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Detritylation and Transtritylation Reactions

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This review deals with various reactions involving the cleavage and certain interesting rearrangements of trityl compounds and the use of trityl protecting groups in the synthesis and reactions of glycerides, carbohydrates, nucleosides, nucleotides, and peptides. The lability of the bond between the trityl group and oxygen, sulphur, nitrogen, carbon, and other atoms has been demonstrated.
The bibliography includes 519 references.

INTRODUCTION

The tendency of compounds containing the labile trityl (triphenylmethyl) group to undergo detritylation and transtritylation reactions has been known for a long time. These reactions are of both theoretical and preparative interest. Various reactions involving the cleavage of trityl compounds and interesting rearrangements have been described. The ease of introduction and removal of the trityl group makes it possible to employ it as a protecting group. Trityl protecting groups have found particularly wide application in the synthesis and reactions of glycerides, carbohydrates, nucleosides, nucleotides, and peptides. They have assisted greatly in the development of the chemistry of natural compounds. The lability of the bond between the trityl group and the carbon atom led to the foundation and development of the chemistry of free radicals.

Until recently there have been no reviews dealing with detritylation and transtritylation reactions. The present review deals with data on the detritylation and transtritylation of oxygen, sulphur, nitrogen, carbon, and other tritylated compounds. The bonds between the trityl group and hydrogen and halogen atoms, the reactions of triphenylmethanol, triphenylmethanethiol, and triphenylmethylamine are not considered, since they are best treated as tritylation reactions.

In view of the enormous number of studies on the subject, the formation of triarylmethyl radicals must also be excluded from consideration. These problems may be the subject of separate reviews.

1. THE BOND BETWEEN THE TRITYL GROUP AND THE OXYGEN ATOM

The bond between the trityl group and the oxygen atom in alkyl trityl ethers dissociates when the latter are heated[1-5], acted upon by potassium[6], hydrogen halides[1,7-9], boron trifluoride[10], aluminium chloride[4], phosphorus pentachloride[9] and pentabromide[11], silica gel[12], formic acid, and acetyl chloride[1,13-15], and also when they are hydrolysed with alkali metal hydroxides[1] and inorganic acids[1,8,9,16]. The reaction products are triphenylmethane, triphenylmethanol, triphenylchloromethane, triphenylbromomethane, and triphenylmethylpotassium. When alkyl trityl ethers were allowed to react with magnesium and propyl iodide, the product was tritylmagnesium iodide[17,18], while the reaction with phenylmagnesium bromide yielded tetraphenylmethane[19]. The electrochemical elimination of a trityl protecting group has been demonstrated for *O*-trityl-*N*-palmitoylethanolamine[20].

When isopropyl trityl ether is allowed to stand with 0.1% solution of hydrogen chloride in methanol, transtritylation takes place[21]:

$$(CH_3)_2CHO{-}C(C_6H_5)_3 + CH_3OH \rightarrow CH_3O{-}C(C_6H_5)_3 + (CH_3)_2CHOH\ .$$

The reactions of alkyl trityl ethers with allyl alcohol, ethylene glycol, glycerol, and phenol yield respectively allyl trityl ether, the trityl ether of ethylene glycol, the α-trityl ether of glycerol, and *p*-hydroxytetraphenylmethane[22]. Methyl and ethyl trityl ethers were used for the tritylation of formamide[23]:

$$RO{-}C(C_6H_5)_3 + HCONH_2 \rightarrow HCONH{-}C(C_6H_5)_3 + ROH$$

Nesmeyanov et al.[24] showed that the reaction of the methyl ether of Crystal Violet with acetaldehyde, propionaldehyde, crotonaldehyde, and nitromethane takes place with formation of a new carbon–carbon bond. For example:

$$CH_3O{-}C[C_6H_4N(CH_3)_2]_3 + CH_3C(=O)H \rightarrow [(CH_3)_2NC_6H_4]_3C{-}CH_2C(=O)H + CH_3OH\ .$$

Cycloalkyl trityl ethers are cleaved by sulphuric[25] and acetic[26,27] acids. Benzyl and diphenylmethyl trityl ethers are hydrogenated catalytically on Raney nickel with dissociation of the bond between the trityl group and the oxygen atom[28]:

$$C_6H_5CH_2O{-}C(C_6H_5)_3 \rightarrow C_6H_5CH_2OH + (C_6H_5)_3CH\ .$$

Aryl trityl ethers are cleaved by water[29], alkali metals[6,30-32], hydrogen chloride[33], zinc chloride[34-36], and hydrochloric acid[5,35-37] with formation of the corresponding phenols and triphenylmethane or its derivatives. With acetyl chloride or hydrogen chloride in the presence of calcium chloride, dityrityl ether gives triphenylchloromethane[38,39].

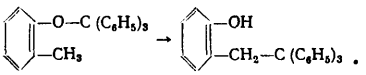
When aryl trityl ethers are heated under different conditions, the corresponding tetraphenylmethane derivatives are obtained[22,30,32,35,40-48]. For example, when phenyl trityl ether is heated in ethylene glycol and glycerol[22,47,48] and also in a mixture of acetic and hydrochloric acids[41], *p*-hydroxytetraphenylmethane forms in 80–100% yield:



Tetraphenylmethane was also isolated in the reaction of phenyl trityl ether with phenylmagnesium bromide[19].

Shorygin[30,49], showed that the reaction of sodium (at 100°C) with *o*-tolyl trityl ether results, apart from the normal decomposition, in a rearrangement which leads to

the migration of the trityl group to the side-chain of *o*-cresol:



A similar rearrangement takes place also under the action of zinc chloride[50].

The reaction of the ditrityl ether of catechol with methanol in the presence of hydrogen chloride yields methyl trityl ether[21]. When phenyl trityl ether reacts with mono-substituted benzenes containing *ortho*- and *para*-directing substituents, the initial ether undergoes rearrangement and the benzene derivative is tritylated[51]. For example:

$$C_6H_5O{-}C(C_6H_5)_3 + C_6H_5N(CH_3)_2 \rightarrow p\text{-}HOC_6H_4{-}C(C_6H_5)_3 + p\text{-}(CH_3)_2NC_6H_4{-}C(C_6H_5)_3 .$$

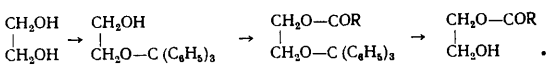
On the basis of the relative amounts of the products, it was concluded that the migration of the trityl group to the *p*-position in both compounds takes place not only by an intermolecular mechanism but partially also by an intramolecular mechanism. The orienting power of the substituents follow the sequence $N(CH_3)_2 > NH_2 > OCH_3$.

Among trityl esters, trityl acetate[15,52-60], trityl benzoate[57,60-63], and others[52,54,60,63-66] have been decomposed. Their pyrolysis yields triphenylmethane[56,62,65]. They are decomposed by water, alcohols, and acetyl chloride with formation of triphenylmethanol, alkyl trityl ethers, and triphenylchloromethane respectively[15,52]. The interaction of trityl acetate with organomagnesium compounds yields, together with detritylation products, the corresponding hydrocarbons[58,59]:

$$CH_3COO{-}C(C_6H_5)_3 + RMgCl \rightarrow (C_6H_5)_3C{-}R + CH_3COOMgCl .$$

Other *O*-trityl compounds have also been decomposed[6,67-75], including peroxides containing one[69] and two[6,70-73] trityl groups and also *O*-trityl organometallic compounds[74].

Trityl protecting groups have been used for the synthesis of monoacyl derivatives of glycol[76]:



Such protection has also found wide application in the synthesis and investigation of the properties of glycerides[9,21,77-115] including lipoamino-acids[107,109,113-115].

It is interesting to note that the elimination of the trityl group from 1,2-diacyl- and 3-trityl-glycerol results in the migration of the acyl group from the 2-position to the 3-position[98,99,108]. However, detritylation with silicic acid avoids migration of acyl groups[93,106,108,110,111,113]. Optically active diglycerides, which are key intermediates in the synthesis of biologically important phospholipids, have been obtained in this way[104,108,111].

Quite recently in a study of the reaction of ethylene glycol and glycerol with their ditritylation products, the hitherto unknown disproportionation reaction of trityl groups leading to the formation of the corresponding monotritylation products, was observed[116]. For example:

$$HOCH_2CH_2OH + (C_6H_5)_3C{-}OCH_2CH_2O{-}C(C_6H_5)_3 \rightarrow 2(C_6H_5)_3C{-}OCH_2CH_2OH .$$

The reaction of the ditrityl ether of glycerol with methanol in the presence of hydrogen chloride yields methyl trityl ether[21].

Trityl protecting groups have found wide application in the synthesis of carbohydrates, in the study of the properties and structure of mono-, di-, and poly-saccharides and also their derivatives and analogues[8,9,12,101,102,117-198]. Their great importance in the chemistry of carbohydrates is due not only to the ease of elimination but also to the fact that they normally combine only with a primary hydroxy-group. The rate of tritylation of the primary alcoholic group in D-galactose is 225 times faster than the rate of tritylation of the hydroxy-group at the C_3 atom, evidently owing to the steric factors[168]. Although side reactions sometimes occur in detritylation[118], the trityl group gives ideal protection of the terminal hydroxy-group of the sugar chain in various syntheses.

Catalytic hydrogenation, refluxing with 80% acetic acid, and treatment at room temperature with hydrogen chloride in chloroform or hydrogen bromide in acetic acid are most often used to cleave the trityl ethers of carbohydrates. For example, when trityl ethers of cellulose and starch are shaken with a solution of hydrogen chloride in chloroform, the trityl residues are split off quantitatively as triphenylchloromethane (when aqueous hydrochloric acid is used, the product is triphenylmethanol)[137]. The methylation of the trityl ether of cellulose with dimethyl sulphate results in rapid elimination of the trityl group, while in the methylation with methyl iodide the elimination is slow[120]. It has been observed that the detritylation of tritylation and acylation products with acid reagents is frequently accompanied by the migration of the acyl groups[101,139-143]. The detritylation of (D-β-5′-*O*-trityl-2′,3′-di-*O*-acetylribofuranosyl)indole, yields, in addition to the normal product, also a small amount of the corresponding ribopyranose derivative—the product of the isomerisation of the carbohydrate ring[122].

Trityl[177,199-294] and also mono- and di-*p*-methoxytrityl[227,295-311] protecting groups have found wide application in the synthesis and the investigation of the properties and structure of nucleosides, nucleotides, and oligonucleotides. When triphenylchloromethane is allowed to react with nucleosides, the product is as a rule a 5′-*O*-trityl derivative, although this reagent, while reacting preferentially with a primary hydroxy-group, is nevertheless not entirely specific with respect to the latter[201,217,246,264,265]. In fact uridine forms a ditrityl derivative[217], shown to be 2′,5′-di-*O*-trityluridine[215]. A certain amount of 3′,5′-di-*O*-trityluridine also forms[201].

The differences between the conditions for the formation and cleavage of trityl and benzyl ethers constitute the basis of Todd's synthesis of uridine diphosphate-glucose[312]. Trityl protecting groups have been used in the synthesis and investigation of the properties and structures of the antibiotic nojirimycin[313], coenzyme A,[314,315], vitamin B_2,[316] lipids[317], and steroids[318-320]. It has been found that the detritylation of certain steroid derivatives is accompanied by the migration of the acetyl group[320]; in the absence of a trityl group such rearrangement does not occur.

2. THE BOND BETWEEN THE TRITYL GROUP AND THE SULPHUR ATOM

The bond between the trityl group and the sulphur atom is cleaved when aryl trityl sulphides are heated[321], refluxed in alcohol in the presence of Raney nickel[322], or acted upon by alkali metals[6], bromine[323], iodine[324], iron(II) chloride[325], aluminium bromide[324], silver nitrate[324], potassium permanganate[325], ruthenium tetroxide[326], chromic[325,327], nitric[325], and sulphuric[321] acids, a mixture of hydrochloric and acetic acids[41], and dichloro- and diacetoxy-iodobenzene[328]. The detritylation products are

triphenylmethane, triphenylmethanol, triphenylchloromethane, triphenylbromomethane, and dityrityl peroxide. The yields of the peroxide reach 90%.

The interaction of phenyl trityl sulphide with *N*-bromosuccinimide gives a 97% yield of *N*-tritylsuccinimide[328]. The reaction of phenyl trityl sulphide with mercury(II) chloride in methanol takes place by the following mechanism[322]:

$$C_6H_5S{-}C(C_6H_5)_3 + HgCl_2 + CH_3OH \rightarrow CH_3O{-}C(C_6H_5)_3 + C_6H_5SHgCl + HCl\ .$$

The decomposition of dityrityl sulphide[329,330], dityrityl disulphide[329-331], trityl thioacetate[329], and trityl thiobenzoate[329,332] has been described. The dissociation of the bond between the trityl group and the sulphur atom in *p*-tolyl trityl sulphone by water has also been observed[3].

The trityl group has been used to protect the mercapto-group in the synthesis of sulphur-containing acids, amino-acids, peptides, and their derivatives[324,333-355]. These protecting groups have been used, for example, in the synthesis of glutathione[342], oxytocin[333], and cyclic cystine peptides[344,345,351]. Selective detritylation permits the elimination of the *S*-trityl protecting groups with retention of the *N*-trityl[334,342] and other protecting groups attached to the sulphur[354] and nitrogen[334,352,354,355] atoms. Thus in the reaction of the methyl ester of *SN*-dityrityl cysteine with silver nitrate in methanol in the presence of pyridine, methanol is tritylated only by the *S*-trityl group[334]. On the other hand, the selective elimination of protecting groups attached to the nitrogen atom with retention of the *S*-trityl protecting group is also possible[353].

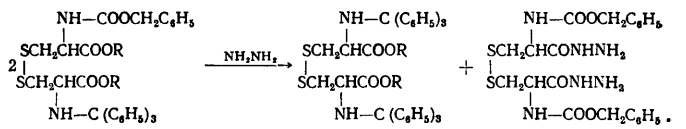
For the synthesis of asymmetric (with respect to the cysteine residues) cystine peptides, the mercapto-groups must be protected in various ways to permit their separate elimination[334,355]. *S*-Tritylcysteine and diphenylmethylcysteine have been proposed for this purpose. *S*-Trityl protecting groups are readily eliminated at room temperature by treatment with heavy metal salts. The *S*-diphenylmethyl group is then unaffected and can be removed separately with trifluoroacetic acid.

3. THE BOND BETWEEN THE TRITYL GROUP AND THE NITROGEN ATOM

As early as 1884, it was known that *N*-trityl groups are readily dissociated in an acid medium[356]. In 1925 trityl derivatives of amino-acids and even of a dipeptide were obtained[8]. However, the effectiveness of trityl protecting groups in the reactions of α-amino-acids and in the synthesis of peptides was not finally recognised until the second half of the present century[333,336,342,344,349-351,354,357-414]. For this reason, the honour and priority in the discovery of trityl protecting groups are attributed not only to Helfferich (1925) but also to Velluse (1955).[415]

N-Trityl protecting groups have been used in the study of the reactions of hydroxy-derivatives[357-359] and mercapto-derivatives[333,334,336,342,344,349-351,354,381,396] of α-amino-acids, diamino-acids[360-362,371,379,401], dicarboxylic[333,342,363-366,370,387,394,395,397-399] and heterocyclic[357,366,370,371,379] α-amino-acids, and also β-amino-acids[411] and cycloserine[369]. They have been also used in the synthesis and the study of the properties of cyclic peptides[344,351,372-378], including gramicidine C and its analogues[375-378]. It has been established that, when trityl protecting groups are employed, the most effective procedure for the synthesis of peptides is the carbodi-imide method.

The principal advantage of the trityl group consists in the ease of its elimination under mild conditions, although steric hindrance of the adjacent carboxy-group sometimes prevents the condensation of tritylamino-acids. With increase of the side chain length in the amino-acid residue, the steric hindrance becomes more pronounced, which is inconvenient from the preparative standpoint. The steric hindrance in αω-diesters of *N*-trityl derivatives of dicarboxylic amino-acids makes it possible to hydrolyse the ω-ester group with retention of that in the α-position[365,387]. The tritylated acid esters obtained in this way have been successfully used for the synthesis of the peptides of asparagine, glutamine, and isoglutamine[365]. On the hypothesis that the bulky trityl group can suppress the reactivity of the adjacent ester group as a result of steric hindrance, an attempt was made to obtain the corresponding monohydrazide by the reaction of hydrazine with the diester of *N*-benzyloxycarbonyl-*N*-tritylcystine[396]. However, the reaction takes place according to the following mechanism:



Evidently, under the action of hydrazine there is a disulphide rearrangement involving two molecules of the asymmetric cystine derivative with formation of two symmetrical derivatives.

The high sensitivity of the *N*-trityl group to the action of acids makes possible its elimination under a wide variety of experimental conditions. *N*-Trityl peptides lose their protecting trityl groups when their solutions are refluxed in anhydrous and aqueous acetic acid for several minutes[357,371,379-382,410]. Aqueous trifluoroacetic acid eliminates the *N*-trityl group even at −5 °C.[375-377] It has been stated that the group is eliminated under the influence of lower alcohols[383]. Depending on the reagent used for its elimination, the trityl group is converted into triphenylmethane, triphenylchloromethane, triphenylbromomethane, triphenylmethanol, triphenylmethyl acetate and trifluoroacetate, alkyl trityl ethers, and also mixtures of these compounds[410].

Anhydrous hydrogen chloride in methanol eliminates *N*-trityl substituents from an α-amino group more readily than from an ω-amino group[361,410] and imidazole[366] and also *O*-trityl substituents from phenol[366]. Thus, when trityl groups of these two types are present in the molecule of the same compound, it is possible under certain conditions to eliminate selectively one *N*-trityl substituent attached to an α-amino group with retention of the *S*-trityl substituent[333,334,342,410] or an *N*-substituent attached to an ω-amino-group[360,410]. For example, when the hydrochloride of the methyl ester of *NS*-dityrityl cysteine reacts with methanol in the presence of hydrochloric acid, methanol is tritylated by the *N*-trityl protecting group[334]. The selective detritylation of the trityl ester of *N*-tritylglycine allows the selective elimination of the trityl group from the nitrogen atom with retention of the ester group[384]. It is also possible to eliminate selectively the *N*-trityl protecting groups without affecting other protecting groups[375-377,385,386,410]. On the other hand, in catalytic hydrogenation the *N*-trityl group is eliminated more slowly than the *N*-benzyloxycarbonyl or *O*-benzyl groups[366,380].

The condensation of amino-acids having amino-groups protected by *N*-substituents with tritylhydrazine yields the corresponding hydrazides[389,398,399,401]. A particular advantage of protecting groups of this type is that, after

the elimination of the trityl group, the resulting derivative may be used directly in peptide synthesis by the azide method.

Under the conditions used to prepare certain oximes of *N*-trityl-α-amino-ketones and also on heating the latter in the presence of hydrogen chloride, ethanol is tritylated[416].

The cleavage of alkyl-[1,14,417], dialkyl-[48,417], alkyl-aryl-[418,419], aryl-[14,417,420-422], and diaryl-[8,423] trityl-amines, trityl-[424,425] and dityrityl-[426,427] hydrazines, trityl azide[428,429], *N*-tritylurethanes[430], *N*-tritylacetamide[431], products of the *N*-tritylation of urea and thiourea[8], phenyl-[426,432-439] and benzoyl-[439] azotriphenylmethanes, quaternary ammonium bases containing the trityl group[440], and other *N*-tritylated compounds[441-445] has been described.

When *N*-tritylaniline[41,422], *N*-(β-cyanoethyl)-*N*-trityl-aniline[419], *N*-trityldiphenylamine, and other *N*-tritylaryl-amines[422,446,447] are heated in an acid medium, in pyridine in the presence of its hydrochloride, or with zinc chloride, *C*-trityl compounds are obtained in yields up to 80%. For example:

$$(C_6H_5)_3C{-}NHC_6H_5 \rightarrow NH_2{-}C_6H_4{-}C(C_6H_5)_3 .$$

The trityl group migrates to the *p*-position when *N*-trityl aniline reacts with monosubstituted benzenes having *ortho*- and *para*-directing substituents[51], as happened in the analogous reaction of phenyl trityl ether. The possibility of the conversion of *N*-trityl aniline into *o*-(phenylamino)-triphenylmethane is also postulated[421]:

$$(C_6H_5)_3C{-}NHC_6H_5 \rightarrow NHC_6H_5{-}C_6H_4{-}CH(C_6H_5)_2 .$$

When *N*-tritylalkylamines[47] and *N*-(β-cyanoethyl)-*N*-tritylalkylamines[48] react with allyl alcohol, ethylene glycol, glycerol, and phenol, transtritylation takes place according to the following mechanism:

$$(C_6H_5)_3C{-}NHR \xrightarrow{HOCH_2CH{=}CH_2} (C_6H_5)_3C{-}OCH_2CH{=}CH_2$$
$$\xrightarrow{HOCH_2CH_2OH} (C_6H_5)_3C{-}OCH_2CH_2OH$$
$$\xrightarrow{HOCH_2CHOHCH_2OH} (C_6H_5)_3C{-}OCH_2CHOHCH_2OH$$
$$\xrightarrow{C_6H_5OH} (C_6H_5)_3C{-}C_6H_4OH\text{-}p .$$

The reaction of arylamines with *N*-(β-cyanoethyl)-*N*-tritylarylamines involves transtritylation by the mechanism[448]:

$$ArNH_2 + Ar'N\begin{matrix}CH_2CH_2CN\\C(C_6H_5)_3\end{matrix} \rightarrow ArNH{-}C(C_6H_5)_3 + Ar'NH{-}CH_2CH_2CN .$$

1-Tritylimidazole and its 4,5-disubstituted derivatives are readily hydrolysed on refluxing with 10% acetic acid to imidazole and its derivatives and also triphenylmethanol[449]. It is suggested that, when 1-tritylimidazole is heated to its melting point, the trityl group may migrate from the nitrogen atom to a carbon atom[449]. The products of the addition of triphenylchloromethane to pyridine and quinoline are decomposed by water and alcohol to the heterocyclic base and triphenylmethanol or an alkyl trityl ether[3,9].

Together with *O*-trityl protecting groups, *N*-trityl protecting groups have found application in the chemistry of nucleosides and nucleotides[391-395].

4. THE BOND BETWEEN THE TRITYL GROUP AND THE CARBON ATOM

The study of the bond between the trityl group and the carbon atom began with the work of Gomberg[450], who obtained in 1900 a free radical of tervalent carbon (triphenylmethyl) in an attempt to synthesise hexaphenylethane by the action of silver on triphenylbromomethane. This quite unexpected discovery demonstrated for the first time the possibility of the existence of free radicals. The discovery, treated by the majority of chemists with considerable disbelief, was confirmed and developed further in the subsequent studies by Gomberg himself and also by Chichibabin, Markovnikov, Kerman, Flürscheim, Schmidlin, Cone, Walden, Wieland, Ullmann and Borsum, Heintschel, Schlenk, Ziegler, A. E. and B. A. Arbuzov, and others[451-453]. It was established that the crystalline colourless hexaphenylethane dissociates reversibly in solution, particularly at elevated temperatures, forming the yellow triphenylmethyl:

$$(C_6H_5)_3C{-}C(C_6H_5)_3 \rightleftarrows 2(C_6H_5)_3C\cdot$$

Gomberg's discovery[450] gave rise to the chemistry of free radicals, which later developed very rapidly. From 1900 up to the present an enormous number of investigations have been carried out in this field. Apart from triphenylmethyl, many free radicals of the triphenylmethane series have been obtained and their properties investigated, including addition, disproportionation, and recombination reactions. These investigations have greatly influenced the development of theoretical concepts in organic chemistry, in particular the study of thermal and photochemical reactions involving chain mechanisms[451-453].

Tetraphenylmethane proved to be a perfectly stable hydrocarbon—its solutions are colourless and the compound itself distils without decomposition at atmospheric pressure at 431 °C. However, under the action of a liquid potassium–sodium alloy, it dissociates even at room temperature with formation of triphenylmethane and other products[454]. On distillation[6] or under the action of oxidising agents[3,455] and potassium[6,456], asymmetric tetraphenylethane yields respectively triphenylmethane, triphenylmethanol, and triphenylmethylpotassium.

Chichibabin[457,458] showed that at an elevated temperature pentaphenylethane decomposes, like hexaphenylethane, at the C–C bond of ethane. The pentaphenylethane molecule then breaks down into radicals, which subsequently recombine in a different manner:

$$2(C_6H_5)_3C{-}CH(C_6H_5)_2 \rightarrow (C_6H_5)_3C{-}C(C_6H_5)_3 + (C_6H_5)_2CH{-}CH(C_6H_5)_2 .$$

According to the observations of Cone and Robinson[459], the reaction of phosphorus pentachloride with this compound yields triphenylchloromethane. The instability of the central C–C bond in pentaphenylethane was later studied also by other chemists[6,460-466].

The thermal decomposition of dityrityl methane yields quantitatively a mixture of triphenylmethane and triphenylethylene[467]:

$$(C_6H_5)_3C{-}CH_2{-}C(C_6H_5)_3 \rightarrow (C_6H_5)_3CH + (C_6H_5)_2C{=}CHC_6H_5 .$$

When two molecules of triphenylmethylsodium react with dichlorodiphenylmethane, the product is octaphenylpropane, which immediately breaks down into triphenylmethyl and pentaphenylethyl[468]:

$$(C_6H_5)_3C{-}C(C_6H_5)_3{-}C(C_6H_5)_3 \rightarrow (C_6H_5)_3C\cdot + (C_6H_5)_3C{-}(C_6H_5)_2C\cdot$$

The products of the *C*-tritylation of mono-, di-, and tri-hydric phenols, *o*-, *m*-, and *p*-cresols, and also their derivatives undergo slight detritylation on oxidation with chromium trioxide, on distillation with zinc dust and soda lime, and on heating with hydriodic, sulphuric, and acetic acids[6,446,447,469-471]. The dissociation of the carbon–carbon bond is influenced in this case by the position of the trityl group.

A number of studies have been made[466,472-483] on the dissociation of alkyl trityl and aryl trityl ketones. In a study of the possibility of using pyridine as a solvent for the reduction with lithium aluminium hydride of ketones which are sparingly soluble in ether and tetrahydrofuran, Lansbury[475-477] discovered an interesting reaction of phenyl trityl ketone. He found that in pyridine solution phenyl trityl ketone undergoes, with lithium aluminium hydride not normal reduction but reductive dissociation with formation of triphenylmethane and benzaldehyde or benzyl alcohol. Phenyltritylmethanol is an intermediate in this reaction[477]. Methyl trityl ketone is also reduced by the above reductant[476]. When organometallic compounds react with phenyl trityl[466,478] and 1-naphthyl trityl[479] ketones, the bond between the trityl group and the carbon atom is dissociated instead of the expected formation of tertiary alcohols. *C*-Tritylated compounds containing an oxo-group in the ring are known to undergo detritylation[484].

The decomposition of triphenylacetic acid and its derivatives has been extensively investigated[466,485-496]. The pyrolysis of ethyl α-tritylpropionate yields triphenylmethane and ethyl acrylate[497]. Methyl α-methyl-α-tritylpropionate decomposes similarly[497]:

$$(C_6H_5)_3C{-}C(CH_3)_2COOCH_3 \rightarrow (C_6H_5)_3CH + CH_2{=}C(CH_3)COOCH_3 .$$

The detritylation process takes place also in the hydrolysis and other reactions of diesters, diamides, and dinitriles of tritylmalonic acid[498-501]. The amide of tritylacetic acid undergoes an interesting transtritylation reaction on heating with sulphuric acid to 200°C:[501]

$$(C_6H_5)_3C{-}CH_2CONH_2 \rightarrow CH_3CONH{-}C(C_6H_5)_3 .$$

The self-condensation of methyl trityl ketone[502], the acyloin condensation of ethyl trityl acetate[503], the thermal decomposition of methylazotritylmethane[503], and the hydrolysis of the acid ester obtained from phenyltritylmethanol and phthalic acid[504] are accompanied by detritylation. For example:

$$(C_6H_5)_3C{-}COCH_3 + CH_3CO{-}C(C_6H_5)_3 \rightarrow (C_6H_5)_3C{-}COCH_2COCH_3 + (C_6H_5)_3CH .$$

The products of the condensation of triarylmethanols (including triphenylmethanol) with 3-methyl-1-phenyl-5-pyrazolone on dissolution in polar solvents dissociate into ions[505] and their reactions with diazo-compounds yield the corresponding diarylmethanol and an azo-dye[506,507]. The reaction of carboxylic acids and magnesium bromide with the condensation products of the methyl ether of the base of Crystal Violet with acetaldehyde, propionaldehyde, crotonaldehyde, and nitromethane involves the dissociation of the carbon–carbon bond and the formation of Crystal Violet[24,508,509].

5. THE BOND BETWEEN THE TRITYL GROUP AND OTHER ATOMS

The dissociation of the bond between the trityl group and lithium[466], boron[510,511], magnesium[512], aluminium[511], silicon[513,514], phosphorus[515,516], nickel[517], zinc[518], and germanium[519] atoms has been investigated. For example, the reaction of tritylaluminium compounds with primary and secondary amines takes place as follows[511]:

$$(R)_3Al{-}C(C_6H_5)_3 + (R')_2NH \rightarrow (R)_2Al{-}N(R')_2 + (C_6H_5)_3CH .$$

When certain tritylated phosphorus compounds are heated with methanol, methyl trityl ether is formed in 88% yield[516]. Treatment of the trityl derivative of zinc with tributyltin bromide resulted in the isolation of tributyltrityltin[518].

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