

THE PREPARATION, REACTIONS, AND PROPERTIES OF TRIPHENYLENES¹

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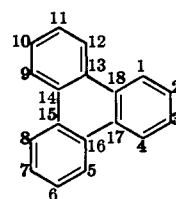
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I. INTRODUCTION

The name "triphenylene" was first used by Schultz (178, 184), who separated the compound from the pyrolytic products of benzene in repeating some work of Berthelot (34). Schultz also obtained a hydrocarbon with similar properties as a byproduct in the preparation of biphenyl from bromobenzene and sodium (184). As will be indicated later, this substance was undoubtedly triphenylene.

Mannich (129, 130) developed the first synthesis of triphenylene (I) and fully appreciated its structure in 1907. The method employed was a two-step reaction from cyclohexanone (Section II,A,1).

The symmetrical nature of triphenylene and some of its fascinating properties—fluorescence, ultraviolet absorption, etc.—led to an early interest in its physical



I
Triphenylene

properties, some of which have been investigated thoroughly. The electronic distribution in triphenylene, with the lack of groupings like the 9,10-positions in phenanthrene and anthracene, make it in several respects more similar to benzene than the compounds containing smaller condensed rings.

Several excellent chemical studies concerning substitution, reaction rates, and other areas of study have been carried out more recently. Other facets for investigation, e.g., the effect of substituents on electrophilic substitution and free-radical attack, have to date been largely neglected. A systematic study of the derivatives

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of triphenylene is lacking, largely owing to difficulties in synthesis. 1-Substituted derivatives are more difficult to obtain than those with 2-substituents, presumably owing to steric hindrance effects in substitution reactions. The stereochemistry of hydrogenated derivatives of triphenylene has apparently not been investigated. An octadecahydrotriphenylene is known (182) but not the cis-trans nature of the product. Various configurations should be capable of existence.

Recent interest in hydrocarbons of this type was stimulated by the recognition that such substances result when biphenyl, terphenyls, and related compounds are subjected to thermal decomposition and radiation. In a way this is an extension of the original observation that triphenylene is obtained from benzene under drastic conditions. Yields from the higher hydrocarbons, although low in most cases, become more significant than from benzene.

Few practical applications have been made of the triphenylenes. The use of dodecahydrotriphenylene as a plasticizer for polystyrene has been suggested (116), and groups of workers in the dye industry have considered the use of certain derivatives (Section IV,B). A number of other uses will certainly be found.

A. NOMENCLATURE

Triphenylene has also been called isochrysene, 1,2,3,4-dibenzonaphthalene, and 9,10-benzophenanthrene. The numbering of the triphenylene ring is uniquely direct and free of variances. The numbering system employed almost universally is shown in formula I. A method for the numbering of the inner ring, when needed, has involved the application of primes to adjacent carbon atoms (e.g., 1', 4', 5', 8', 9', 12'), but the method shown above seems preferable.

B. SCOPE OF REVIEW

Triphenylene and its hydrogenated and univalently substituted derivatives are included in this review. The chemistry of the keto-substituted hydrotriphenylenes is also covered, but not that of the benzo derivatives or larger ring systems.

The chemistry of the triphenylenes has been summarized completely to 1946, with some later references to 1951, in Elsevier's *Encyclopaedia of Organic Chemistry* (73). The literature prior to 1946 has been included here only when needed for correlation with later work.

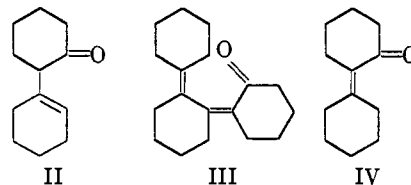
II. SYNTHESSES OF TRIPHENYLENES AND HYDRO DERIVATIVES

A. FROM CYCLOHEXANONE

1. Direct condensation to dodecahydrotriphenylene

Cyclohexanone was first converted to 1,2,3,4,5,6,7,8-, 9,10,11,12-dodecahydrotriphenylene in 8 per cent yield by Mannich (129, 130), who employed methanolic sul-

furic acid as the reaction medium. The low yield is due to the simultaneous formation of fractions with the molecular formulas $C_{12}H_{18}O$ and $C_{18}H_{26}O$. The former



fraction is mainly 2-(1-cyclohexenyl)cyclohexanone (II) or isomers such as 2-cyclohexylidenecyclohexanone (IV). The higher-boiling fraction must contain some 2-(2-cyclohexylidene)cyclohexylidene)cyclohexanone (III) (possibly with displaced double bonds), since it yields some dodecahydrotriphenylene on treatment with sodium ethoxide (117). The question of the positions of the double bonds is of considerable importance in other syntheses of triphenylene and homologs and is discussed in Section II,A,5.

Several attempts to improve the yield of dodecahydrotriphenylene by varying the reaction conditions have been made. Other condensing agents tested, with the yields claimed in parentheses, include thorium oxide at 300°C. (6.4 per cent) (110), zinc chloride (4 per cent) (117), calcium and aluminum oxides with cerium and thorium oxide (32 per cent) (75, 76, 79), aluminum oxide at 320°C. and 30 atm. (23 per cent) (148), and polyphosphoric acid (32 per cent yield of the crude product, which on dehydrogenation gave a 2 per cent yield of triphenylene) (21). Dodecahydrotriphenylene has also been mentioned as a minor product from reactions of cyclohexanone in the presence of 1 per cent sulfuric acid (0.5 per cent yield) (136), *p*-toluenesulfonic acid (1.5 per cent yield) (152), activated aluminosilicate (120), and acetyl chloride in nitromethane (19).

A thorough study of the available methods has recently been made (17). The best yield obtained was 13 per cent, and this was accomplished in the presence of aluminum oxide containing 4.5 per cent thorium oxide at 280°C. and 57 atm. for 32 hr. Mannich's original conditions still represent the most convenient small-scale laboratory method. The yield is improved to 10.5 per cent by modifying the method of isolation (67).

2. Dehydrogenation of hydrotriphenylenes

For the dehydrogenation of dodecahydrotriphenylene, zinc dust and copper (130), selenium (70), and nickel on chromium oxide with benzene as a hydrogen acceptor (3) were used in earlier studies. With the ready availability of active palladium catalysts, which act generally in high yields in the liquid state, this catalyst for the dehydrogenation of dodecahydrotriphenylene as well as other hydro derivatives is now preferred. Almost quantitative yields of products which are nearly pure may generally be obtained.

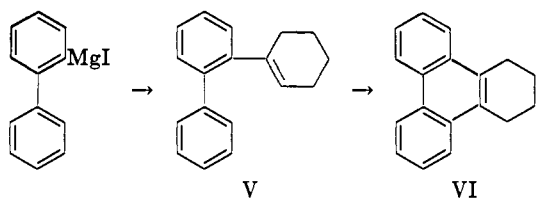
3. Via 2-cyclohexylcyclohexanone

2-Cyclohexylcyclohexanone is obtained by the reduction of II or IV and, when condensed with phenylmagnesium bromide, gives 1-phenyl-2-cyclohexylcyclohexanol in 38 per cent yield. When heated with selenium, this tertiary alcohol yields no *o*-terphenyl but undergoes cyclodehydrogenation as well as dehydrogenation and dehydration to give triphenylene directly (143).

This contrasts with the results obtained when the unsaturated ketones, II and IV, are condensed with the phenyl Grignard reagent and the product is dehydrogenated with palladium on alumina. The condensation yields a liquid and a solid alcohol. Dehydrogenation of the crystalline alcohol with palladium activated by boiling for a short time with 5 per cent aqueous potassium carbonate or by washing with dilute hydrochloric acid yields mainly *o*-terphenyl and only small amounts of triphenylene. Similar results are obtained with the liquid isomer and alkaline palladium. Under similar conditions dodecahydrotriphenylene is smoothly dehydrogenated, but *o*-terphenyl does not yield triphenylene when heated at 360–370°C. for 1 hr. (153).

4. With biphenyl-2-magnesium iodide

Condensation of the Grignard reagent from 2-iodobiphenyl with cyclohexanone followed by dehydration of the product gives a 29 per cent yield of 2-(1-cyclohexenyl)biphenyl (V). Epoxidation of the hydrocarbon, followed by ring closure with hydrobromic and acetic acids, gives 1,2,3,4-tetrahydrotriphenylene (VI) in 30 per cent yield (40).

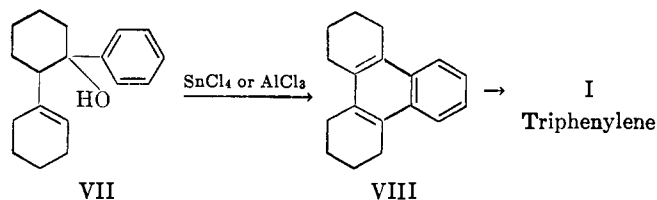


5. Via 2-(1-cyclohexenyl)cyclohexanone or isomer

Before the syntheses are discussed, the structures of the bimolecular condensation products of cyclohexanone deserve some comment. In acidic or alkaline media cyclohexanone yields a liquid unsaturated ketone (204, 205). In most work this product has been considered to be 2-(1-cyclohexenyl)cyclohexanone (II). The structure of this material and of a solid isomer obtained by treating 2-(1-chlorocyclohexyl)cyclohexanone with sodium methoxide was assigned on the basis of chemical evidence (166). The solid isomer yields an epoxide when treated with a limited amount of alkaline hydrogen peroxide and was considered to be 2-cyclohexylidenecyclohexanone (IV). The liquid similarly treated yields 6-(1-cyclohexenyl)-6-ketocaproic acid by oxidation in the cyclohexanone ring along with a smaller amount of an epoxide which is apparently the same compound as

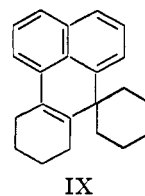
that obtained from the solid. This assignment has recently been questioned on the basis of infrared and ultraviolet absorption studies (170). The two samples are considered to be different stereochemical forms of IV. Needless to say, the nature of the compound bears greatly on the results described below. The "cyclohexenylcyclohexanone" is usually obtained by treatment of cyclohexanone with anhydrous hydrogen chloride and dehydrochlorination with pyridine. It is used after fractionation and corresponds to the liquid isomer. Actually, the fractions used may contain both cyclohexenylcyclohexanone and cyclohexylidenecyclohexanone.

The attempted preparation of 1- and 2-methoxytriphenylene through the use of appropriate biphenyl compounds (Section II,A,4) failed (164). Condensation of II or IV with the phenyl Grignard reagent followed by dehydration and dehydrogenation of the product also resulted in low yields of triphenylene (153, 164). Better yields are obtained when the triphenylene nucleus is formed from 2-(1-cyclohexenyl)-1-phenylcyclohexanol (VII) by ring closure in the presence of stannic or aluminum chloride prior to dehydrogenation (164).



The structure of 1,2,3,4,5,6,7,8-octahydrotriphenylene (VIII), the formation of which requires dehydrogenation as well as dehydration, has been confirmed (21). The cyclization may also be carried out in the presence of polyphosphoric acid or anhydrous hydrogen fluoride (21).

This method is applicable to the preparation of 2-fluorotriphenylene (23) and methoxytriphenylenes (164; Section IV,B). Similarly, through the use of the β -naphthyl Grignard reagent, 1,2-benzotriphenylene is prepared (21). The alcohol obtained with the α -naphthyl Grignard reagent, however, yields with aluminum chloride 8,9,10,11-tetrahydrospiro[7H]benz[d,e]anthracene-7,1'-cyclohexane (IX).



An improvement in the Rapson synthesis is made by epoxidation of the intermediate unsaturated alcohol (VII). The octahydrotriphenylene is then prepared from the epoxide through the use of a mixture of acetic and

hydrobromic acids. Dehydrogenation with palladium affords triphenylene in 50 per cent yield from VII (17). Similarly prepared were the 1-methyl and 2-methyl derivatives using *o*- and *p*-bromotoluene and in 15 per cent and 32 per cent yields, respectively, from II or IV. 1,2,3,4,5,6,7,8-Octahydro-9,12-dimethyltriphenylene is readily prepared similarly, but the hydrocarbon is not dehydrogenated smoothly. In contrast to the results of the experiments without epoxidation described above, either 1- or 2-naphthylmagnesium bromide yielded 1,2-benzotriphenylene (17). 2-Hydroxytriphenylene was prepared in an analogous manner, using *p*-methoxyphenylmagnesium bromide (16).

Epoxidation furnishes a ready path for the elimination of the two hydrogen atoms and this may be the explanation of the improved yields. If the starting material contains no II, the cyclization reaction becomes more difficult to explain.

6. Other methods

Electrolytic oxidation of cyclohexanone in dilute sulfuric acid yields along with other substances small amounts of a hydrocarbon of the molecular formula $C_{18}H_{12}$, which is apparently triphenylene (151). Cyclopentanecarboxaldehyde is isomerized in concentrated sulfuric acid to cyclohexanone and yields small amounts of dodecahydrotriphenylene (203).

B. BY FRIEDEL-CRAFTS REACTIONS WITH BENZENE

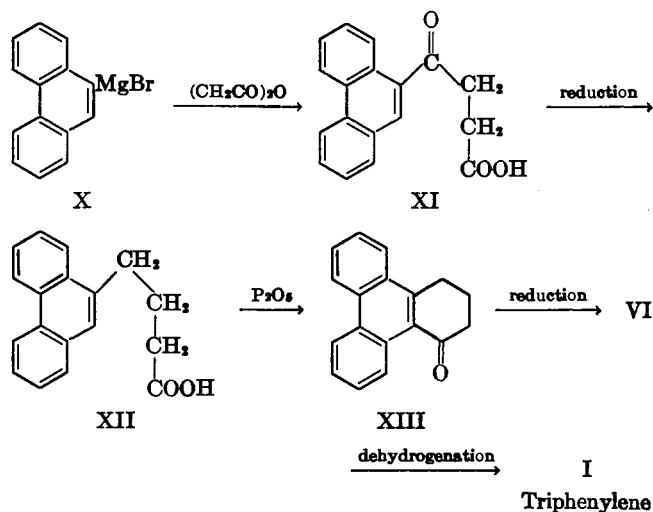
Dodecahydrotriphenylene is obtained along with octahydrophenanthrenes and octahydroanthracenes by the reaction of benzene with 1,4-dichlorobutane in the presence of aluminum chloride. A 77 per cent yield of dodecahydrotriphenylene is claimed (169). Another report states that triphenylene is also obtained. Under the mildest conditions studied 20.4 per cent of the dodecahydro derivative is isolated, with 4.2 per cent of triphenylene as a side-product. Under more vigorous conditions the products obtained include triphenylene (20 per cent yield) and dodecahydrotriphenylene (14 per cent yield) (191). The reaction with 1-bromo-4-chlorobutane also yields the dodecahydro derivative (200). The formation of a hexahydrotriphenylene through the use of 1,4-dichloro-2-butene has also been reported (169).

The claim that dehydrogenation takes place under some conditions in the presence of Friedel-Crafts catalysts bears substantiation.

C. FROM PHENANTHRENE

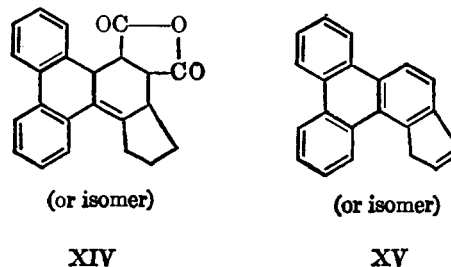
The expansion of the phenanthrene nucleus to that of triphenylene constituted in 1937 an independent proof of structure. 9-Phenanthrylmagnesium bromide (X) and succinic anhydride yield XI, which is reduced through the semicarbazone to XII. Ring closure with phosphorus pentoxide yields 1-keto-1,2,3,4-tetrahydrotriphenylene

(XIII). Clemmensen reduction of XIII affords 1,2,3,4-tetrahydrotriphenylene (VI), which is dehydrogenated to triphenylene (I) (27, 208).

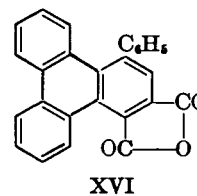


A byproduct obtained in the Clemmensen reduction is presumably bis-1,1'-(1,2,3,4-tetrahydrotriphenylenyl).

In related work it was found that 9-(1-cyclopentenyl)phenanthrene undergoes Diels-Alder addition with maleic anhydride to yield 9,10,15,16-tetrahydro-11-cyclopenta[*a*]triphenylene-9,10-dicarboxylic anhydride (XIV) (24), which is converted by oxidation with lead tetraacetate and decarboxylation to 13(or 11)-cyclopenta[*a*]triphenylene (XV). XV is also prepared by the treatment of 1-[2-(9-phenanthryl)ethyl]cyclopentene with aluminum chloride followed by dehydrogenation (25, 26).



1-(9-Phenanthryl)-1-phenylethylene also gives small amounts of an adduct with maleic anhydride (198). Aromatization with sulfur yields an anhydride, which may be 4-phenyltriphenylene-1,2-dicarboxylic anhydride (XVI). Although this might seem to be the more



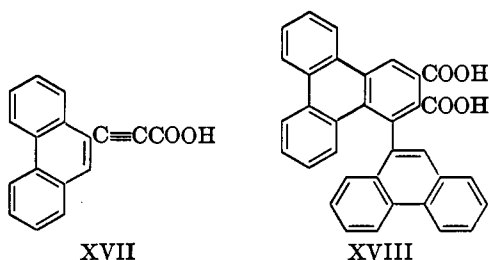
probable structure, the similar reaction with 1-(1-naphthyl)-1-phenylethylene yields after aromatization

and decarboxylation 1,1'-binaphthyl. Here the addition occurred at the diene system involving the phenyl rather than the 1-naphthyl ring. This effect is presumably due to a steric factor, which may also be operative with the phenanthryl derivative. In that case the product would be 4-(9-phenanthryl)naphthalene-1,2-dioic anhydride. The yields of products isolated were low in all cases, however.

The synthesis of triphenylene involving the reaction of phenanthrene with succinic anhydride is adaptable to the preparation of 1- and 2-methyltriphenylene (81). The former is obtained by reaction of the methyl Grignard reagent with XIII and the latter through the use of methylsuccinic anhydride. The method is further extended (80) through the use of dimethylsuccinic anhydride to the synthesis of 2,3-dimethyltriphenylene. 1,2,3-Trimethyl- and 1-hydroxy-2,3-dimethyltriphenylene were prepared by reaction of the ketone analogous to compound XIII with the methyl Grignard reagent and with hydrogen, respectively.

Phenanthrene is usually substituted in the 2- or 3-position in the Friedel-Crafts reaction; therefore, this reaction cannot be used directly in syntheses of triphenylene. However, 1,2,3,4-tetrahydrophenanthrene reacts with succinic anhydride chiefly at the 9-position (8). Reduction of tetrahydrophenanthroylpropionic acid, ring closure, and reduction yield 1,2,3,4,5,6,7,8-octahydrotriphenylene, which is smoothly dehydrogenated to the parent compound. 1-Methyltriphenylene, which is obtained through the use of a Grignard reagent (above), may also be prepared by the succinoylation of 4-methyl-1,2,3,4-tetrahydrophenanthrene followed by the appropriate sequence of steps (7).

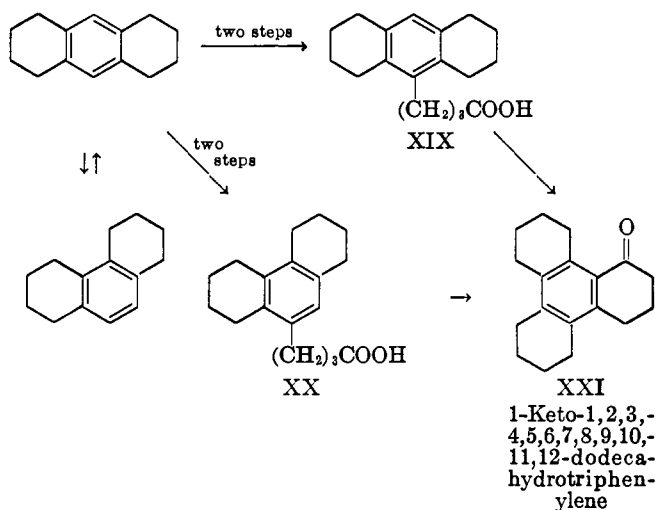
An interesting triphenylene derivative is formed by the dimerization of 9-phenanthrenepropionic acid (XVII) in acetic acid to 1-(9-phenanthryl)triphenylene-2,3-dicarboxylic anhydride (XVIII) (148). Decarboxylation of a salt of this acid yielded in addition to 1-(9-phenanthryl)triphenylene some tetrabenzo[*a,c,f,g,o,p*]naphthalene by dehydrogenation.



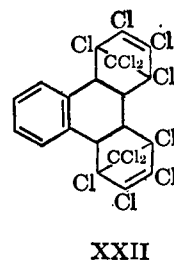
A related reaction of methyl 2-(9-phenanthryl)vinylcarbamate in the presence of phosphorus pentoxide yields 2-(9-phenanthryl)triphenylene (88).

Treatment of 1,2,3,4,5,6,7,8-octahydroanthracene with aluminum chloride yields an equilibrium mixture of the octahydroanthracene and 1,2,3,4,5,6,7,8-octahydrophenanthrene (89, 183). A small amount of do-

decahydrotriphenylene may also be isolated from this reaction mixture. The product from the interaction of octahydroanthracene with succinic anhydride in carbon disulfide with aluminum chloride is thus not the expected octahydroanthranoylpropionic acid, but the corresponding derivative of octahydrophenanthrene (10, 202). When the reaction is carried out in tetrachloroethane, both products may be isolated. The corresponding substituted butyric acids, 4-(1,2,3,4,5,6,7,8-octahydro-9-anthryl)butyric acid (XIX) and 4-(1,2,3,4,5,6,7,8-octahydro-9-phenanthryl)butyric acid (XX), are prepared by Clemmensen reduction, and either compound yields the triphenylene derivative when treated with hydrogen fluoride.



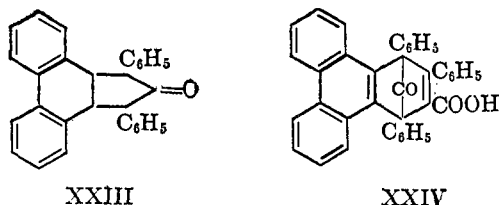
In the patent literature, Diels-Alder addition of hexachlorocyclopentadiene to naphthalene is claimed to yield under appropriate conditions a 2:1 adduct, 1,4,5-bis(endodichloromethano)-1,2,3,4,5,6,7,8-octachloro-1,4,5,8,15,16,17,18-octahydrotriphenylene (XXII) (106). Compounds of this type are claimed to be useful as insecticides or in the manufacture of glue.



D. FROM PHENANTHRAQUINONE

In an adaptation of work in which highly phenylated benzenes were obtained from substituted cyclopentenones, the action of acetylenes with 1,3-diphenyl-2-cyclopenta[*e*]phenanthren-2-one (XXIII) was studied (71, 72). XXIII is readily obtained from phenanthraquinone and dibenzyl ketone. Phenylacetylene condenses with XXIII at about 100°C. with the elimination

of carbon monoxide, and 1,2,4-triphenyltriphenylene is obtained.

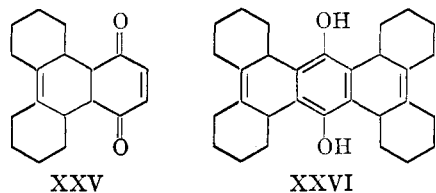


The use of diphenylacetylene similarly yielded 1,2,3,4-tetraphenyltriphenylene. Under these conditions phenylpropionic acid, however, adds to the cyclone, yielding the corresponding endocarbonyl compound (XXIV) or its lactone. When this product is heated (or when the starting materials are caused to react at 150–170°C.), 1,3,4-triphenyltriphenylene-2-carboxylic acid is obtained.

Although the above reaction has apparently not been applied to acetylene, XXIII condenses with di(alkylmercuri)acetylene (1). Again carbon monoxide is readily ejected and 1,4-diphenyl-2,3-di(alkylmercuri)triphenylenes are obtained. The methyl, ethyl, and phenyl derivatives have been reported.

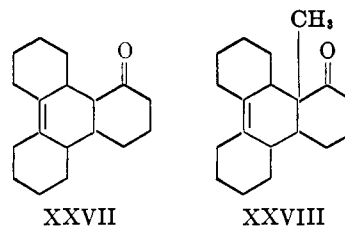
E. FROM BI(1-CYCLOHEXEN-1-YL)

The Diels–Alder addition to the readily available bi(1-cyclohexen-1-yl) suggests an interesting approach in building up the triphenylene nucleus, but efforts in this direction have to date met with limited success as far as the preparation of hydrocarbons is concerned. *p*-Benzoquinone, as well as α -naphthoquinone, readily yields adducts (18). The adduct of benzoquinone is formulated as 1,4-diketo-1,4,5,6,7,8,9,10,11,12,13,16,17,18-tetradecahydrotriphenylene (XXV) and is readily converted to a diacetate, which is a decahydrotriphenylene derivative. The yield of XXV isolated is low. This has been explained on the basis that redox reactions occur simultaneously with the addition. It has been claimed that dehydrogenated forms of the adducts, such as 1,2,3,4,5,6,7,8,8*a*,8*b*,9*b*,10,11,12,13,14,15,16,17,17*a*,18*a*,18*b*-docosahydro-tetra-benz[*a,c,h,j*]anthracene-9,18-diol (XXVI) from the 2:1 bicyclohexenyl–quinone adduct, may be isolated (31, 208). Another explanation is that the product isolated was only one stereochemical form. In other work four different forms of XXV were claimed to be separable (9). Apparently these results bear re-investigation.



2-Cyclohexenone undergoes Diels–Alder addition to bi(1-cyclohexen-1-yl), giving 1-keto-1,2,3,4,5,6,7,8,9,-

10,11,12,13,16,17,18-hexadecahydrotriphenylene (XXVII) but with difficulty and in low yield (141). The resulting ketone is reduced with zinc and acetic acid to hexadecahydrotriphenylene. 2-Methyl-2-cyclohexenone condenses similarly to give low yields of 1-keto-18-methyl-1,2,3,4,5,6,7,8,9,10,11,12,13,16,17,18-hexadecahydrotriphenylene (XXVIII), a triphenylene derivative with an angular methyl group.



Attempted addition of *p*-benzoquinonemonobenzene-sulfonimide to bi(1-cyclohexen-1-yl) gives only a gum and a small amount of *p*-benzenesulfonamidophenol (2).

A recent, promising innovation involves the addition of cyclohexene-1,2-dicarboxylic anhydride to bi(1-cyclohexen-1-yl) (193). The adduct when treated with phosphorus pentoxide yields dodecahydrotriphenylene. 1,4-Diphenyltriphenylene-2,3-dicarboxylic anhydride may be decarboxylated by refluxing with quinoline in the presence of basic copper carbonate (167, 168).

1,2-Dihydronaphthalene yields with bi(1-cyclohexen-1-yl) a small amount of a hydrocarbon which is partially dehydrogenated by selenium to a crystalline hydrocarbon, probably a tetrahydro-1,2-benzotriphenylene (28).

F. FROM *o*-TERPHENYL AND DERIVATIVES

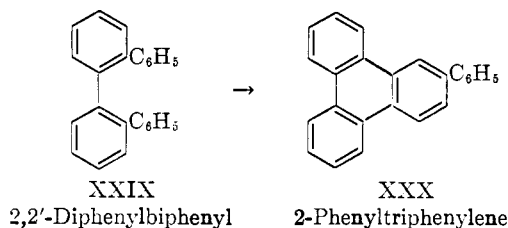
In many of the reactions of *o*-terphenyl and its derivatives dehydrogenation across the 2-positions of the terminal rings occurs and triphenylene derivatives are obtained, sometimes in low yields and occasionally in substantial yields. Allen and Pingert (4) state: "The cyclization is concomitant with substitutions and rearrangements, and is accomplished by most dehydrogenating and condensing agents such as ozone, nitric acid, bromine and aluminum chloride. Triphenylene and its derivatives are common components of the pasty and tarry residues of the reactions of *o*-terphenyl."

As mentioned previously, treatment of 1-phenyl-2-cyclohexylcyclohexanol with selenium yields no *o*-terphenyl, but a substantial amount of triphenylene may be isolated from the reaction mixture (see Section II,A,4). This is in contrast to the formation of *m*- and *p*-terphenyl by the dehydrogenation of 1,3- and 1,4-diphenylcyclohexane, respectively, under similar conditions. *o*-Terphenyl is obtained by the dehydrogenation of 1-(2-xenyl)-1-cyclohexene with chloranil, but even under these conditions triphenylene may be isolated in certain runs (4).

With an aluminum chloride–sodium chloride melt

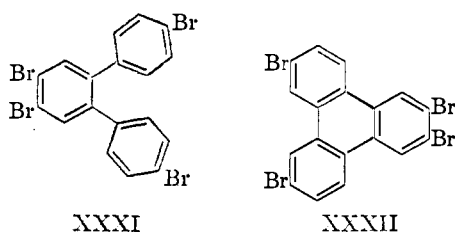
o-terphenyl at 130°C. is isomerized mainly to *p*-terphenyl, but at 200°C. tarry condensation products from which triphenylene may be isolated in 20 per cent yield are obtained (4).

o-Terphenyl is also cyclodehydrogenated on chromia-alumina at 625°C. (95). 2,2'-Diphenylbiphenyl (XXIX) similarly yields a phenyltriphenylene. The authors considered rearrangement of the expected 1-phenyltriphenylene to 2-phenyltriphenylene (XXX) very likely. This proves to be the case (121).

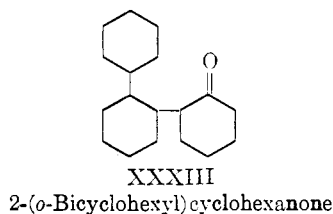


Attempted cleavage of 4'-benzoyl-*o*-terphenyl with sodium amide in benzene yields no *o*-terphenyl but gives some triphenylene (4).

Aqueous bromination of *o*-terphenyl yields eventually a tetrabromo derivative, 4,4',4'',5'-tetrabromo-*o*-terphenyl (XXXI), in which the positions of the bromine atoms are known. This derivative on further treatment with bromine is converted quantitatively to 2,3,7,10-tetrabromotriphenylene (XXXII), which may be reduced to the parent compound (5). The position originally assigned to one of the bromine atoms in the triphenylene derivative is apparently erroneous, owing to a typographical error.



2-(*o*-Bicyclohexyl)cyclohexanone (XXXIII) is dehydrated in the presence of zinc chloride to the hexadecahydrotriphenylene, which may be hydrogenated to a completely saturated octahydro derivative (182).

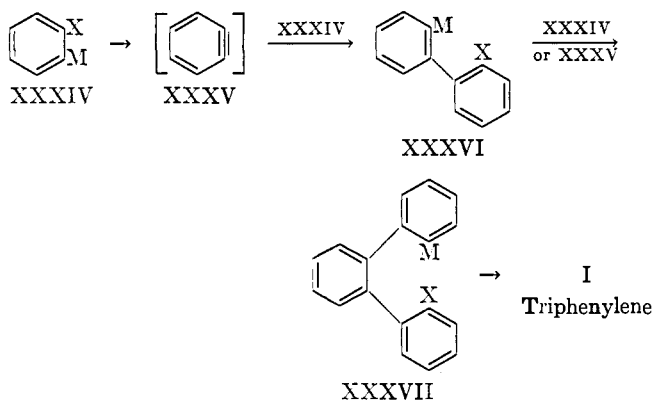


G. BY METALATION REACTIONS AND METAL-HALOGEN INTERCONVERSIONS

Triphenylene is obtained in a variety of metalation and halogen interconversion reactions. The explanation

of the formation of the hydrocarbon led early to the postulation of *o*-phenylene radicals (6). Studies of these reactions have dealt with benzyne or dehydrobenzene chemistry (for leading references see 105, 107, 215).

In the metalation reactions it appears that ortho-metalation is followed by ejection of the inorganic salt. A possible reaction sequence is illustrated:



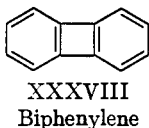
It appears that the reaction sequence does not involve three molecules of XXXV, as originally thought.

The action of sodium on chlorobenzene yields, in addition to biphenyl, *o*-terphenyl, 2,2'-diphenylbiphenyl, and triphenylene (6, 178). Triphenylene is also obtained when the reaction is carried out in the presence of anisole (137, 138) and in the reaction of chlorobenzene with phenyllithium (214). Sodium with bromobenzene gives similarly low yields of triphenylene (38). Metalation of diphenyl ether with a sodium-potassium alloy yields triphenylene and 4,5,9,10-dibenzopyrene in addition to phenols and ethers (123, 124).

Under the milder conditions needed to effect halogen-metal interconversion reactions, the *o*-halometalobenzenes are capable of existence. Thus at temperatures of about -60°C. to -90°C. *o*-fluorobromobenzene and *o*-chlorobromobenzene react with butyllithium to yield *o*-fluorophenyllithium and *o*-chlorophenyllithium, respectively (87). The existence of the organometallic compounds is shown by carbonation and by reaction with benzophenone. *o*-Bromophenyllithium is obtained similarly at lower temperatures and in lower yield. After solutions of the organolithium compounds are allowed to become warm, triphenylene may be isolated as a product.

The reaction of *o*-dihalobenzenes with lithium and magnesium at ambient temperatures has also been studied. *o*-Diiodobenzene and *o*-bromiodobenzene yield with lithium considerable quantities of triphenylene (97, 98). From the reaction of *o*-bromiodobenzene with lithium triphenylene may be obtained in 54.5 per cent yield along with a 12 per cent yield of biphenyl. The hydrocarbons may be separated by steam distillation of the latter. The method is very direct and was recently (1957) claimed to be the best synthetic route to

triphenylene. The action of magnesium and butyllithium on these *o*-dihalobenzenes does not yield triphenylene. When magnesium is used, some biphenylene (XXXVIII) is obtained (98). Magnesium and 4-iodo-3-bromotoluene react to produce 2,6-dimethylbiphenylene, while lithium with this halogen compound affords some 2,6,11-trimethyltriphenylene (100).



Small amounts of triphenylene result when *o*-chloriodobenzene is treated with copper under the conditions of the Ullmann reaction (144).

o-Dilithiobenzene is obtained from *o*-phenylenemercury (209). Reaction of either organometallic compound with a variety of salts yields considerable quantities of triphenylene (211, 212). The highest yields are 33.5 per cent by reaction of the lithium compound with cobaltous chloride and 33 per cent with titanium(IV) chloride. Higher phenylenes (e.g., octaphenylene) are obtained in minute amounts. In similar reactions biphenylene is the major product (215).

In the preparation of the Grignard reagent from *o*-fluorobromobenzene in tetrahydrofuran in the presence of anthracene, both triptycene and triphenylene are formed. Triptycene may be isolated in 28 per cent and triphenylene in 11 per cent yield (213). The two hydrocarbons are also obtained after the reaction of fluorobenzene with butyllithium in the presence of anthracene (210).

2,2'-Dibromobiphenyl gives with phenyllithium an 8 per cent yield of triphenylene (19). With *p*-tolyllithium a low yield of 2-methyltriphenylene is obtained. On the other hand, 9,10-dichlorophenanthrene affords with magnesium in tetrahydrofuran a 60 per cent yield of hexabenzotriphenylene (50).

A review of the Grignard and organolithium compounds derived from dihalogen compounds has appeared (135).

H. MISCELLANEOUS SOURCES

Triphenylene is present in coal tar (197) and marine sediments (132). The liquid-solid phase diagram of 1,2-dibenzophenanthrene-triphenylene, which is of interest in the isolation of these hydrocarbons from coal tar, has been recorded (197). Mellitic acid, found in some asphalts, is thought to have been formed by the oxidation of triphenylene (128).

The formation of triphenylene in the pyrolysis of benzene was mentioned earlier (34, 178, 184). Under pyrolytic and dehydrogenation conditions, biphenyl (119), 1-phenyl-1,3-butadiene (12), and cyclooctadecane (158) similarly give low yields of triphenylene.

The action of boron trifluoride on anisole (hexahydro anisole?) yields a compound which may be a methoxydimethyl-dodecahydrotriphenylene (103).

III. REACTIONS

A. HALOGENATION

Both monofluorotriphenylenes are known, but these have been obtained by indirect methods (Section IV,A). Polychlorotriphenylene, prepared in a study of cyclic fluorocarbons, is obtained under rather drastic conditions in the presence of ferric chloride at 200–250°C. (195, 196). Through the use of silver difluoride and antimony pentafluoride the polychlorotriphenylene is converted to fluorinated oils and resins containing some residual chlorine.

The low-temperature chlorination involving only substitution deserves more study from a synthetic point of view. The kinetics of chlorination in acetic acid has been compared with that of related compounds (66) and is in line with the calculated reactivity (65).

Triphenylene reacts readily with bromine under suitable conditions. The bromination with one mole of bromine in carbon disulfide with iron present has been described (185). The product obtained is a mixture of 2-bromotriphenylene (isolated chromatographically in 56 per cent yield) and dibromotriphenylene (16). 1-Bromotriphenylene, not isolated in these experiments, may be formed in small amounts, since a mixture of 10 per cent of synthetic 1-bromotriphenylene with 2-bromotriphenylene is not separable by the method used.

The bromination of *o*-terphenyl yields under some conditions bromotriphenylene derivatives (5).

B. SULFONATION

Sulfonation of triphenylene yields 2-triphenylenesulfonic acid (174). Comparison of the phenol obtained by alkali fusion of its salt (186) with synthetic 2-triphenylenol confirms the orientation assigned to the sulfonic acid group (16).

C. NITRATION

Triphenylene readily yields a trinitro derivative (130). It is difficult to restrict the reaction to mononitration, but by heating the hydrocarbon in acetic anhydride at 60°C. with the theoretical amount of nitric acid, 27 per cent and 23 per cent yields of 1- and 2-nitrotriphenylene, respectively, are obtained (16). Similar results are obtained using acetyl nitrate in acetic anhydride at 25°C. (23). The two nitro compounds are separable chromatographically. Evidence of oxidation is observed in these experiments (16), but no dinitro compounds are obtained.

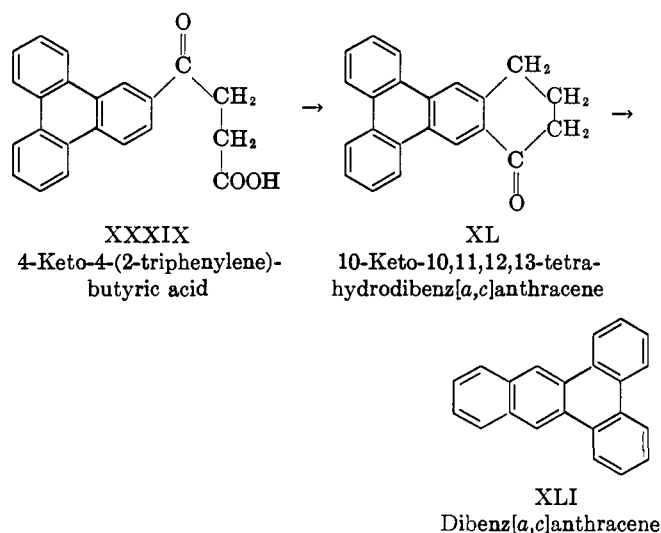
Competitive nitration studies of triphenylene-naphthalene and triphenylene-phenanthrene have been reported (67). The ratio ($k_{\text{triphenylene}}/k_{\text{naphthalene}}$) is 4.4; the

corresponding ratio relative to phenanthrene is 2.3. These results have been compared with calculations of reactivity (68).

D. FRIEDEL-CRAFTS REACTIONS

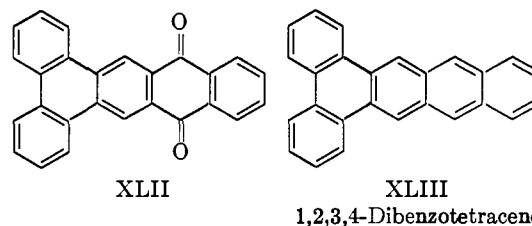
Apparently the first Friedel-Crafts reaction on triphenylene studied was with oxalyl chloride in an attempt to prepare more highly condensed ring systems (61). The reaction, however, does not form a new ring involving carbon atoms 1 and 12, but yields a triphenylenecarboxylic acid. A triphenylenecarboxylic acid with the same melting point has been reported in the patent literature (77). This is obtained by condensing triphenylene with carbamyl chloride under Friedel-Crafts conditions, a reaction which yields the amide. 2-Triphenylenecarboxylic acid may be obtained by sodium hypobromite oxidation of 2-acetyltriphenylene of known orientation (45). The acid prepared in this way is identical with that obtained using oxalyl chloride.

2-Acetyltriphenylene is obtained in good yield by a Friedel-Crafts reaction (16, 45). The position of the acetyl group is known, since the ketone undergoes the Willgerodt-Kindler reaction to a triphenyleneacetic acid, which is decarboxylated to 2-methyltriphenylene. Propionyl- and succinoyltriphenylene, obtained similarly, were presumed to be 2-substituted derivatives also (45). The position of the succinoyl group is now established, since the succinoyl derivative is converted as shown to dibenz[*a,c*]anthracene:

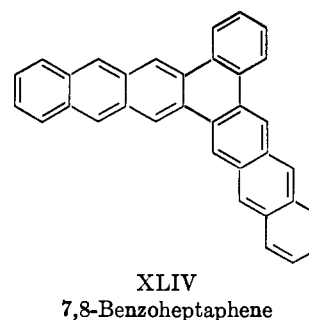


This result establishes the facts that the succinoyl group attaches to the 2-position and that cyclization occurs at the adjacent, unhindered 3-position (46)

Similar results are obtained with phthalic anhydride. The orientation of 2-phthaloyltriphenylene is known, as it may be cyclized to a quinone, 10,15-diketo-10,15-dihydrodibenzo[*a,c*]naphthacene (XLII), and this product may be converted to 1,2,3,4-dibenzotetracene (XLIII) (54). With two moles of phthalic anhydride a mixture,



apparently of the 2,6-, 2,7-, and 3,6-diphthaloyltriphenylenes, is obtained. This mixture is converted to a homogeneous bisquinone, which may be converted to a hydrocarbon, probably 7,8-benzoheptaphene (XLIV) (55).



Thus, to date, the entering group in all known Friedel-Crafts reactions of triphenylene substitutes at the 2-position.

E. WITH SODIUM

Reaction of triphenylene as well as a number of other hydrocarbons with sodium in tetrahydrofuran yields a free-radical negative ion as the primary product (145). The absorption spectrum of a paramagnetic solution of $C_{18}H_{12}^-Na^+$ has been given.

F. OXIDATION

Triphenylene is not exceptionally reactive toward oxidizing agents. Dodecahydrotriphenylene (129, 130) and triphenylene are oxidized at 160°C. by fuming nitric acid to mellitic acid. In fact, the oxidation of triphenylene by nitric acid, followed by oxidation by potassium permanganate, proves to be one of the better oxidative methods for preparing mellitic acid (108). Triphenylene is not oxidized as rapidly by alkaline permanganate as is naphthacene or pyrene (206).

Dodecahydrotriphenylene is oxidized by chromic acid to the 1-keto compound (202).

G. REDUCTION

Triphenylene appears to be relatively resistant to hydrogenation, as might be expected from its structure. In contrast to naphthalene and phenanthrene, it is not affected by dicobalt octacarbonyl in the presence of carbon monoxide and hydrogen (83). This system generally reduces condensed polynuclear hydrocarbons in which benzene rings are not isolated.

Triphenylene is reduced to the dodecahydro compound in cyclohexane at 185°C. in the presence of large amounts of Raney nickel (206). The liquid octadecahydro derivative has been obtained only by reduction of the hexadecahydro compound (181, 182).

Triphenylene is attacked by sodium in amyl alcohol, yielding 1,2,3,4-tetrahydrotriphenylene and probably a dihydrotriphenylene (42).

The results with triphenylene obtained in a study of the polarographic reduction of hydrocarbons agree with the calculated reactivity of the hydrocarbon (101).

H. WITH FREE RADICALS

The perbenzoic acid-initiated reaction of carbon tetrachloride with 1-hexadecene is not strongly inhibited by triphenylene; thus triphenylene does not appear to be very susceptible to attack by the trichloromethyl free radical (111).

IV. SYNTHETIC APPLICATIONS

A. AMINOTRIPHENYLENES

1-Aminotriphenylene is obtained by reduction with tin and hydrochloric acid of the corresponding nitro compound (16) or by reduction with hydrazine and Raney nickel of the same compound (23). The 2-amino derivative is obtained by the latter method.

2-Aminotriphenylene is also prepared from the acetyl derivative by oxidation to the carboxylic acid, conversion to the azide, and decomposition of the latter compound (16). Conversion of 2-triphenylenecarboxamide to the amine by means of sodium hypobromite fails, owing to the insolubility of the amide, but rearrangement yielding the urethan occurs in methanol. The urethan may be hydrolyzed to the amine (16). The oxime of 2-acetyltriphenylene is converted to 2-acetamidotriphenylene by means of phosphorus pentachloride, and the amide also may be hydrolyzed (23).

The aminotriphenylenes may be diazotized, and thus a method of preparation of halo and related derivatives is available. The conversion to the 2-fluoro (22), 1-bromo, and 2-bromo (16) compounds by this method has been reported.

B. TRIPHENYLENOLS AND ETHERS

Syntheses of the 1-methoxy (164), 2-methoxy (164), and 2-hydroxy (16) derivatives of triphenylene have been reported. By the method of epoxidation (Section II), which involves the use of a mixture of hydrobromic and acetic acids, the 2-hydroxy compound is obtained directly in the synthesis starting with *p*-bromoanisole. Neither the 1-methoxy nor the 1-hydroxy compound could be obtained by this method (16). The 1-methoxy derivative is resistant to ether cleavage (164), a fact which is attributed to steric hindrance at the 1-position. 2-Triphenylenol is also available by alkali fusion of the

sulfonic acid (186) and by means of the diazo reaction on 2-aminotriphenylene (16).

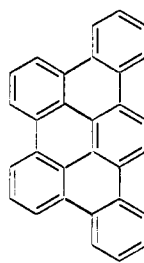
Under the conditions of the Kolbe-Schmidt reaction 2-triphenylenol is converted to an *o*-hydroxytriphenylenecarboxylic acid (175). The acid may be converted to a number of anilides, which have been claimed to be useful in the dye industry (78, 176, 177). 2-Triphenylenol and the derived acid couple with a variety of diazotized anilines (187, 188).

2-Triphenylenol cannot be oxidized directly to a quinone with potassium nitrosodisulfonate, $\text{NO}(\text{SO}_3\text{K})_2$. However, 1,2-triphenylenequinone is obtained by the action of this oxidizing agent on 1,2-triphenylenediol, which may be prepared from the product obtained by the reaction of diazotized sulfanilic acid with 2-triphenylenol (199).

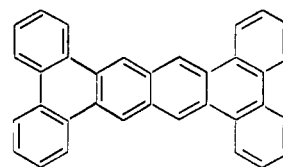
C. CARBOXYLIC ACIDS

1-Triphenylenecarboxylic acid is unknown. 2-Triphenylenecarboxylic acid (Section II,D) and several derivatives, the acid chloride, the amide, the azide, and the methyl ester (16, 61, 77), are known.

1,4-Diphenyltriphenylene, obtainable from the 2,3-dicarboxylic anhydride, is cyclodehydrogenated in a sodium chloride-aluminum chloride melt to yield 1,12-, 2,3,10,11-tribenzoperylene (XLV) (167, 168). Friedel-Crafts condensation of 2-triphenylenecarboxylic acid chloride with 9-methylphenanthrene yields a ketone which may be pyrolyzed to 1,2,3,4,7,8,9,10-tetrabenzonaphthacene (XLVI) (58).



XLV



XLVI

D. ACYLTRIPHENYLENES

2-Acetyl- and 2-propionyltriphenylenes are reduced to 2-ethyl- and 2-propyltriphenylenes by the Huang-Minlon modification of the Wolff-Kishner method (45). 2-Acetyltriphenylene may also be converted to 2-methyltriphenylene and its phenylhydrazone to 2-(2'-indolyl)triphenylene by the Fischer method (45).

V. PHYSICAL AND BIOLOGICAL PROPERTIES AND THEORETICAL STUDIES

Triphenylene is a planar molecule (133, 134) with an orthorhombic crystal structure (15). These results are listed with those of two other independent x-ray investigations:

	Banerjee (15)	Chorghade (51)	Klug (114)
	A.	A.	A.
a.....	13.20	13.16	13.20
b.....	16.81	16.78	16.84
c.....	5.26	5.27	5.28

Space group = $P 2_12_12_1$.

The original solution of the x-ray data (115) yielded abnormally low intermolecular distances. In recalculations with recently developed instruments these distances are found to be normal (96, 149, 150, 201). The carbon-carbon bond lengths of the various bonds are undoubtedly different, but the values assigned are subject to a rather large experimental error.

The dodecahydrotriphenylene crystal is hexagonal (51, 52, 91). The crystal structure is disordered in one direction, and diffuse lines are obtained in single-crystal x-ray photographs (90).

The ultraviolet absorption spectrum of triphenylene is characteristic (53, 56, 59, 82, 100). Careful studies in heptane (113) and on the solvent effects in chloroform, ethyl alcohol, and iso-octane (179) have been recorded. The band shifts are not a function of the refractive indices of the solutions. The band displacements at low temperatures in the solid state in hydrocarbons (37) and in ether-alcohol at -196°C ., as well as in aqueous sodium cholate solutions at room temperature (14), have been recorded. In aqueous solutions the shifts are all negative, while at low temperatures the displacements are irregular. The bands are narrower and the differences in intensities between maxima and minima are more than doubled at -170°C . (37).

The spectrum has been compared with those of related polycyclic hydrocarbons (165). The absence of "quinonoid rings" in triphenylene is indicated by comparison of spectra of a group of hydrocarbons (62). The planarity of the molecule is indicated by the fine structure in the long ultraviolet wave region (133, 134). Changes in the ultraviolet absorption may be used to follow the hydrogenation of triphenylene and hexahydrocoronene (84).

Marked similarities between the spectrum of triphenylene and that of 1-azatriphenylene have been noted (11). References to the ultraviolet absorption of derivatives of triphenylene are listed in the tables.

The spectra of dodecahydrotriphenylene (59, 82) and iodine complexes of this compound at normal and low temperatures (92) are available.

The fluorescent and phosphorescent spectra of condensed aromatic hydrocarbons have been the subject of a number of investigations (39, 60, 69, 180). In triphenylene a mirror-image relationship between the fluorescent and the ultraviolet absorption bands exists (180). Thus the ultraviolet band of longest wavelength corresponds to the fluorescent band of shortest wave-

length. The recorded fluorescent data include values in crystalline paraffins at -180°C . (39) and relations between the phosphorescent bands, *p*-bands, singlet-triplet differences, and the average life of phosphorescence (60). Dodecahydrotriphenylene is included in this last study.

The flash photolysis technique affords useful information about the triplet states of triphenylene and other aromatic hydrocarbons (154, 155, 156, 157). The photomagnetism (74) and absorption spectrum (125) of triplet states are related to phosphorescent decay. The calculated frequencies of the two longest absorption bands agree satisfactorily with the observed values (160). Separation of the two lowest singlet states, as calculated by the Slater-Pauling approximation, correlates with light absorption values (190). Recent calculations of the main ultraviolet transitions have been recorded (93, 94).

The infrared spectra with a rock salt prism (49) and in the low-frequency region (122) are interesting. A strong

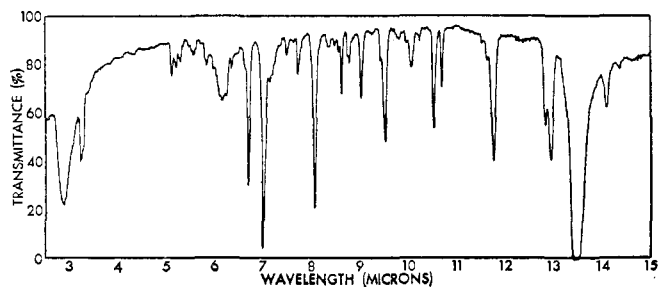


FIG. 1. Infrared absorption spectrum of triphenylene (potassium bromide pellet).

band at 738 cm^{-1} and weak ones at 620 and $1020\text{--}1035\text{ cm}^{-1}$ are observed. The curve obtained by the authors in a potassium bromide pellet is illustrated in figure 1.

Nine Kekulé structures may be written for triphenylene. The number of mesomeric structures for each degree of excitation of condensed aromatic hydrocarbons has been calculated (160). The heat of combustion of triphenylene is $2138.11 \pm 0.52\text{ kcal./mole}$ (constant pressure, 20°C .) and the calculated resonance energy is 135.8 kcal./mole (126, 127). The theoretical resonance energy agrees well with the experimental value (99). The specific mesomerism energy (energy per π electron) increases in the series benzene, naphthalene, phenanthrene, triphenylene (194). Asymmetric annellation effects are also noted in β -band shifts (57, 58).

Attempts have been made to correlate calculations of diamagnetic anisotropy with experimental values (36, 146, 147). The calculated values are somewhat higher than the experimental ones and do not correlate simply with resonance energies in a series of hydrocarbons.

The electron distribution in triphenylene and other hydrocarbons has been the subject of a number of studies (13, 20, 35, 41, 47, 65, 159, 171, 173). The results have been correlated with chemical reactivity (163) and

applied to nonreaction in Diels–Alder addition (20) and to an expected low activity with osmium tetroxide and ozone (41). It is generally concluded from the calculations that the 1-positions should be more active. The fact that substitution seldom occurs there is attributed to steric effects (44).

No carcinogenic triphenylene derivative has been found (140, 192). This is attributed to the lack of areas of electron delocalizability (35, 140, 162). The ease of polarographic reduction of a series of aromatic hydrocarbons, including triphenylene, correlates well with electron distribution (101).

Two broad proton peaks are observed in the nuclear magnetic resonance spectrum of triphenylene (32, 33). These are undoubtedly due to the two types of hydrogen atoms present. The peak of higher frequency is due to the hydrogen atoms in positions 1, 4, 5, 8, 9, and 12.

Triphenylene has been included in studies on the scintillation counting behavior of various compounds (172), on electron emission produced by high fields (139), and on electron and methyl affinities and ioniza-

tion energies (131). The exaltation of the molar refraction of triphenylene is 81.5 (29), the dipole moment is 0 (30), and the solubility in water is 38 γ per liter (64). Measurements on the absorption of triphenylene at mercury–solution boundaries (85), solubilization in soap solutions (112), and interaction with sterols in surface films (63) have been recorded.

Other studies include the molar refraction (189) and specific viscosities of solutions (118) of dodecahydrotriphenylene. The effects of temperature on viscosity in 2 per cent solutions in nitrobenzene and *p*-xylene are large.

VI. TABLES OF TRIPHENYLENES

Melting points and other pertinent data on the triphenylene derivatives, together with literature references, are listed in tables 1 to 6. The compounds are divided into various classes and arranged within each table according to the number and kind of functional groups and according to increasing molecular formulas.

TABLE 1
Hydro-, alkyl-, and aryltriphenylenes

Derivative	Molecular Formula	Melting Point °C.	Other Data	References
Unsubstituted.....	C ₁₈ H ₁₂	199	Boiling point, 425°C.	See Section V (27, 40)
1,2,3,4-Tetrahydro.....	C ₁₈ H ₁₆	122–123		(169)
α -Hexahydro.....	C ₁₈ H ₁₈			(8, 21, 164)
1,2,3,4,5,6,7,8-Octahydro.....	C ₁₈ H ₂₀	129–130		
Picrate.....		196–197		
<i>sym</i> -Dodecahydro.....	C ₁₈ H ₂₄	232–233		See Section V (141, 182, 193)
1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16-Hexadecahydro.....	C ₁₈ H ₂₈	87–90	Boiling point, 140–145°C./1.5 mm., 186–188.5°C./12 mm.	
Octadecahydro.....	C ₁₈ H ₃₀	Liquid	Boiling point, 175–176°C./7 mm.	(182)
1-Methyl.....	C ₁₉ H ₁₄	93–94	Ultraviolet	(7, 8, 17, 81, 142, 192)
Picrate.....		176–177		
2-Methyl.....	C ₁₉ H ₁₄	102.6–103.6	Ultraviolet	(17, 19, 45, 81, 164)
Picrate.....		192–193		
2-Methyl-1,2,3,4-tetrahydro.....	C ₁₉ H ₁₈	116.2–116.8		(81)
1-Methyl-1,2,3,4,5,6,7,8-octahydro.....	C ₁₉ H ₂₂	91–92		(7)
Picrate.....		164–165		
2-Methyl-5,6,7,8,9,10,11,12-octahydro.....	C ₁₉ H ₂₂	93–94		(164)
Picrate.....		195.5		
1,2-Dimethyl.....	C ₂₀ H ₁₆	86.8–87.4		(81)
Picrate.....		154–155		
2,3-Dimethyl.....	C ₂₀ H ₁₆	156.7–157.2		(80)
Picrate.....		210–211		
Trinitrobenzene derivative.....		237–237.7		
1,4-Dimethyl.....	C ₂₀ H ₁₆	108.4–109.2		(80)
Picrate.....		148.4–149.4		
2,6-Dimethyl.....	C ₂₀ H ₁₆	89–90	Ultraviolet	(142)
Picrate.....		194–195		
2-Ethyl.....	C ₂₀ H ₁₈	90		(45)
Picrate.....		144		
2,3-Dimethyl-1,2,3,4-tetrahydro.....	C ₂₀ H ₂₀	158–167		(80)
Picrate.....		154–158		
Trinitrobenzene derivative.....		158–160		
1,4-Dimethyl-5,6,7,8,9,10,11,12-octahydro.....	C ₂₀ H ₂₄	123–124		(17)
1,2,3-Trimethyl.....	C ₂₁ H ₁₈	109.8–110.6		(80)
Picrate.....		186–186.5		
Trinitrobenzene derivative.....		203.7–204.1		
2,6,10-Trimethyl.....	C ₂₁ H ₁₈	187–188	Ultraviolet	(17, 100, 121, 142)
Picrate.....		208–209		

TABLE 1—Continued

Derivative	Molecular Formula	Melting Point	Other Data	References
		°C.		
2,6,11-Trimethyl.....	C ₂₁ H ₁₈	128.5–129.5	Ultraviolet	(100, 142)
Picrate.....		85–86		
2-Propyl.....	C ₂₁ H ₁₈	191–192		
Picrate.....		78	Boiling point, 212–214°C./0.5 mm.	(45)
2,6,10-Trimethyl-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro.....	C ₂₁ H ₃₀	195		(100, 121)
2-Phenyl.....	C ₂₄ H ₁₈	183–184		(95, 121)
1,4-Diphenyl.....	C ₂₆ H ₂₀			(167, 168)
1,2,4-Triphenyl.....	C ₂₆ H ₂₄	250		(71)
1,2,3,4-Tetraphenyl.....	C ₂₈ H ₂₈	292–293		(71)
1-(9-Phenanthryl).....	C ₂₂ H ₂₀	216–217	Ultraviolet	(48)
Trinitrobenzene derivative.....		178		
2-(9-Phenanthryl).....	C ₂₂ H ₂₀	214–216	Ultraviolet	(88)

TABLE 2

Halotriphenylenes

Derivative	Molecular Formula	Melting Point	Other Data	References
		°C.		
1-Fluoro.....	C ₁₈ H ₁₁ F	174–175	Ultraviolet	(22, 23)
2-Fluoro.....	C ₁₈ H ₁₁ F	185–185.5	Ultraviolet	(22, 23)
1-Bromo.....	C ₁₈ H ₁₁ Br			(16)
2-Bromo.....	C ₁₈ H ₁₁ Br	131–132		(16, 185)
<i>α,α</i> -Dibromo.....	C ₁₈ H ₁₀ Br ₂			(185)
2,3,7,10-Tetrabromo.....	C ₁₈ H ₈ Br ₄	>450		(5)
2-Fluoro-5,6,7,8,9,10,11,12-octahydro.....	C ₁₈ H ₁₉ F	146–147		(23)
Picrate.....		180		
<i>α</i> -Chloro-2,6,10-trimethyl.....	C ₂₁ H ₁₇ Cl			(185)
<i>α</i> -Bromo-2,6,10-trimethyl.....	C ₂₁ H ₁₇ Br			(185)
1,4,5,8-Bis(endodichloromethylene)-1,2,3,4,5,6,7,8-octachloro-1,4,5,8,15,16,17,18-octahydro.....	C ₂₀ H ₈ Cl ₁₂	210–211		(106)
Perchloro.....				(195, 196)
Perfluorochloro.....				(195, 196)

TABLE 3

Hydroxy-, methoxy-, amino-, and nitrotriphenylenes

Derivative	Molecular Formula	Melting Point	Other Data	References
		°C.		
2-Hydroxy.....	C ₁₈ H ₁₂ O	215–217	Ultraviolet	(16, 164, 186, 199)
Picrate.....		224–225		
Acetate.....		129		
1,2-Dihydroxy.....	C ₁₈ H ₁₂ O ₂	242–243	Ultraviolet	(199)
1-Methyl-1-hydroxy-1,2,3,4,9,10,11,12-octahydro.....	C ₁₉ H ₂₂ O	104–105		(8)
2,3-Dimethyl-1-hydroxy.....	C ₂₀ H ₁₆ O	167.5–168.5		(80)
Picrate.....		210.5–211.5		
Trinitrobenzene derivative.....		239–240		
1-Methoxy.....	C ₁₉ H ₁₄ O	172		(164)
Picrate.....		196–198		
2-Methoxy.....	C ₁₉ H ₁₄ O	97–98		(164)
1-Methoxy-5,6,7,8,9,10,11,12-octahydro.....	C ₁₉ H ₂₂ O	96–97		(164)
Picrate.....		204–205		
2-Methoxy-5,6,7,8,9,10,11,12-octahydro.....	C ₁₉ H ₂₂ O	120–121		(164)
Picrate.....		193–194		
1-Amino.....	C ₁₈ H ₁₃ N	103–104		(16, 23)
<i>N</i> -Acetyl.....		252		
Benzylidene derivative.....		140–140.5		
2-Amino.....	C ₁₈ H ₁₃ N	142–143		(16, 23)
<i>N</i> -Acetyl.....		260–261		
Methyl carbamate.....		188–189		
Benzyl carbamate.....		169–170		
1-Nitro.....	C ₁₈ H ₁₁ NO ₂	168.5–169.5	Ultraviolet	(16, 22, 23)
2-Nitro.....	C ₁₈ H ₁₁ NO ₂	165.5–166	Ultraviolet	(16, 22, 23)
<i>α</i> -Trinitro.....	C ₁₈ H ₉ N ₃ O ₆	335 (d.)		(130)

TABLE 4
Acyl- and ketotriphenylenes

Derivative	Molecular Formula	Melting Point	Other Data	References
		°C.		
2-Acetyl.....	C ₂₀ H ₁₄ O	152-153		(16, 45)
Oxime.....		202		
2,4-Dinitrophenylhydrazone.....		>325		
2-Propionyl.....	C ₂₁ H ₁₆ O	123		(45)
2-[9-(10-Methylphenanthroyl)].....	C ₃₃ H ₂₀ O			(58)
1-Keto-1,2,3,4-tetrahydro.....	C ₁₈ H ₁₄ O	101		(27, 81)
1-Keto-1,2,3,4,9,10,11,12-octahydro.....	C ₁₈ H ₁₈ O	121-122		(8)
1-Ketododecahydro.....	C ₁₈ H ₂₂ O	222-222.5		(10, 202)
1,4-Diketo-1,4,5,6,7,8,9,10,11,12,13,16,17,18-tetradeca-	C ₁₈ H ₂₂ O ₂	114		(18)
Diacetate.....		161		
1-Keto-1,2,3,4,5,6,7,8,9,10,11,12,13,16,17,18-hexadeca-	C ₁₈ H ₂₆ O	211-212	Boiling point, 150-158 °C./1 mm.	(141)
2,4-Dinitrophenylhydrazone.....				
2-Methyl-1-keto-1,2,3,4-tetrahydro.....	C ₁₉ H ₁₆ O	85-86.5		(81)
4-Methyl-1-keto-1,2,3,4-tetrahydro.....	C ₁₉ H ₁₆ O	99-100.5		(81)
1-Keto-9-methyl-1,2,3,4,9,10,11,12-octahydro.....	C ₁₉ H ₂₀ O	130-131		(7)
Oxime.....		173-175		
1-Keto-18-methyl-1,2,3,4,5,6,7,8,9,10,11,12,13,16,17,18-hexadeca-	C ₁₉ H ₂₆ O	162-165	Boiling point, 150-155 °C./1.5 mm.	(141)
2,4-Dinitrophenylhydrazone.....				
2,3-Dimethyl-1-keto-1,2,3,4-tetrahydro.....	C ₂₀ H ₁₈ O	132-138		(80)
2-Phenyl-1,4-diketo-1,4,5,6,7,8,9,10,11,12,13,16-dodeca-	C ₂₄ H ₂₄ O ₂	140-141		(208)
2-Phenyl-1,4-diketo-1,4,5,6,7,8,9,10,11,12,13,16,17,18-tetradeca-	C ₂₄ H ₂₆ O ₂	207-208		(208)
2-Benzoyl-1,4-diphenyl-1,4-endocarbonyl-1,4-dihydro.....	C ₃₈ H ₂₄ O ₂	312-315		(4)
2-Benzoyl-1,4-diphenyl-1,4-endocarbonyl-1,2,3,4-tetrahydro.....	C ₃₈ H ₂₆ O ₂	273		(4)

 TABLE 5
Triphenylenecarboxylic acids and derivatives

Derivative	Molecular Formula	Melting Point	References		
		°C.			
2-Carboxylic acid.....	C ₁₉ H ₁₂ O ₂	336-338	(16, 45, 61, 77, 185)		
Methyl ester.....		171-172			
Acid chloride.....		130-131			
Amide.....		292-293			
Azide.....		135			
1-(Anthraquinonyl)amide.....		277-278			
2-Acetic acid.....	C ₂₀ H ₁₄ O ₂		(45)		
2-(4-Butyric acid).....	C ₂₂ H ₁₈ O ₂	168	(45, 46)		
2-(4-Keto-4-butyric acid).....	C ₂₂ H ₁₆ O ₃	224	(45)		
1,3,4-Triphenyl 2-carboxylic acid.....	C ₂₇ H ₂₄ O ₂	314-315	(71)		
3-Hydroxy 2-carboxylic acid.....	C ₁₉ H ₁₂ O ₃	309-310	(78, 175, 176, 177, 187, 188)		
Anilide.....		269-270			
<i>o</i> -Toluidide.....		235-236			
<i>m</i> -Toluidide.....		235-237			
<i>p</i> -Toluidide.....		307-308			
<i>p</i> -Chloroanilide.....		308-309			
<i>o</i> -Aniside.....		236-237			
<i>p</i> -Aniside.....		272-273			
2,5-Dimethoxyanilide.....		232-234			
2-Naphthylamide.....		258-259			
2-Phthaloyl.....		C ₂₆ H ₁₆ O ₃		248-250	(54)
2,6-, 3,6- and 2,7-Diphthaloyl.....		C ₃₄ H ₂₀ O ₆		230-250	(55)
1,2,3,4-Tetrahydro 1,2-dicarboxylic acid.....		C ₂₀ H ₁₆ O ₄		218-220	(27)
1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,18-Hexadeca-		C ₂₀ H ₂₀ O ₃		150-151	(193)
hydro 1,2-dicarboxylic anhydride.....					
3-Methyl-1,2,3,4(or 1,2,3,18)-tetrahydro 1,2-dicarboxylic anhydride.....		C ₂₁ H ₁₆ O ₃		264	(24)
4-Methyl-1,2,3,4(or 1,2,3,18)-tetrahydro 1,2-dicarboxylic anhydride.....		C ₂₁ H ₁₆ O ₃		262	(27)
3-Phenyl-1,2,3,4(or 1,2,3,18)-tetrahydro 1,2-dicarboxylic anhydride.....	C ₂₆ H ₁₆ O ₃	249-250	(24)		
1-(9-Phenanthryl) 2,3-dicarboxylic anhydride.....	C ₃₄ H ₁₈ O ₃	325-327	(48)		
3-(9-Phenanthryl)-1,2,3,4(or 1,2,3,18)-tetrahydro 1,2-dicarboxylic anhydride.....	C ₃₄ H ₂₂ O ₃	310	(31a)		
1,4-Diphenyl 2,3-dicarboxylic acid.....	C ₃₂ H ₂₀ O ₄	330-335	(72, 168)		
Anhydride.....		348-350			
Anilide.....		358			
<i>p</i> -Toluidide.....		341			
<i>p</i> -Dimethylaminophenylimide.....		338			
4'-Aminobiphenylimide.....		360-361			
<i>o</i> -Phenylenediamine derivative.....		312			
1,8-Naphthalenediamine derivative.....	319				
1,4-Diphenyl-2,3-dihydro 2,3-dicarboxylic anhydride.....	C ₃₂ H ₂₀ O ₃	298-300	(72)		
1,4-Diphenyl-1,4-endocarbonyl-1,2,3,4-tetrahydro 2,3-dicarboxylic acid.....	C ₃₃ H ₂₂ O ₅	276-277	(72)		
Anhydride.....		286-287			
1,3,4-Triphenyl-1,4-endocarbonyl-1,4-dihydro 2-carboxylic acid (or hydroxy lactone).....	C ₃₈ H ₂₄ O ₃	206-212	(71)		

TABLE 6

Miscellaneous triphenylene derivatives

Derivative	Molecular Formula	Melting Point °C.	References
2-Sulfonic acid.....	C ₁₈ H ₁₂ O ₃ S		(16, 174, 186)
1,2-Quinone.....	C ₁₈ H ₁₀ O ₂	188-190	(199)
1-(2-Hydroxy)azobenzene-4-sulfonic acid.....	C ₂₄ H ₁₆ N ₂ O ₄ S	255-256	(199)
Other azo couples with 2-triphenylenol and its carboxylic acid.....			(187, 188)
2-(2-Indolyl).....	C ₂₆ H ₁₇ N	225	(45)
Picrate.....		227-228 (d.)	
1,4-Diphenyl-2,3-di(methylmercuri).....	C ₃₂ H ₂₄ Hg ₂	257-258	(1)
1,4-Diphenyl-2,3-di(ethylmercuri).....	C ₃₄ H ₂₈ Hg ₂	210-212	(1)
1,4-Diphenyl-2,3-di(phenylmercuri).....	C ₄₂ H ₂₈ Hg ₂	>400	(1)
1,1'-Bis(1,2,3,4-tetrahydro).....	C ₃₆ H ₃₀	300	(27)

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