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AN INVESTIGATION INTO THE SYNTHESIS OF AN

OPTICALLY ACTIVE TRITYL SYSTEM

BY

PAUL L. FITZGERALD

A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment
of the Requirements for the Degree of
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ABSTRACT

Several possible routes to obtain an optically active trityl system have been studied. Model systems, using triphenylcarbinol and 4-bromo-4'-chlorotriphenylcarbinol, were employed. Several routes to break down the glycolic acid derivatives of these alcohols were studied. These involve the preparation of the silver salt of the acid and its reaction with bromine; the reaction of the acid with mercuric oxide and bromine and the thermal decomposition of the silver salts of the acids.

ACKNOWLEDGEMENTS

The author would like to express his most sincere gratitude to Dr. K. G. Rutherford for his patience and guidance during the course of this work.

Appreciation is also shown to the University of Windsor for a Graduate Teaching Assistantship which was held for each of the years during which these studies were undertaken.

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CHAPTER I

Introduction

Optically active systems arise from the fact that molecules which have the same constitution may still differ, as isomers, in the way in which their atoms are arranged in space. The one main condition for this type of isomerism to take place is met when a molecule is not superimposable on its mirror image. Such a molecule is called dissymmetric and the simplest way a molecule can attain dissymmetry is to contain a carbon atom to which are attached four different atoms or groups. There are other ways in which dissymmetry can be attained but this work only concerns itself with this type of molecule. Compounds of the general formula RR_1R_2C-X are of this type. These compounds, in general exist as a racemic mixture of optical antipodes which can be separated by mechanical means. Each optical antipode is identical to the other as regards chemical properties but rotates the plane of polarized light in opposite directions. The separation of optical isomers usually involves the formation of a diastereomeric pair by reaction with an optically active compound. The diastereomers usually differ in physical properties to the extent that they can be separated by fractional crystallization. Regeneration of the optically active antipode is usually effected easily with mineral acid or base.

Resolution of Alcohols

Satisfactory methods of resolution have been reported for all types of alkyl and arylalkyl secondary alcohols.[1] These methods of resolution, however, do not apply to all cases and it is left up to the individual researcher to determine the best method for the resolution of the compound in question. Of the three methods that are outlined by Ingersoll it will be found that only one of them has any practical importance.

The first method involves the separation of the enantiomers by means of crystallization. This method must necessarily involve a solid racemic mixture which upon crystallization deposits crystals of each of the active components. These crystals may then be separated by sorting them out mechanically or by partial crystallization. Separating the enantiomers by this means has proved practical only in a few cases and for that reason is not generally used.

The formation of diastereomers and the subsequent fractional crystallization of the diastereomeric derivatives is the second method of resolution mentioned by Ingersoll. It has been shown to be the most useful and practical of all the methods. The first step involves the formation of a semi-permanent linkage between the optically active

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1   A.W. Ingersoll, Organic Reactions, Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1944, p.376

resolving agent and the two enantiomers of the substance to be resolved. This linkage must be strong enough to remain intact during the fractional crystallization but also must be capable of being readily broken so that the desired optically active substance may be regenerated. Esterification of an alcohol (or phenol) with an acid or acid derivative usually provides the linkage that meets these requirements. The alcohol can be esterified with an optically active acid and separated with the recovery of the alcohol and the resolving agent by alkaline hydrolysis. This method is limited in that the esters formed must be crystalline.

Phthalic acid or succinic acid are two of the most common substances with which derivatives of alcohols have been formed. Resolution of the alcohol is effected through the salt of the acid ester. The ester is resolved through the acid portion using an alkaloid, usually brucine or strychnine, as the resolving agent. When the optically active salts have been purified they are hydrolysed and the acid ester is saponified or reduced (in the case where racemization of the alcohol might take place with base) to regenerate the optically active alcohol. The procedure for the use of the hydrogen phthalate derivatives is out-lined in the following scheme. This scheme has been applied to alcohols of nearly all types except tertiary. Tertiary alcohols were found generally to dehydrate or not form derivatives by this method.

(±) R-OH + [phthalic anhydride] —pyridine→ (±) R-O-C(=O)-C₆H₄-C(=O)-OH —Brucine→

R-O-C(=O)-C₆H₄-C(=O)-O⁻ Brucine·H⁺ —(1) Fractionation / (2) HCl→ R-O-C(=O)-C₆H₄-C(=O)-OH (active)

fractionation

NaOH Δ

LiAlH₄

R-OH + NaOOC-C₆H₄-COONa (active)

R-OH + C₆H₄(CH₂OH)₂ (active)
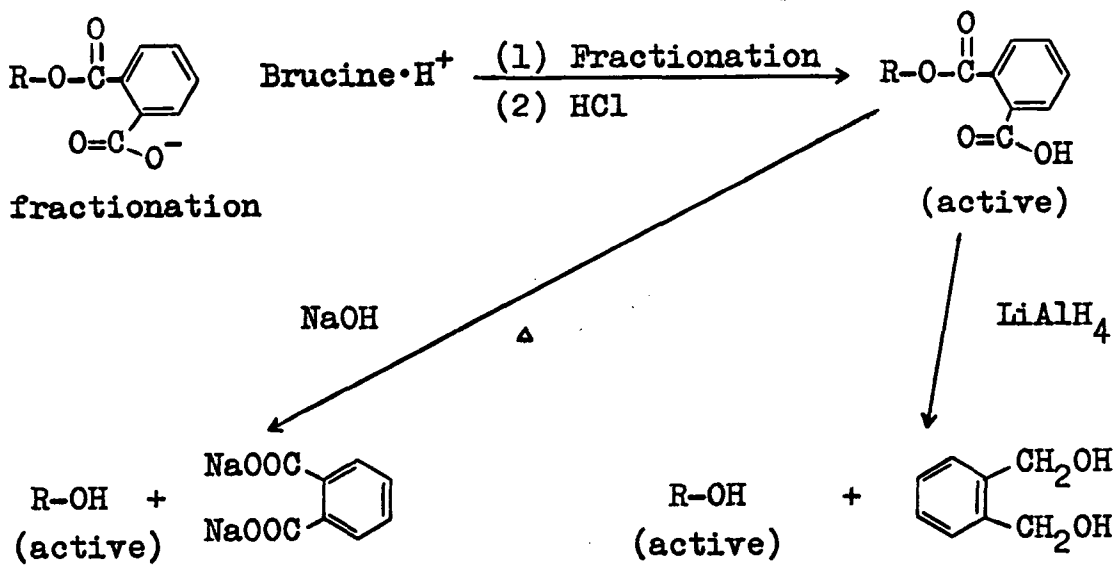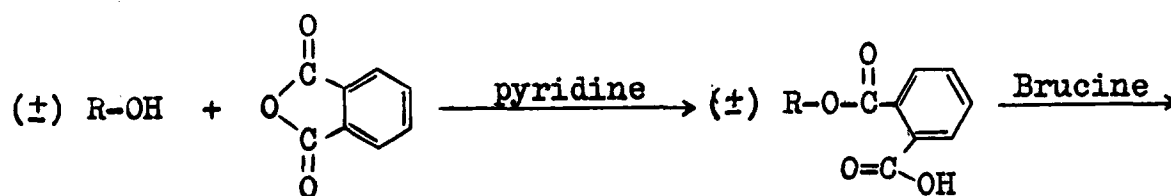
Ingersoll's third method involves the reaction of the racemic substance with an optically active agent under different conditions. The enantiomers might be found to react with the reagent at different rates and thus partial resolution may be obtained. Fractional reaction with an optically active agent, fractional decomposition by an optically active catalyst or fractional absorption on an optically active surface could all lead to partial resolution. In following with the same principle, optically active compounds can be produced by the interaction of a living organism or by an enzyme. These methods rarely show

practicality.

Although many alcohols have been resolved by these methods the fractionation of the diastereomeric derivative has proved to be the most useful. In fact nearly all types of secondary alcohols have been resolved using this method. In 1950 Green and Kenyon[2] reported the preparation and the resolution of an aryl carbinol, 4-chlorobenzhydrol. Their method involved the use of the hydrogen phthalate derivative and the subsequent resolution and regeneration of the alcohol. 2,4-Dimethylhexan-4-ol[3] and 2-phenyl-2-butanol[4] are two examples of aliphatic or mixed aliphatic-aromatic tertiary alcohols that have been reported to have been resolved. The resolutions were effected by preparing the potassium salt of the alcohol, then adding phthalic anhydride to the mixture and resolving the resultant hydrogen phthalate ester. In general, derivatives of the tertiary alcohols are hard to form and although several derivatives of tertiary alcohols have been formed,[5][6] those of a purely aromatic nature have been reported in only a few cases in the literature.

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2 G. H. Green and J. Kenyon, *J*. *Chem*. *Soc*., 751 (1950).

3 W. von E. Doering and H. H. Zeiss, *J*. *Am*. *Chem*. *Soc*., 72, 147 (1950).

4 H.H. Zeiss, *J*. *Am*. *Chem*. *Soc*., 73, 2391 (1951).

5 J. Hickman and J. Kenyon, *J*. *Chem*. *Soc*., 2051 (1955).

6 J. Kenyon, A. G. Davies and K. Thaker, *J*. *Chem*. *Soc*., 3396 (1956).

Resolution of Triarylcarbinols

The optically active trityl system is most attractive for studies of the stereochemistry of substitution processes involving ion pairs since the system does not suffer from side reactions (S_N2 type processes and elimination reactions [7,8,9]). Again, kinetic and sterochemical studies on the solvolysis of optically active trityl systems should provide information concerning the mechanism of substitution of trityl compounds. Certainly interest in stereochemical studies has been heightened by recent studies of Swain[10], Smith[11] and Streitweiser[12]. Thus attempts to find synthetic routes to optically active trityl systems are desirable.

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7 E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai Y. Pocker, J. Chem., Soc., 1220 (1957).

8 S. Winstein and G. C. Robinson, J. Am. Chem. Soc., 80, 169 (1958).

9 C. G. Swain and E. E. Pegues, J. Am. Chem. Soc., 80 812(1958).

10 C. G. Swain and G. Tsuchihashi, J. Am. Chem. Soc., 84, 2021 (1962).

11 S. G. Smith, Tetrahedron Letters, No. 21, 979 (1962).

12 A. Streitweiser Jr. and T. D. Walsh, Tetrahedron Letters, No. 1, 27 (1963).

Hydrogen phthalate ester derivatives of trityl systems
can be prepared[13] by using a strong base, triphenylmethyl
sodium, and adding phthalic anhydride to the system. After
stirring the system, the solid derivative is obtained.
Having now obtained a hydrogen phthalate ester derivative,
it would now be conceivable that resolution of the alcohol
might be possible.

More recently Thaker and Dave[14] have reported the
preparation of hydrogen phthalate esters. The alcohols
ethylphenyl p-tolylmethanol and α-napthylphenyl p-tolyl-
methanol were studied. They reacted each of these with
phthalic anhydride in the presence of triethylamine at 90-
96° for a period of sixteen to eighteen hours. Their method
of preparing these derivatives was contrary to the claims
of Balfe and Kenyon[15]. Attempts in this laboratory to
repeat the work of Thaker and Dave has also failed to give
the reported results under a variety of conditions.

In our research the problem of finding a synthetic
route to optically active trityl systems was approached
from another point of view. Wallis[16] had reported the

13 K. G. Rutherford, J. M. Prokipcak and D. P.C.
Fung, J. Org. Chem., 28, 582 (1963).

14 K. A. Thaker and N. S. Dave, J. Sci. Industr. Res.,
21B, 374 (1962).

15 M. P. Balfe, J. Kenyon, and E. M. Thain, J. Chem.
Soc., 386 (1951).

16 E. S. Wallis, Proc. Nat. Acad. Sci., 16, 215 (1930).

resolution of phenylbiphenyl-α-napthylmethylthioglycolic
acid and the subsequent resolution[17] of phenylbiphenyl-α-
napthylcarbinol. In a later paper[18] he reported the res-
olution of 12-phenyl-12-β-benzoxanthenethioglycolic acid,
which was prepared by reacting the chloride with thiogly-
colic acid and resolving the acid with brucine from acetone
solution. Attempts to break down the resolved thioglycolic
acid derivative to the alcohol with mineral acids caused
racemization. Wallis and Adams also tried to resolve the
thioglycolic acid derivative of methylphenylbiphenylcarbinol
in the same manner but it was found that the brucine salt
decomposed into unsaturated hydrocarbons and alkaloid
thioglycolates. This method of resolution seemed reasonable
as the acid functional group was present for resolution
and the conversion of the acid derivative to the alcohol
seemed possible.

In our laboratory similar work was done on the glycolic
acid derivative[19]. Triphenylcarbinol and also 4-bromo-4'-
chlorotriphenylcarbinol were used in these studies. The
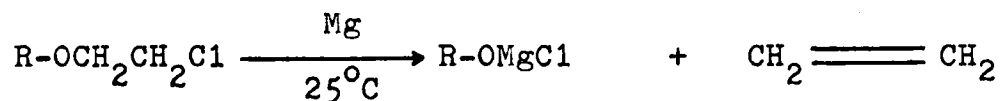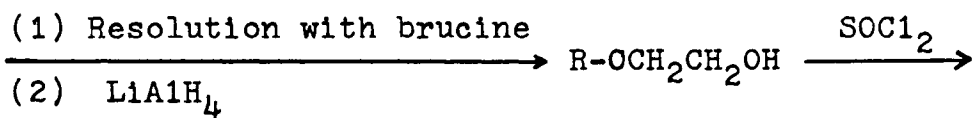study was carried out according to the following reaction
schemes:

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17 E. S. Wallis, J. Am. Chem. Soc., 54, 1695 (1932).

18 E. S. Wallis and F. H. Adams, J. Am. Chem. Soc., 55, 3838 (1933).

19 J. M. Prokipcak, Ph. D. Thesis, Faculty of Graduate Studies, University of Windsor, 1964, pp. 50-71.

R= triphenylmethyl or the substituted derivative.

$$R\text{-}OH \xrightarrow{CH_3COCl} R\text{-}Cl \xrightarrow[\text{Pyridine}]{HOCH_2COOH} R\text{-}OCH_2COOH$$

$$\xrightarrow[\text{(2) LiAlH}_4]{\text{(1) Resolution with brucine}} R\text{-}OCH_2CH_2OH \xrightarrow{SOCl_2}$$

$$R\text{-}OCH_2CH_2Cl \xrightarrow[25^\circ C]{Mg} R\text{-}OMgCl \quad + \quad CH_2 = CH_2$$

and

$$R\text{-}Cl + HOCH_2CH_2COOH \xrightarrow{\text{Pyridine}} R\text{-}OCH_2CH_2COOH$$

$$\xrightarrow[\text{(2) CH}_2N_2]{\text{(1) Resolution}} R\text{-}OCH_2CH_2COOCH_3 \xrightarrow[\text{Reverse Michael}]{(C_6H_5)_3C^-Na^+}$$

$$R\text{-}O\overset{\curvearrowright}{-}CH_2\underset{\curvearrowleft}{-}CH\overset{\|}{\underset{O}{C}}\text{-}OCH_3 \longrightarrow \begin{array}{c} R\text{-}ONa \\ \text{optically} \\ \text{active} \end{array} + \quad CH_2 = CH\text{-}\overset{\|}{\underset{O}{C}}\text{-}OCH_3$$
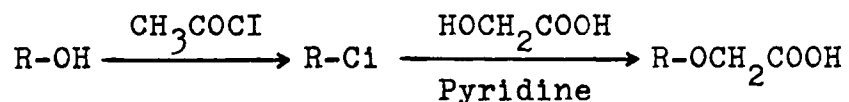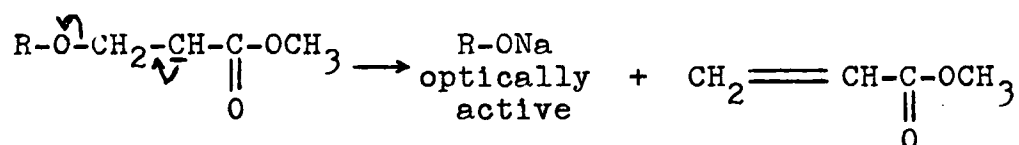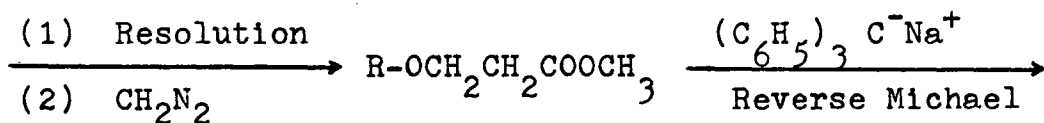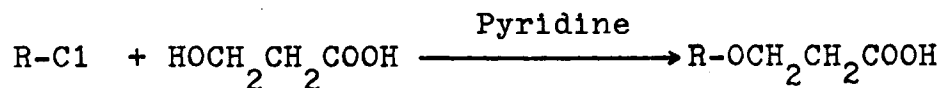
At least in principle the above methods show a feasible route to an optically active trityl system and would be very good if the difficulties could be overcome. The latter route appears more practical as it furnishes a better yield.

Murr[20] recently has reported a successful synthesis
for an optically active trityl system. His work was done
on the glycolic acid derivative of phenylbiphenyl-α- napthyl-
carbinol and the reaction scheme that he used is outlined
below:

R= phenylbiphenyl- α- napthylmethyl.

$$\text{R-OH} \xrightarrow[\text{chloride}]{\text{acetyl}} \text{R-Cl} \xrightarrow[\text{HOCH}_2\text{COOCH}_3]{\text{pyridine-benzene}} \text{R-OCH}_2\text{COOCH}_3 \quad .$$

$$\xrightarrow[\text{65\% MeOH-H}_2\text{O}]{\text{KOH}} \text{R-OCH}_2\text{COOH} \xrightarrow[\text{(3)} \quad \text{H}_2\text{SO}_4, \text{ ether.}]{\substack{\text{(1)} \quad \text{Brucine} \\ \text{(2)} \quad \text{Resolution}}} \text{1-R-OCH}_2\text{COOH}$$
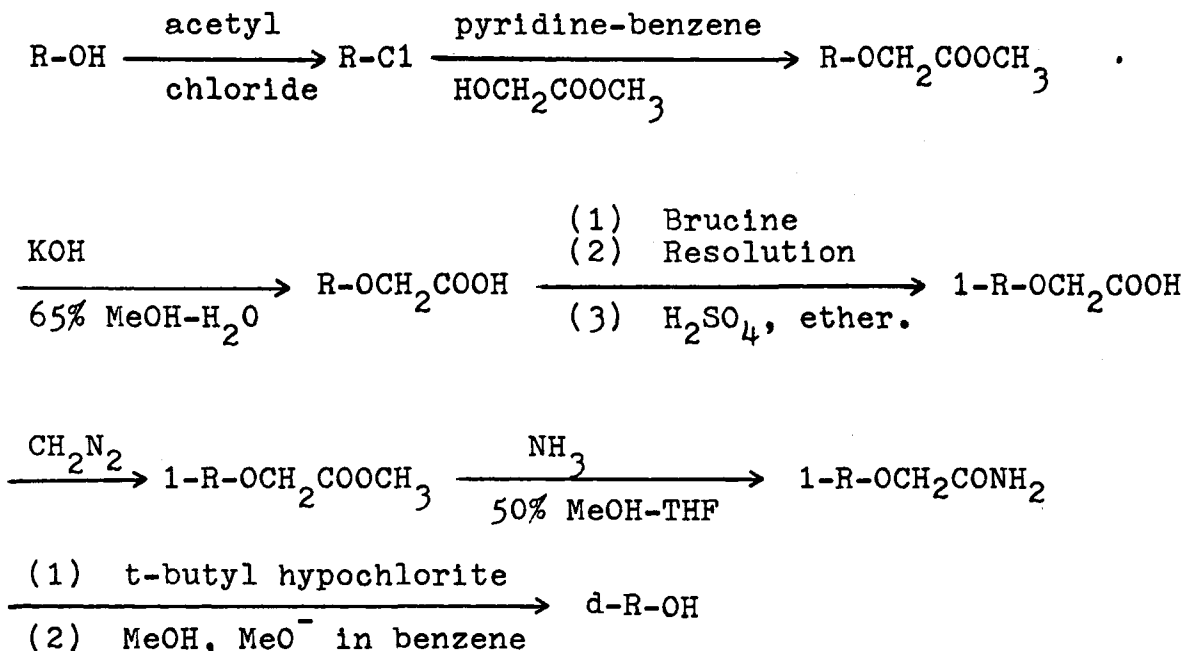
$$\xrightarrow{\text{CH}_2\text{N}_2} \text{1-R-OCH}_2\text{COOCH}_3 \xrightarrow[\text{50\% MeOH-THF}]{\text{NH}_3} \text{1-R-OCH}_2\text{CONH}_2$$

$$\xrightarrow[\text{(2)} \quad \text{MeOH, MeO}^- \text{ in benzene}]{\text{(1)} \quad \text{t-butyl hypochlorite}} \text{d-R-OH}$$

The overall yield of the alcohol obtained from the glycolic
acid derivative was approximately 36% and the yield of alcohol
obtained from the optically active acid was 60%.

Murr's reaction scheme appeared to have all the
characteristics favorable to the resolution of trityl
alcohols. The yields were fairly good and except for the
last step the reactions appeared simple. The last step

20 B.L. Murr, J. Am. Chem. Soc., 85, 2866, (1963).

involved the procedure of Baumgarten[21] using tertiary butyl
hypochlorite in the Hofmann rearrangement.

The method of Murr indeed looked excellent and it was
decided to carry out the reaction sequence using 4-bromo-
4'-chlorotriphenylcarbinol although it was decided to
investigate other methods as well.

The glycolic acid derivative of a triarylcarbinol
seemed inviting as regards other possible synthetic routes
to optically active trityl systems. Thus it was thought that
if the silver salt of the optically active acid was prepared
and a Hunsdieker reaction[22] were performed then facile
breakdown of the alcohol could take place. The Hunsdieker
reaction involves the action of halogens with dry metal
salts, particularly silver salts of carboxylic acids, and
it has been reviewed in the literature.[23, 24] It is possible
to obtain from these silver salts organic halides containing
one less carbon atom than the original acid, and it requires
reaction conditions in which the ratio of the silver salt
to the halogen is one to one. The initial product of this
reaction is an acyl hypohalite which is then thermally
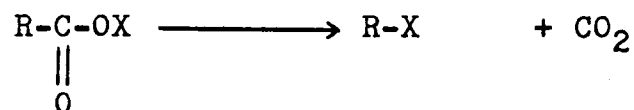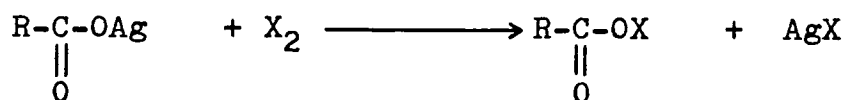cleaved to form an alkyl halide and carbon dioxide as
follows:

21 H. E. Baumgarten, J. E. Dirks, J. M. Petersen and
D. C. Wolf, J. Am. Chem. Soc., 82, 4422 (1960).

22 C. V. Wilson, Organic Reactions, Vol IX, John Wiley
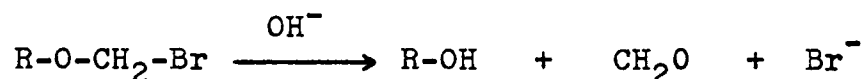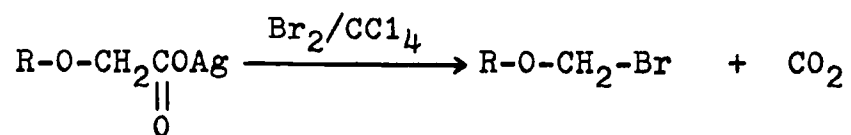and Sons, Inc., London 1957, p. 332.

23 J. Kleinberg, Chem. Rev., 40, 381 (1947).

24 R. G. Johnson and R. K. Ingham, Chem. Rev., 56, 219
(1956).

$$R-\underset{\underset{O}{\|}}{C}-OAg \quad + X_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OX \quad + \quad AgX$$

$$R-\underset{\underset{O}{\|}}{C}-OX \longrightarrow R-X \quad + CO_2$$

The reaction is believed to proceed via a free radical mechanism by studies on optically salts and on model compounds that rearranged due to the formation of free radicals and through other experiments reported by Wilson.[22] Wilson also reports that substituents in the aliphatic chain, other than the α-position do not interfere with the reaction. Also any aryl substituents such as phenyl or deactivated phenyl do not interfere, but with an activated phenyl group present the aromatic ring is easily halogenated and carbon dioxide is not liberated. Usually these Hunsdieker reactions are run in boiling carbon tetrachloride with the silver salt forming a slurry and the bromine is added dropwise. Then the whole mixture is heated at reflux for a period of about two-three hours.

The silver salt of the glycolic acid derivative could possibly decarboxylate and form the α-halo ether in the Hunsdieker manner. This α-halo ether could then be hydrolysedin a basic solution and yield the desired alcohol, formaldehyde, and halide, according to the following reaction sequence:

$$R-O-CH_2\underset{\underset{O}{\|}}{C}OAg \xrightarrow{Br_2/CCl_4} R-O-CH_2-Br \quad + \quad CO_2$$

$$R-O-CH_2-Br \xrightarrow{OH^-} R-OH \quad + \quad CH_2O \quad + \quad Br^-$$

The Hunsdieker reaction could be modified in another manner. Hunsdieker[25] reported in 1942 that the mercuric salts of acids treated in the same manner as silver salts could decarboxylate in the same manner and possibly through the same intermediate when treated with halogens. This method still involved the preparation of these salts followed by a scrupulous drying process since any water present would decrease yields in the reaction.

In 1961 Cristol and Firth [26] reported a much simpler procedure for carrying out the Hunsdieker reaction. They treated a refluxing solution of stearic acid in carbon-tetrachloride, containing a slurry of excess red mercuric oxide, with approximately an equivalent of bromine. The reaction was carried out in the dark and a 93% yield of the crude heptadecyl bromide was obtained. Their work was repeated by Davis and coworkers[27] and the results were the

---

25 H. Hunsdieker, and C. Hunsdieker, Ber., 75, 291 (1942).

26 S. J. Cristol and W. C. Firth, Jr., J. Org. Chem., 26, 280 (1961).

27 J. A. Davis, J. Herynk, S. Carroll, J. Bunds, and D. Johnson, J. Org. Chem., 30, 415 (1965).

same. Davis and workers also tried other metal oxides and solvents but reported that the best yields were obtained with red mercuric oxide and carbontetrachloride or tetrachloroethane as solvents. Their reactions were not carried out in the dark and yet their results were comparable. The proposed stoichiometric equation for Cristol and Firth's modification of the Hunsdieker reaction is given as:

$$2\ RCOOH\ +\ HgO\ +\ 2\ Br_2 \longrightarrow$$
$$2\ RBr\ +\ HgBr_2\ +\ H_2O\ +\ 2\ CO_2$$
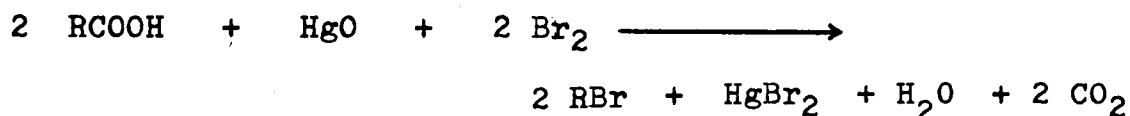
Since water is formed in the reaction products it would seem that the acyl hypohalite (RCOOBr) proposed as the intermediate would break down. Cristol and Firth say that this formation of water does not propose any difficulty. Therefore, it would seem that their reaction would not proceed in a manner similar to that of Hunsdieker. This reaction also would be very useful in the synthesis of an optically active trityl alcohol. The alkyl halide formed could be hydrolysed by base and the desired alcohol obtained.

Summary

Although synthetic routes to optically active trityl systems have been studied such as hydrogen phthalate, glycolic acid, and hydracrylic acid derivatives and several resolutions have been reported[8,11,14] it is still desirable to find a shorter and more efficient synthesis. The methods

mentioned above could all provide routes to optically
active systems and could all prove very useful. It was,
however, thought that the Hunsdieker method of preparing
alkyl halides followed by basic hydrolysis could lead to
an optically active trityl system in a more facile manner.
This method should be easy to carry out and because of its
relative simplicity (it involves fewer steps) should give
better yields. This method is of concern in this work and
the results along with other attempts will be discussed in
the following chapter.

CHAPTER II

Discussion of Experimental Results

In view of Murr's[1] successful synthesis of optically
active phenylbiphenyl-α- napthylcarbinol, a concerted effort
was made to find new general routes which would involve
shorter reaction sequences and better yields for the
synthesis of optically active trityl systems. Murr's
reaction sequence was however applied to both triphenyl-
carbinol and 4-bromo-4'-chlorotriphenylcarbinol. In the
case of triphenylcarbinol, the method proved feasible with
the exception of the Hofmann Rearrangement which proceeded
in only 14% yield. With 4-bromo-4'-chlorotriphenylcarbinol,
the Hofmann Rearrangement step could not be effected under
the conditions employed.

Since the glycolic acid derivative of both trityl-
carbinols under investigation was quite simple to prepare
it was decided to investigate possible methods of degradation
of this intermediate. One of the methods employed involved
the use of the Hunsdiecker Reaction, the sequence of which
was shown in Chapter I. The preparation of the silver salt
of triphenylcarbinol proceeded quite smoothly to give near
quantitative yields. The subsequent reaction with bromine
in boiling carbon tetrachloride followed by base hydrolysis

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1 B. L. Murr., J. Am. Chem. Soc., 85, 2866 (1963).

gave only 44% yield of triphenylcarbinol. It was decided then to abandon the silver salt method.

The modification of the Hunsdiecker Reaction as reported by Cristol and Firth[2] proved quite promising in the case of the glycolic acid derivative of triphenylcarbinol. A 67% yield of carbinol was obtained from the reaction of the corresponding glycolic acid derivative with mercuric oxide and bromine in carbon tetrachloride. Similarily a 50% yield of 4-bromo-4'-chlorotriphenylcarbinol was obtained from the corresponding glycolic acid derivative. Thus it would appear that this modification of the Hunsdiecker Reaction will be useful for future work in the synthesis of optically active trityl systems.
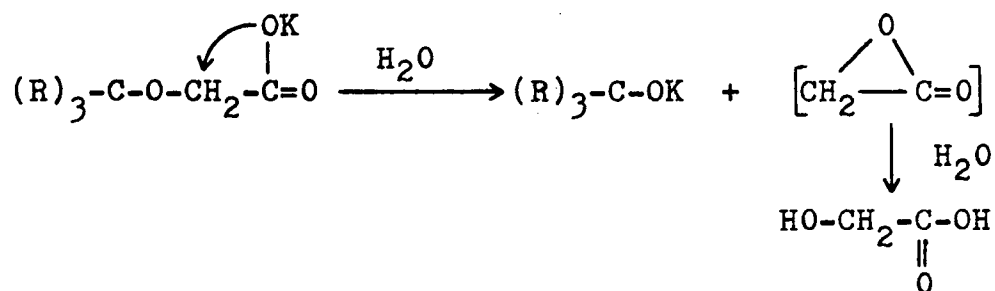
Another method which may eventually prove to be even more useful and practical than the Hunsdiecker modification for the synthesis of optically active trityl systems resulted from the observation that the silver salts of both glycolic acid derivatives of the carbinols investigated decomposed below 200°C. Thus silver-triphenylmethoxyacetate decomposed at 165-169° while silver-4-bromo-4'-chlorotriphenylmethoxy-acetate decomposed within the range 150-154°. The addition of water to the residue in both cases followed by extraction with chloroform gave a 47% yield of triphenylcarbinol in the one case and a 75% yield of 4-bromo-4'-chlorotriphenyl-carbinol in the other. The isolation and semiquantitative

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2 S. J. Cristol and W. C. Firth, Jr., J. Org. Chem., 26, 280 (1961).

determination of the inorganic residue indicated elemental
silver as one of the products of decomposition. The gases
which resulted from the decomposition were not determined.
The mechanism of this decomposition would prove an
interesting study.

Another method which did not prove fruitful involved
the reaction of the glycolic acid derivatives with boiling
potassium hydroxide (3%). It was hoped that neighbouring
group participation of carboxylate anion would occur in
the following manner and result in recovery of the carbinols.

$$(R)_3-C-O-CH_2-C=O \xrightarrow{H_2O} (R)_3-C-OK \;+\; \left[CH_2 \overset{O}{\diagdown} C=O\right]$$

$$\downarrow H_2O$$

$$HO-CH_2-C-OH \underset{\|}{\overset{}{}} O$$

However only starting acid materials were isolated.

Conclusions

Two new methods have been found which may prove useful
as general syntheses for optically active tritylcarbinols.
No attempt was made to study the stereochemistry of either
method, but this area would be a required study for future
work.

CHAPTER III

EXPERIMENTAL PROCEDURE

All starting materials for the initial compounds were
certified reagents obtained from the Fisher Scientific
Company. All melting points and decomposition points were
taken on the Fisher-Johns melting point apparatus. The
infrared absorption spectra were all taken on the Beckman
Midek IR-10 infrared spectrophotometer.

4-Bromo-4'-Chlorobenzophenone. - This compound was prepared
according to the method of Gomberg and Bailer.[1] 4-Chloro-
benzoyl chloride (100 g., 0.57 mole) and bromobenzene
(89.7 g., 0.57 mole) were placed in a one-litre, three-
necked flask which was equipped with a mechanical stirrer,
a condenser (drying tube attached), and a flask from which to
introduce a solid powder. Anhydrous aluminum·chloride
(87 g., 0.65 mole) was added in 5-10 gram portions. The
reaction mixture was placed on a steam bath and stirred
until the mixture turned solid. The solid was broken into
small pieces and cracked ice was added to the flask. When
the solid was completely hydrolysed the resultant precipitate
was recovered by filtration, washed with 5% sodium carbonate,
distilled water and air dried. The crude product was
recrystallized from a chloroform-petroleum ether (b.p.30-60°)

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1 M.Gomberg and J. C. Bailer Jr., J. Am. Chem. Soc.,
51, 2233 (1929).

solvent pair and 4-bromo-4'chlorobenzophenone, m.p. 148-149.5°, was recovered as a white flakey precipitate (110.1 g., 66%). This melting point corresponds closely to that obtained by Gomberg and Bailer.[1] The infrared absorption spectrum showed a carbonyl absorption band at 1660 cm.$^{-1}$ and aromatic ring skeletal absorption bands at 1485 and 1590 cm.$^{-1}$.

4-Bromo-4'-Chlorotriphenylcarbinol. - Into a one-litre, three necked, round bottomed flask were placed magnesium turnings (20 g., 0.87 mole), and anhydrous ether (400 ml.). The flask was equipped with a reflux condenser, dropping funnel and a powder flask. A solution of bromobenzene (75 g., 0.48 mole) in anhydrous ether (200 ml.) was added from the dropping funnel so that a steady reflux was maintained. When all the bromobenzene had been added the phenyl magnesium bromide that was formed was heated at reflux for a period of an hour. The phenyl magnesium bromide solution was cooled to room temperature and by means of a powder flask the solid 4-bromo-4'-chlorobenzophenone (109 g., 0.37 mole) was added and the mixture was stirred at reflux temperature for two hours. The reaction mixture was then poured into a mixture of cracked ice and concentrated hydrochloric acid to destroy the Grignard complex and the excess magnesium. The ether layer was separated and washed successively with 5% sodium carbonate and distilled water. The ether was then removed in vacuo and the resultant oil

was subjected to steam distillation to remove any biphenyl
formed as a by-product. A small amount of the oil was
dissolved in chloroform after the water had been decanted.
The chloroform solution was dried over anhydrous sodium
sulphate and the latter was removed by filtration.
Petroleum ether (b.p. 30-60°) was added to form a solvent
pair and the solution was allowed to crystallize at room
temperature. A white powder came out of solution so
slowly that crystallization of the remaining oil would not
have been practical. The powder melted at 102-103° which
agrees with previous work[2]. The infrared absorption
spectrum showed a free -OH stretching band at 3600 cm.$^{-1}$,
aromatic skeletal absorption bands at 1482 cm.$^{-1}$ and 1595
cm^{-1}, and a C-O stretching band at 1016 cm.$^{-1}$.

4-Bromo-4'-Chlorotriphenylmethylchloride. - Into a 500 ml.,
single-necked, round bottomed flask, fitted with a reflux
condenser, were placed 4-bromo-4'-chlorotriphenylcarbinol
(139 g., 0.37 mole) as an oil and anhydrous chloroform
(100 ml.). The solution was heated and acetyl chloride
26.5 ml., 0.37 mole) was added slowly. Upon completion of
the addition the mixture was heated at reflux temperature
for four hours. The solvent was then removed in vacuo

2 J. M. Prokipcak, Ph. D., Thesis, Faculty of Graduate Studies, University of Windsor, 1964, p. 97.

and 4-bromo-4'chlorotriphenylmethylchloride was recovered
(131.8 g., 90%) as a heavy oil. Repeated attempts to
recrystallize the 4-bromo-4'-chlorotriphenylmethylchloride
did not yield any crystals. The infrared absorption
spectrum showed an absence of free -OH or C-O stretching
bands.

Triphenylmethoxyacetic Acid. - Triphenylmethyl chloride
(55.5 g., 0.20 mole) was placed in a one-litre, single-
necked, round bottomed flask containing anhydrous pyridine
(300 ml.). The flask was fitted with a reflux condenser
(drying tube attached) and warmed while glycolic acid
(16.7 g., 0.22 mole) was added. The reaction mixture was
heated at reflux temperature for approximately seventeen
hours, cooled, and poured into a mixture of cracked ice
and concentrated hydrochloric acid. The resultant oil was
extracted with two portions of ether (200 mls. each) and
the ether extracts were combined. The ether was made
concentrated by evaporation at atmospheric pressure and
was washed successively with 5% sodium hydroxide (100 mls.)
and water. The aqueous layer was poured into a mixture
of ice and concentrated hydrochloric acid and the resultant
precipitate was filtered and dried in air. The
triphenylmethoxyacetic acid was recrystallized from a
chloroform-petroleum ether (b.p. 30-60°) solvent pair and
the white powder which resulted was filtered and dried in
air. The triphenylmethoxyacetic acid (28.6 g., 45%) showed

a m.p. 152-153° in agreement with other workers.[3] The infrared absorption spectrum showed a very broad hydrogen bonded O-H stretching band beginning at 3600 cm.$^{-1}$ and merging with the C-H stretching band at 3060 cm.$^{-1}$. The carbonyl stretching band was observed at 1730 cm.$^{-1}$, and aromatic ring skeletal absorption bands at 1595, 1488, and 1445 cm.$^{-1}$.

4-Bromo-4 -Chlorotriphenylmethoxyacetic Acid. - In a manner similar to the above, 4-bromo-4'-chlorotriphenylmethoxyacetic acid was prepared. 4-bromo-4'-chlorotriphenylmethyl chloride (49.7 g., 0.13 mole) was reacted with glycolic acid (10.0 g., 0.13 mole) to yield the crude product (23.9 g., 42%). Difficulty was encountered in extracting the acid from the ether with sodium hydroxide. This was overcome by pouring the ether on ice and concentrated hydrochloric acid and by evaporating the ether at atmospheric pressure. The crude product was recrystallized from a chloroform-petroleum ether (b.p. 30-60°) solvent pair. A white powder (m.p. 154-155°) was obtained which closely agreed with previous work.[4] The infrared absorption spectrum showed a very broad hydrogen bonded O-H stretching band beginning at 3550 cm.$^{-1}$ and merging with the C-H stretching band at

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3 J. M. Prokipcak, Ph. D. Thesis, Faculty of Graduate Studies, University of Windsor, 1964, p. 88.

4 J. M. Prokipcak, Ph. D. Thesis, Faculty of Graduate Studies, University of Windsor, 1964, p. 98.

3100 cm. $^{-1}$. The carbonyl stretching band was observed

at 1740 cm.$^{-1}$, and aromatic ring skeletal absorption bands

at 1580, 1492, and 1450 cm.$^{-1}$.

Resolution of($\pm$) 4-Bromo-4'-Chlorotriphenylmethoxyacetic-

Acid. - Into a 500 ml. Erlenmeyer flask were placed the

acid (42.0 g., 0.097 mole) and acetone (200 ml.). To this

mixture was added anhydrous brucine (37 g., 0.094 mole) in

acetone (200 ml.). The solution was heated to boiling

temperature. When the flask had cooled to room temperature

the brucine salt of the acid was recovered as crystals,

m.p. 133-136°, (74 g., 96%). The brucine salt (74 g.),

representing the sum of the two diastereoisomers, was

dissolved in acetone (1.5 1.) and after leaving this sit

at zero degrees for two days the brucine salt, m.p. 135 -

137°, (23 g.) was recovered. This salt was recrystallized

twice from acetone and gave $[\alpha]_D^{25}$ - 14.2° (1, 2; c, 5.28 in

chloroform) which was unchanged on further recrystallization.

The resolved acid was regenerated by dissolving the

brucine salt (9.2 g., 0.011 mole) in acetone (300 ml.) and

this solution was poured over cracked ice and concentrated

hydrochloric acid. The solution was made concentrated

by evaporating the acetone at atmospheric pressure and

a white precipitate formed. This precipitate was recovered

by filtration and was recrystallized from a chloroform-

petroleum ether (b.p. 30-60°) solvent pair and optically

pure 4-bromo-4'-chlorotriphenylmethoxyacetic acid (3.81 g.,

80% was recovered, m.p. 150-151°, $[\alpha]_D^{25}$ - 0.243° (1, 2;

c 14.35 in chloroform). These results agree closely with previous work.[5]

N-Nitrosomethyl Area. - Arndt's[6] method was used in the preparation of N-nitrosomethyl urea. Into a weighed one-litre flask was placed a solution of 24% aqueous methylamine (200 g., 1.5 mole). Concentrated hydrochloric acid was added until the solution was acid to methyl red and water was added to bring the total weight to 500 grams. Urea (300 g., 5 mole) was added to the solution which was boiled gently at reflux temperature for two and three-quarter hours and then vigorously for one-quarter hour. The solution was then cooled to room temperature and 95% sodium nitrite (110 g.) was dissolved in it. The whole solution was then cooled to zero degrees.

A mixture of ice (600 g.) and concentrated hydrochloric acid (100 g., 1 mole) was placed in a three-litre beaker which was immersed in a dry ice-acetone bath. The cold reaction mixture was siphoned into the ice-acid bath over a period of an hour. A foamy pink precipitate floated to the surface and this was filtered, washed once with water and pressed dry. The N-nitrosomethyl urea prepared was

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5 J. M. Prokipcak, Ph. D. Thesis, Faculty of Graduate Studies, University of Windsor, 1964, p. 102

6 F. Arndt, Organic Syntheses, Coll. Vol. II, John Wiley and Sons, Inc., London (1943) p. 461.

recovered (112 g., 73%) with m.p. 114-116°, (reported[7] m.p. 123-124°) accompanied by the evolution of gas.

Methyl-(Triphenylmethoxy)-Acetate. - The method of Bachman and Struve[8], using diazomethane was employed in the preparation of the ester. A simple distillation apparatus was set up in the fume hood as shown below in figure 1.
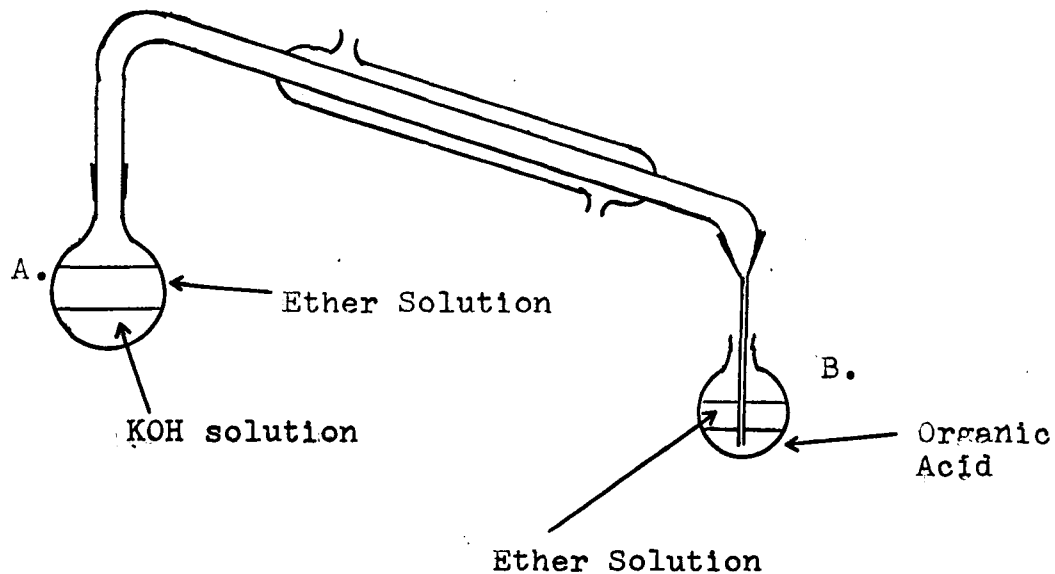

Fig. 1. - Preparation and Use of Diazomethane.

7 E. D. Arnstatz and R. R. Myers, Organic Syntheses, Coll. Vol. II, John Wiley and Sons, Inc., London (1943) p.462.

8 W. E. Bachman and W. S. Struve, Organic Reactions, Vol. II, John Wiley and Sons, Inc., New York, N.Y. (1942) p. 469-509.

Into a 100 ml. round-bottomed flask (B) were placed triphenylmethoxacetic acid (1.33 g., 0.0042 mole) and ether (25 ml.). Into the 50 ml. round bottomed flask (A) were placed potassium hydroxide (50% solution, 4 ml.) and ether (15 ml.). N-nitrosomethyl urea (2-3g.) was added in excess to flask (A) and a vigorous reaction took place. The diazomethane that was formed caused the ether layer to turn yellow and this solution was distilled into flask (B) by warming with warm water when necessary. When the solution in flask (B) had a persistant yellow color, due to the excess diazomethane, the reaction was halted and the excess diazomethane was destroyed by changing flask (B) with one containing benzoic acid in ether. The ether solution of the methyl ester was left to stand in the fume hood for a period of an hour. The solution was then dried over anhydrous sodium sulphate and the ether was removed in vacuo. The desired product was recrystallized from a chloroform-petroleum ether (b.p. 30-60°) solvent pair. The methyl-(triphenylmethoxy)-acetate was dried in air and had a melting point 93-96° and was recovered in almost quantitative yield. The infrared absorption spectrum showed no acid hydroxyl absorption band, and a carbonyl stretching band shift to 1755 cm.$^{-1}$ from the 1740 cm.$^{-1}$ band shown in the acid. This shows that the compound is the desired ester.

Methyl-(4-Bromo-4'-Chlorotriphenylmethoxy)-Acetate. - In a manner similar to that above the methyl ester of 4-bromo-4'-chlorotriphenylmethoxyacetic acid was prepared. The acid

(3.4 g., 0.0079 mole),$[\alpha]_D^{25}$ + 0.42 (1.2; c, 9.52 in
chloroform.) was reacted with potassium hydroxide and
excess N-nitrosomethyl urea. When the ether had been
stripped off the oil that was recovered (2.8 g., 80%) was
put into solution and repeated attempts to recrystallize
it failed. The infrared spectrum showed no acid hydroxyl
absorption band. It did show a carbonyl stretching shift to
1750 cm.$^{-1}$ from the acid band of 1725 cm.$^{-1}$. This indicated
that the methyl-(4-bromo-4'-chlorotriphenylmethoxy)-acetate
had been obtained. The specific rotation of the ester was
$[\alpha]_D^{25}$ - 0,195 (1,2; c, 11.2 in chloroform).

Triphenylmethoxyacetamide. - Into a 125 ml. Erlenmeyer flask
was placed 100 ml. of 50% ammonium hydroxide solution.
Methyl-(triphenylmethoxy)-acetate (0.56 g., 0.0017 mole)
was added and the solution was stirred for a period of
approximately three hours. A white solid precipitated from
solution and this was recovered by filtration. The precip-
itate was washed with water and dried. Triphenylmethoxy-
acetamide (0.26 g., 49%) was recovered (m.p. 176-179°).
The infrared spectrum exhibited a carbonyl stretching band
at 1790 cm.$^{-1}$, free N-H stretching band at 3530 cm.$^{-1}$,
bonded N-H stretching at 3410 cm.$^{-1}$, and aromatic ring
skeletal absorption bands at 1565 cm.$^{-1}$ and 1490 cm.$^{-1}$.

4-Bromo-4'-Chlorotriphenylmethoxyacetamide. - Methyl-(4-
bromo-4' chlorotriphenylmethoxy)-acetate (2.0 g., 0.0045
mole),$[\alpha]_D^{25}$- 0.195 (1.2; c, 11.2 in chloroform) was dissolved
in a 50% methanol-tetrahydrofuran solution (100 ml.).

This solution was added to concentrated ammonium hydroxide (100 ml.) and the mixture immediately turned cloudy. The solution was stirred for approximately two hours when it turned clear and a white precipitate formed. The precipitate was recovered by filtration, washed with water and dried. Upon recrystallization from a chloroform-petroleum ether (b. p. 30-60°) solvent pair white crystals (m.p. 184 - 187°) were recovered (1.3 g., 67.5%); $[\alpha]_D^{25}$ + 0.478 (1,2; c,5.33 in chloroform).

> Analysis: Calcd. for $C_{21}H_{17}BrClNO_2$: C, 58.55; H, 3.95; N, 3.26.
>
> Found: C, 58.11; H, 4.01; N, 3.08.

The infrared spectrum showed a carbonyl stretching band at 1692 cm.$^{-1}$, free N-H stretching band at 3530 cm.$^{-1}$, bonded N-H stretching at 3410 cm.$^{-1}$, and aromatic ring skeletal bands at 1565 and 1485 cm.$^{-1}$.

<u>Tertiary-Butyl Hypochlorite</u>. - Tertiary-butyl hypochlorite was prepared according to the method of Teeter and Bell.[9] The reaction was carried out in a fume hood using all ground glass connections. Into a two-litre, round-bottomed three-necked flask equipped with a gas inlet tube extending to the bottom of the vessel, a gas outlet tube, and a

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9 H. M. Teeter and E. W. Bell, <u>Organic Syntheses</u>, Coll. Vol. IV, John Wiley and Sons, Inc., New York, N.Y. (1963) p. 125.

mechanical stirrer) was placed sodium hydroxide (5.0g., 0.25 mole) in 100 ml. of water. The reaction vessel was placed in a cold water bath (15-20°) and tertiary-butyl alcohol (9.25 g., 0.125 mole) in 75 ml. of water was added to form a homogeneous solution. The solution was stirred constantly while chlorine gas was passed through at a rate of approximately one litre per minute for the first thirty minutes and then about half that for the next thirty minutes. The upper layer was a yellow oil and this was separated and washed twice with 10% sodium carbonate and twice with water. The oil was then dried over anhydrous calcium chloride and distilled. The t-butyl hypochlorite, b.p. 77-79°, η_D^{20} = 1.4019 (11.0 g., 81%) was recovered. (reported[9] b.p. 77-78°; η_D^{20} = 1.403). The infrared spectrum showed an O-Cl stretching band at 685 cm.$^{-1}$, a band at 839 cm.$^{-1}$ attributed to t-butyl and an absence of a free O-H stretching band. This was in agreement with previous workers.[10]

Reaction of t-Butyl Hypochlorite with Triphenylmethoxy-acetamide. - This reaction was run according to the precedure of Murr.[11] Triphenylmethoxyacetamide (0.5 g., 0.0016 mole) was dissolved in 200 ml. of anhydrous benzene and

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10 L. Denivelle, R. Fort, and J. Favre, Compt. rend., 237, 722-24 (1953).

11 B. L. Murr, J. Am. Chem. Soc., 85, 2867 (1963)..

placed in a 500 ml.-round bottom flask equipped with a condenser, drying tube attached. To this solution was added t-butylhypochlorite (0.35 g., 0.0032 mole) and the mixture was heated at 65°. Methanolic sodium methoxide (0.005 g.-atoms of sodium in 20 ml. of methanol) was added to the mixture and it was heated at reflux temperature for two hours. The sodium chloride was removed by filtration and upon concentrating the solvent crystals formed. Triphenylcarbinol (0.06 g., 14.4%) was obtained and from the infrared spectrum it appeared that some unreacted triphenylmethoxacetamide was still in solution.

Reaction of 4-Bromo-4'-Chlorotriphenylmethoxyacetamide with Tertiary-Butyl Hypochlorite.

- In the same manner as that described above, 4-bromo-4'-chlorotriphenylmethoxy-acetamide was reacted with t-butyl hypochlorite. The amide (0.80 g., 0.0018 mole) was placed in 200 ml. of benzene. t-Butyl hypochlorite (0.29 g., 0.0027 mole) was added to the benzene solution and also methanolic sodium methoxide (0.0055 g.-atoms of sodium in 20 mls. of methanol). The reaction mixture was heated for two hours at reflux temperature. The product was recovered in a similar manner to that described above. 4-Bromo-4'-chlorotriphenyl-methoxyacetamide (0.7 g.) was recovered as shown by the infrared spectrum which was identical with that of pure 4-bromo-4'-chlorotriphenylmethoxacetamide.

Silver (Triphenylmethoxy)-Acetate.- The method described by Barnes and Prochaska[12] was followed in this preparation. Into a 500-ml. Erlenmeyer flask was placed 250 ml. of a 1% sodium hydroxide (2.51 g., 0.0628 mole) solution. To this solution was added the triphenylmethoxyacetic acid (20.0 g., 0.0628 mole). When all the acid had been dissolved 100 ml. of silver nitrate (11.71 g., 0.069 mole) solution was added very slowly with constant stirring. A white cloudiness immediately appeared and upon continued addition of silver nitrate a white slurry was obtained. The solution was filtered and the white fluffy precipitate was washed twice with water and twice with ethanol. It was then pressed dry and allowed to dry in air for one day and dried in vacuo for a day. The white silver-(triphenylmethoxy)-acetate was recovered (26.4 g., 98.5%) and this showed a softening at 132-134° and decomposed at 165-169°.

Analysis: Calcd. for $C_{21}H_{17}AgO_3$: C, 59.5; H, 4.0; Ag, 25.35.

Found: C, 57.20; H, 4.05; Ag, 27.44.

Silver (4-Bromo-4'-Chlorotriphenylmethoxy)-Acetate.- In a manner similar to that described, silver (4-bromo-4'-chloro-triphenylmethoxy)-acetate was prepared. Potassium hydroxide (0.78 g., 0.0139 mole, 1% solution), 4-bromo-4'-chloro-

12 R. A. Barnes and R. J. Prochaska, J. Am. Chem. Soc., 72, 3188 (1950).

triphenylmethoxyacetic acid (6.0 g., 0.0139 mole) and

silver nitrate (2.71 g., 0.016 mole) were reacted to give

the silver salt (6.2 g., 84%) which had a m. p. 134-139°

and decomposed at 150-154°.

Analysis: Calcd. for $C_{21}H_{15}AgBrClO_3$: C, 46.8; H, 2.78;

Ag, 20.02.

Found: C, 47.32; H, 2.97; Ag, 19.70.

Reaction of Silver (Triphenylmethoxy)-Acetate with Bromine.-

This reaction was carried out according to the method of

Barnes and Prochaska.[12] The silver salt (10.0 g., 0.023

mole) was added to form a slurry in dry carbon tetrachloride

(300 ml.) in a 500-ml., three-necked, round-bottomed flask.

The flask was fitted with a condenser (drying tube attached)

and a syringe. Bromine (3.74 g., 0.023 mole) was added

dropwise from the syringe at room temperature. The suspension

of silver salt immediately became dark red. This dark red

solution was heated very slowly with constant stirring and

maintained at reflux temperature for a period of three hours.

The hot solution was filtered and a solid (4.5 g.), probably

silver bromide, was recovered. The solution was allowed to

cool to room temperature and a 1% solution of sodium

hydroxide (2.8 g., 0.07 mole) was added dropwise to the

cooled reaction mixture. The resultant solution was heated

at reflux overnight. The colour changed from a dark red to

a pale yellow.

The mixture was cooled and the carbontetrachloride

layer was separated, washed with water and dried over anhydrous calcium chloride. The carbontetrachloride was then removed in vacuo and the oil was recrystallized from a chloroform-petroleum ether (b.p. 30-60°) solvent pair. White crystals, m.p. 158-160°, were recovered (2.7 g., 44%). The infrared spectrum of these crystals was the same as that of triphenylcarbinol.

Pyrolysis of Silver (Triphenylmethoxy)-Acetate.- Silver (triphenylmethoxy)-acetate (10.2 g., 0.024 mole) was placed in a large test tube and immersed in an oil bath. The temperature of the bath was raised slowly until a maximum of 200° was reached. Gases were observed to escape from the tube and condensation was observed on the walls when the temperature was above 170°. The test tube was removed from the flask and allowed to cool and then the contents were taken up in a chloroform-petroleum ether (b.p. 30-60°) solvent pair. An insoluble residue (2.55 g.) was recovered by filtration. This was determined to be a silver compound by dissolving it in hot concentrated nitric acid and precipitating the silver as silver chloride by the addition of concentrated hydrochloric acid. A rough analysis of this residue showed it to contain 96.7% silver.

Crystallization of the chloroform soluble product yielded triphenylcarbinol (3.05 g., 47%), m. p. 161-163° with an infrared spectrum identical to that of the pure compound.

Pyrolysis of Silver-(4-Bromo-4'-Chlorotriphenylmethoxy)-

Acetate.- In a manner similar to the preceding silver-
(4-bromo-4'-chlorotriphenylmethoxy)-acetate (1.9 g., 0.0035
mole) was decomposed. Condensation on the side of the test
tube and escaping gases were again observed. The test tube
and contents were weighed both before and after pyrolysis
and it was observed that 0.1 gram was lost as gases. The
residue was taken up in chloroform and an insoluble precip-
itate was recovered (0.24 g.). This precipitate was shown
to contain silver in a manner similar to before. The
chloroform solution was evaporated in vacuo. The remaining
oil (1.40 g.) was then purified by chromatography using a
column of alumina (50 g.). The 4-bromo-4'-chlorotriphenyl-
carbinol (0.99 g., 75.0%) was recovered as an oil as shown
by the similarities in the infrared spectra of the product
and the pure compound.

Reaction of Triphenylmethoxyacetic Acid with Mercuric

Oxide and Bromine.- This reaction was carried out follow-
ing the procedure used by Davis and coworkers.[13] A 500-ml.,
three-necked, round bottomed flask was fitted with a reflux
condenser and a dropping funnel. Into the flask was placed
dry carbon tetrachloride (150 ml.), red mercuric oxide
(3.65 g., 0.0157 mole) and triphenylmethoxyacetic acid

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13 Davis, John A., J. Herynk, S. Carroll, J. Bunds, and
D. Johnson, J. Org. Chem., 30, 415 (1965).

(2.5 g., 0.0078 mole). The mixture was warmed and stirred

constantly while a solution of one equivalent of bromine

(1.25 g., 0.0078 mole) in carbontetrachloride (50 ml.) was

added dropwise from the dropping funnel. After the addition

of the bromine was completed the reaction mixture was

heated at reflux temperature for a period of an hour. The

reaction mixture was then cooled and filtered. The carbon

tetrachloride layer was heated at reflux temperature with a

5% sodium hydroxide (7.5 g., 0.187 mole) solution for a period

of twelve hours. The organic layer was then separated,

washed with water and dried over anhydrous sodium sulphate.

The carbon tetrachloride solution was evaporated in vacuo

and the resultant oil was recrystallized from a chloroform-

petroleum ether (b. p. 30-60°) solvent pair and crystals,

m. p. 160-163°, were obtained. These crystals (1.40 g., 68%)

had an identical infrared spectrum to that of triphenyl-

carbinol.

Reaction of 4-Bromo-4'-Chlorotriphenylmethoxyacetic Acid

with Mercuric Oxide and Bromine.- In a manner similar to the

above, 4-bromo-4'-chlorotriphenylmethoxyacetic acid (2.8 g.,

0.0065 mole) was reacted with red mercuric oxide (3.0 g.,

0.0104 mole) and bromine (1.035 g., 0.0065 mole). The

reaction mixture was heated at reflux temperature for a period

of an hour, filtered and the carbon tetrachloride was

removed in vacuo. The remaining oil was taken up in chloroform

and 3% potassium hydroxide (150 ml.) was added. This mixture

was stirred at room temperature for a period of a day and then the organic layer was separated and concentrated. The resultant oil was crystallized from methanol and crystals, m. p. 87 -90 $^{\circ}$, were obtained. The infrared absorption spectrum was identical to that of pure 4-bromo-4'-chloro-triphenylcarbinol. The crystals obtained were a small fraction of the yield. The remaining oil (1.20 g., 49.6%) had an identical infrared spectrum to the crystals obtained.

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