoid modification. This theory was subsequently used to explain the formation of color in the sulfates, nitrates and perchlorates of the triarylcabinols, and has received much attention and support especially from the work of Gomberg, Cone and Anderson.⁶

However, there are experiments⁷ recorded in the literature which are difficult to explain on the basis of this theory of constitution. These results have led to a different interpretation for the formation of color in these compounds. On the basis of this "carbonium ion theory" it is assumed that triarylmethyl compounds can exist in two forms—a colorless modification in which the negative group, X, is directly bound to the central carbon atom, and a colored modification of a true salt-like character (carbonium salt). The colorless solutions of the triarylmethyl halides are of the former type. The colored solutions of these compounds as well as the colored sulfates, nitrates, perchlorates, and double salts are of the latter type. According to Hantzsch⁸ and Dilthey⁹ this colored form can be best represented by the formula, $\left[\begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R} \end{array} - \text{R} \right] \text{X}$, where X may be Cl, ClO₄, OSO₃H, SnCl₅, etc.

In the light of these two different interpretations, therefore, it seemed that it would be of interest if further investigations were made on this problem along somewhat different lines. If a triarylmethyl compound could be prepared in which the four groups around the central carbon atom were all different, the molecule would then contain an asymmetric carbon atom and it should be possible to resolve it into its enantiomorphic forms. Such a compound would still have the property of forming halochromic double salts with metallic halides, and the behavior of such salts toward polarized light could be easily studied. If the above quinonoid theory be correct for the explanation of color in halochromic salts, we would expect

⁵ Kehrman and Wentzel, *Ber.*, **34**, 3815 (1901).

⁶ Gomberg and Cone, *ibid.*, **39**, 3274 (1906); **42**, 406 (1909); Gomberg, *ibid.*, **40**, 1847 (1907); Anderson and Gomberg, *THIS JOURNAL*, **50**, 203 (1928); Anderson, *ibid.*, **51**, 1889 (1929); **52**, 4567 (1930).

⁷ A. Baeyer and Villiger, *Ber.*, **35**, 1189, 3013, 3054 (1902); A. Baeyer, *ibid.*, **38**, 569 (1905); **40**, 3083 (1907); Tschitschibabin, *ibid.*, **40**, 3965 (1907); Schlenk and Weikel, *Ann.*, **368**, 295 (1909); Conant, Small and Taylor, *THIS JOURNAL*, **47**, 1959 (1925).

⁸ Hantzsch, *Ber.*, **54**, 2573, 2613 (1921); **63B**, 1181 (1930).

⁹ Dilthey, *J. prakt. Chem.*, [2] **109**, 273 (1925); **118**, 321 (1928); **124**, 81 (1929).

such salts on hydrolysis to the colorless benzenoid form to give optically inactive products due to the fact that in the halochromic state the asymmetry of the central carbon atom has been destroyed. In the investigations which I now wish to report this was found under certain conditions not to be the case.

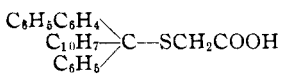
Phenylbiphenyl- α -naphthylcarbinol was prepared according to the method of Schlenk.¹⁰ Several attempts were made to resolve the carbinol itself by combining it directly with brucine, quinine, camphorsulfonic acid, etc., but only negative results were obtained. Experiments were carried out in an attempt to make the carbinol in the form of its chloride combine with silver salts of optically active acids, but this method of approach proved unsatisfactory. Phenylbiphenyl- α -naphthylchloromethane, however, was found to combine with thioglycolic acid giving a stable derivative which was easily resolved.¹¹ *l*-Phenylbiphenyl- α -naphthylmethylthioglycolic acid, $(\text{C}_6\text{H}_5\text{C}_6\text{H}_4)(\text{C}_{10}\text{H}_7)(\text{C}_6\text{H}_5)\text{C}-\text{SCH}_2\text{COOH}$, has the following specific rotation in carbon tetrachloride: $[\alpha]_{\text{D}}^{20} -13.63^\circ$; in ether, $[\alpha]_{\text{D}}^{25} -12.93^\circ$. Experiments with this substance show that it forms halochromic salts. Concentrated sulfuric acid, perchloric acid and mercuric chloride unite with it forming deep blue-violet halochromic compounds which on pouring into ice water yield the carbinol, $(\text{C}_6\text{H}_5\text{C}_6\text{H}_4)(\text{C}_{10}\text{H}_7)(\text{C}_6\text{H}_5)\text{COH}$, in its optically inactive form. A solution of titanium tetrachloride in chloroform when added to a chloroform solution of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid produces a deep blue-violet halochromic salt which on decomposition with ice water yields inactive phenylbiphenyl- α -naphthylmethylthioglycolic acid. However, when a solution of ferric chloride in glacial acetic acid is added to a chloroform solution of the levo thioglycolic acid derivative, the deep blue-violet halochromic compound so formed, on pouring into ice water, produces the original *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid with no racemization. This is also true in the case of the zinc chloride halochromic salt. If an ether solution of zinc chloride be added to an ether solution of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid, the deep blue-violet compound so produced is optically active and on hydrolysis produces the original *l*-thioglycolic acid compound with no change in rotation.

If we accept the statement that the formation of color in the double salt of triarylmethyl compounds with metallic halides is caused by a tautomerism of the molecule into a quinonoid modification, the two forms of phenylbiphenyl- α -naphthylmethylthioglycolic acid would be represented by the formulas¹²

¹⁰ Schlenk, *Ann.*, 394, 196 (1912).

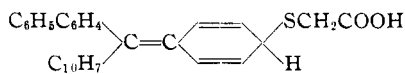
¹¹ Wallis, *Proc. Nat. Acad. Sci.*, 16, 215 (1930).

¹² Other possible quinonoid formulas can be written, but it makes no difference which group undergoes quinonoidation so far as the present discussion is concerned.



I

Colorless benzenoid



II

Colored quinonoid

On hydrolysis of the colored double salts, which according to this theory are represented by form II, compounds of type I are produced. According to theories of stereochemistry the asymmetric carbon atom in I has lost its asymmetry in form II. However, a construction of a model of the molecule of form II shows that it possesses an asymmetry of a different type known as "centroasymmetry" or molecular asymmetry, although it contains no asymmetric carbon atom. Therefore, theoretically, it could exist in two optically active modifications, but these two modifications would in all probability be produced in the rearrangement of the colorless benzenoid form, and, therefore, a racemic product would result. The question as to what will occur when an optically active substance of which the enantiomorphism of molecular configuration is associated with one particular type of asymmetry is converted into a second substance of which the optical activity arises from the exhibition by the molecule of enantiomorphism of a quite different type is not new. Perkin and Pope¹³ have shown that an optically active compound whose activity is due to molecular asymmetry undergoes racemization during its conversion into the isomeride which contains only an asymmetric carbon atom.

l-1-Methyl-cyclohexylidene-4-acetic acid, $\begin{array}{c} \text{H} \\ \text{HOOC} \end{array} \text{C}=\text{C} \begin{array}{c} \text{CH}_2\text{---CH}_2 \\ \text{CH}_4\text{---CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \\ \text{H} \end{array}$ was found by them to rearrange to *dl*-1-methyl- Δ^3 -cyclohexene-4-acetic acid, $\text{HOOCCH}_2\text{---C} \begin{array}{c} \text{CH} \text{---} \text{CH}_2 \\ \text{CH}_2\text{---CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \\ \text{H} \end{array}$. During the rearrangement complete racemization took place, even though the rearrangement product contains a true asymmetric carbon atom. In the light of such experiments, if the quinonoid theory for the explanation of color be correct, we would expect that a compound of Formula I on conversion into its halochromic salt and subsequent hydrolysis would be racemized, and would yield an optically inactive product.¹⁴ That this is not the case is readily seen from the experimental results on the halochromic compounds of ferric chloride and zinc chloride.¹⁵ In these instances not even partial racemiza-

¹³ Perkin and Pope, *Trans. Chem. Soc.*, **99**, 1515 (1911).

¹⁴ Similar reasoning has been used by Phillips (*ibid.*, **127**, 2563 (1925)), to explain the fact that certain optically active sulphinates racemize rapidly.

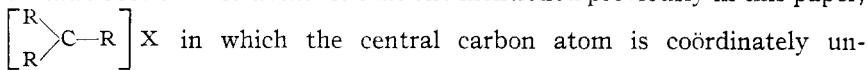
¹⁵ The fact that the double salt with titanium tetrachloride behaves differently than the double salts with ferric chloride and zinc chloride is perhaps to be expected. Titanium tetrachloride is a compound which is itself unstable in aqueous solution and is hydrolyzed with liberation of much energy and a large concentration of hydrochloric acid. Hydrolysis of the double salt of such a compound could easily be imagined to produce racemization. That this interpretation may be correct is strengthened by the

tion takes place. It therefore appears that whatever may be the cause of color in these halochromic compounds *we must not assign a structure or configuration which in any manner disturbs fundamentally the arrangement of groups around the central carbon atom.*

The alternative theory of color formation usually called the carbonium ion theory at first sight might not appear to be invalidated by these results. There is some evidence from optically active sulfonium compounds¹⁶ that at least with a sulfur atom a positive ion maintains an asymmetric configuration. It is plausible that in both the optically active methylthethylthetines and in the optically active sulfinates, the tercovalent sulfur atoms are associated with free electric charges. From this it might be imagined that a carbonium ion could maintain a structure approaching that of an asymmetric molecule. Experimental evidence¹⁷ has been found which seems to support this view. However, if this be true we would expect that the halochromic compounds produced by the action of sulfuric acid, perchloric acid and mercuric chloride on *l*-phenylbiphenyl- α -naphthylthioglycolic acid would produce on hydrolysis the optically active modification of the carbinol. But in these three cases the racemic compound is formed. It must be noted that the sulfonium ion if present in the thetines and sulfinates possesses a complete octet of valency electrons whereas in the carbonium ion only a sextet of valency electrons is present. Therefore the carbonium ion may possess a far less rigid structure than the sulfur atom in the thetine ion. In fact, recent evidence of Kenyon and Phillips¹⁸ leads to the view that tercovalent carbonium ions are optically unstable.

Another argument which could be put forward against this view that a carbonium ion is always produced in the colored salts of the triarylcarbinols is the fact that the halochromic compounds with zinc chloride and ferric chloride on hydrolysis do not produce the carbinol, but the original *l*-thioglycolic acid derivative. We should expect the carbinol to be formed if a carbonium ion were produced in the production of the halochromic salt, for hydrolysis of a compound containing the carbonium ion generally produces the corresponding carbinol.

It therefore would appear from these results on halochromic salts of an optically active derivative of a triarylcarbinol that the most likely representation for their structure is that one mentioned previously in this paper,



fact that an acetic acid solution of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid containing hydrogen chloride racemizes.

¹⁶ Pope and Peachey, *Trans. Chem. Soc.*, **77**, 1072 (1900); Phillips, *ibid.*, **127**, 2552 (1925).

¹⁷ Jones and Wallis, *THIS JOURNAL*, **48**, 169 (1926); McKenzie, Rogers and Wills, *Trans. Chem. Soc.*, **129**, 779 (1926).

¹⁸ Kenyon and Phillips, *ibid.*, **133**, 1676 (1930).

saturated. In such a compound the molecule is heteropolar as compared with the colorless homopolar modification. The C—X bond may or may not be a true ionic linkage depending on whether the particular inorganic acid or salt used causes a complete transference of an electron to the octet of the group X, or only a partial distortion from the normal position.

Experimental Results

Preparation of *l*-Phenylbiphenyl- α -naphthylmethylthioglycolic Acid, (C₆H₅C₆H₄)(C₁₀H₇)(C₆H₅)C—SCH₂COOH.—*l*-Phenylbiphenyl- α -naphthylmethylthioglycolic acid was prepared according to the method of Wallis.¹⁹ Seventeen grams of the pure *levo* compound was obtained from 39 g. of the brucine salt; 1.0242 g. dissolved in 25 cc. of dry ether solution gave a rotation of -1.06 at 25° in a 2-dm. tube, $[\alpha]_D^{25} -12.93^\circ$; 1.0020 g. dissolved in 25 cc. of carbon tetrachloride solution gave a rotation of -1.09 at 20° in a 2-dm. tube, $[\alpha]_D^{20} -13.63^\circ$; 0.4215 g. dissolved in 25 cc. of glacial acetic acid solution gave the following rotations at 20° in a 2-dm. tube: $\alpha_{558} -0.23$, $\alpha_{589} -0.29$, $\alpha_{546} -0.36$, $\alpha_{4861} -0.50$, $\alpha_{4358} -0.70$; $[\alpha]_{558}^{20} -6.82$, $[\alpha]_{589}^{20} -8.60$, $[\alpha]_{546}^{20} -10.68$, $[\alpha]_{4861}^{20} -14.83$, $[\alpha]_{4358}^{20} -20.76^\circ$.

An ether solution of this substance on standing at room temperature for two weeks showed no change in rotation. However, a solution of this material in glacial acetic acid on standing slowly decreased in rotatory power.

The residues from the fractional crystallizations were worked up and gave 20 g. of a mixed dextro phenylbiphenyl- α -naphthylmethylthioglycolic acid,²⁰ $[\alpha]_D^{20} +10.13^\circ$ in ether.

Action of Concentrated Sulfuric Acid.—Two grams of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid was dissolved in 5 cc. of concentrated sulfuric acid previously cooled to -20° . A deep violet color developed. As soon as solution was complete the contents of the flask were poured into ice water. The deep violet color of the halochromic sulfate disappeared immediately and a white precipitate was formed. This was filtered off and dried; 1.7 g. of crude product was obtained. One-half gram of this material dissolved in 25 cc. of benzene solution gave no observable rotation in a 2-dm. tube. Recrystallization of a second portion from benzene gave a compound which melted at 161 – 162° . A mixed melting point determination of this substance with *dl*-phenylbiphenyl- α -naphthylcarbinol showed no change in melting point.

Action of Perchloric Acid.—Two grams of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid was dissolved in 30 cc. of glacial acetic acid and cooled to the freezing point of the mixture; 10 cc. of a 60% aqueous solution of perchloric acid previously cooled to 0° was then added, and the deep violet halochromic compound was poured immediately into ice water. It melted at 138 – 145° ; 0.5 g. of this crude product in 25 cc. of benzene solution gave no observable rotation in a 2-dm. tube. Recrystallization of the material from benzene (60 – 80°) gave a compound which melted at 160 – 161° . A mixed melting point determination with the *dl*-carbinol showed no change in melting point.

Action of Mercuric Chloride.—A solution of 1.0 g. of mercuric chloride dissolved in 30 cc. of dry ether was cooled to 0° and added to a solution of 1.0 g. of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid in 10 cc. of ether. The deep violet mixture was poured immediately into ice water. The ether layer was separated, washed and dried with anhydrous sodium sulfate. A portion of this solution in a 2-dm. tube gave

¹⁹ Wallis, *Proc. Nat. Acad. Sci.*, 16, 215 (1930).

²⁰ The dextro modification was not obtained in a pure form. Fractional crystallization of the brucine salt gives only the pure *l*-isomer.

no observable rotation. On partial evaporation a compound was deposited which contained ether of crystallization. It melted at 113° and contained no sulfur. The ether was removed by warming and the product crystallized from benzene ($60-80^{\circ}$). The product so obtained melted at 160° . A mixed melting point determination of this substance with *dl*-phenylbiphenyl- α -naphthylcarbinol²¹ showed no change in melting point.

Action of Titanium Tetrachloride.—0.45 g. of titanium tetrachloride in 10 cc. of pure chloroform was cooled to 0° and added to a solution of 1.0 g. of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid dissolved in 15 cc. of chloroform. The deep violet solution was poured into ice water. The colorless chloroform layer was separated, washed three times with water and dried over anhydrous sodium sulfate. A portion of this solution in a 2-dm. tube gave no observable rotation. The chloroform was evaporated and the product crystallized from toluene. A white crystalline compound was obtained which melted at 114° . This compound contained sulfur, and was identical in its properties with *dl*-phenylbiphenyl- α -naphthylmethylthioglycolic acid. Similar experiments at -70° gave the same results. The product formed was inactive.

Action of Ferric Chloride.—A qualitative study of the ferric chloride and zinc chloride double salts of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid showed that these compounds on hydrolysis gave solutions which were optically active. Therefore, quantitative experiments were carried out in order to determine whether partial racemization took place during the formation and hydrolysis of the double salts. The following experiments will serve as typical examples: 0.50 g. of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid was dissolved in dry ether. The volume of the solution was made up accurately to 25 cc. A portion of this solution in a 2-dm. tube gave α_D at 20° -0.59° . The two solutions were then carefully poured into a 50-cc. Erlenmeyer flask and cooled to 0° . All receptacles were washed with ether to insure no loss of the thioglycolic acid derivative. One gram of ferric chloride previously dissolved in 10 cc. of glacial acetic acid was added. A deep violet halochromic compound formed immediately. The mixture was then poured into ice water. The color disappeared at once. The ether layer was removed, washed with distilled water and dried with anhydrous sodium sulfate. The aqueous layer was extracted three times with ether. This extract was washed twice with distilled water and dried. The ether solutions were united and concentrated by evaporation to 20 cc. The solution was then made up accurately to a volume of 25 cc. and the rotatory power determined, $\alpha_D^{20} -0.56$. The solution was evaporated and the material which separated out was crystallized from benzene. The compound was found to contain sulfur. It melted at $107-108^{\circ}$. A mixed melting point with *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid showed no appreciable change in melting point. Other experiments were carried out varying the concentrations of the reactants and the solvents, but in no case was appreciable racemization observed.

Action of Zinc Chloride.—0.61 g. of *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid was dissolved in ether and the solution accurately made up to a volume of 25 cc.; α_D^{20} in a 2-dm. tube was -0.73 . The solution was cooled to 0° and to it was added an ether solution of 0.50 g. of zinc chloride previously cooled to 0° . The deep violet solution was poured into ice water and the colorless ether layer removed. This was washed twice with distilled water and dried. The aqueous layer was extracted with ether and the ether solution was washed and dried with anhydrous sodium sulfate. The two solutions were united and concentrated to 20 cc. The volume was then made up to 25 cc. and the rotatory power determined, α_D^{20} in a 2-dm. tube, -0.70° . The solution was evaporated and treated as described in the experiments on the ferric chloride

²¹ Phenylbiphenyl- α -naphthylcarbinol crystallizes from ether with ether of crystallization. This compound melts at $115-116^{\circ}$.

double salt. A mixed melting point determination with *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid showed no change in melting point.

Other experiments were carried out varying the amount of zinc chloride, but in no case was racemization observed.

Conclusions

Certain derivatives of triarylcarbinols containing an asymmetric carbon atom have been prepared. Phenylbiphenyl- α -naphthylmethylthioglycolic acid has been resolved into a pure levo form, $[\alpha]_D^{20} - 13.63^\circ$, and a mixed dextro isomer $[\alpha]_D^{20} + 10.13^\circ$. Experiments with this substance show that it forms halochromic compounds. Concentrated sulfuric acid, perchloric acid and mercuric chloride unite with it to form deep violet halochromic compounds which on pouring into ice water yield the carbinol in its optically inactive form. Titanium tetrachloride produces a deep violet halochromic salt which on decomposition with water yields the racemic phenylbiphenyl- α -naphthylmethylthioglycolic acid. However, the double salts with ferric chloride and zinc chloride on hydrolysis give *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid with no racemization.

A discussion of these facts is given with special reference to the quinonoid theory and carbonium ion theory of formulation for the explanation of color.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

SOME CHLORINE DERIVATIVES OF BENZYLPHENOLS. I. DICHLORO DERIVATIVES OF ORTHO AND PARA BENZYLPHENOLS

BY R. C. HUSTON AND E. F. ELDRIDGE

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This paper is the first of a series dealing with the chlorination and the chlorine derivatives of the benzylated phenols. Only a comparatively few of these compounds have been reported.

A chlorobenzyl phenol¹ was made by treating benzylphenol with sulfuric chloride. The investigator reported that the chlorine probably entered the ring in the ortho position, giving the formula $C_6H_5CH_2C_6H_4ClOH$, but gave no proof of structure. Beilstein reports its formula as $C_6H_5-CHClC_6H_4OH$ with the chlorine on the CH_2 group. Richter's Lexicon shows the substitution in the meta position.

Sentinis prepared a benzyl chlorophenyl ether² by passing chlorine into an alcoholic solution of the ether to which some mercuric oxide had been added as a catalyst. This was later shown by Baw³ to be benzyl *p*-chlorophenyl ether.

¹ Peratoner and Vitaei, *Gazz. chim. ital.*, **28**, 197 (1898).

² Sentinis, *Ann.*, **161**, 345 (1872).

³ Baw, *Quart. J. Indian Chem. Soc.*, **3**, 101 (1926).