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Advances in the Chemistry of Triptycene

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Information is presented on the preparation of triptycene, its homologues, and substituted derivatives. The spectroscopic, X-ray, optical, and other physical properties of these compounds are discussed. A systematic account is given of the behaviour of substituents located at a bridgehead, and of the differing reactivities of α- and β-positions in the aromatic rings on nucleophilic and electrophilic substitution. Reactions involving opening of the bridge system, the polarographic reduction of triptycenequinones, and the catalytic hydrogenation of triptycene are considered. The list of references contains 247 items.

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I. INTRODUCTION

Triptycene, which was first described in 1942,[1] has now become readily available thanks to the well known work of Wittig[2-9] on the preparation of dehydrobenzene and its interaction with anthracene.

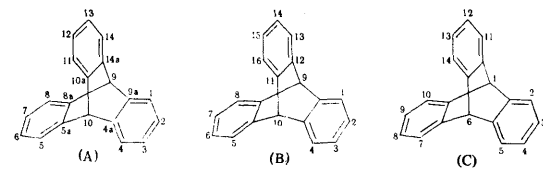
The specific properties of triptycene—the low mobility of bridge substituents, the difference in reactivity towards substitution between α- and β-positions in aromatic rings, steric peculiarities due to the rigidity of the molecule—attracted the attention of research workers. The large number of differently substituted isomeric compounds is due to the presence of three equivalent aromatic rings in the triptycene molecule. The bulky structure of the thermally stable triptycene suggests that certain polymers containing a triptycene fragment may possess valuable specific properties.

The chemistry of triptycene has been studied in comparative detail. A considerable quantity of interesting work of fundamental character has appeared during recent years, but only one review paper has hitherto been published on triptycene, which is small in scope and not readily accessible to a wide range of readers[10]. The present Review examines methods for constructing the triptycene system, together with the reactivity, spectral characteristics, and certain physicochemical properties of compounds of this series.

II. CONSTRUCTION OF TRIPTYCENE SYSTEM

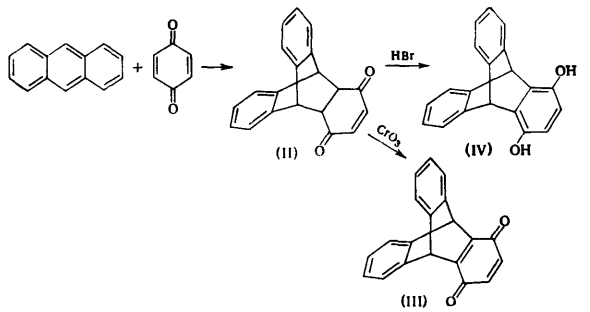
The most general method for building up the polycyclic triptycene system—9,10-*o*-benzo-9,10-dihydroanthracene† (I)—is diene synthesis between anthracene or a substituted derivative and a sufficiently active six-membered carbocyclic dienophile. Thus Clar[14] was the first to isolate the adduct (II) of anthracene with *p*-benzoquinone,

† A nomenclature which regards triptycene as a derivative of dihydroanthracene is now generally accepted[11,12], with the carbon atoms numbered as in (A) (used in the present Review) or (B):

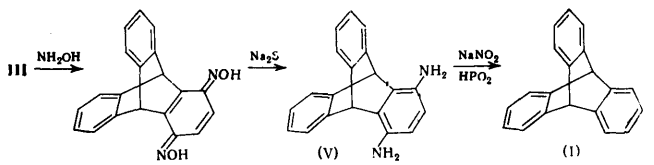


In some publications triptycene compounds have been regarded as substituted bicyclo[2,2,2]octanes, with the carbon atoms numbered as in (C).[1,13]

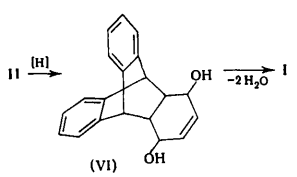
which he converted into triptycene derivatives—triptycenequinone (III) and triptycenequinol (IV):



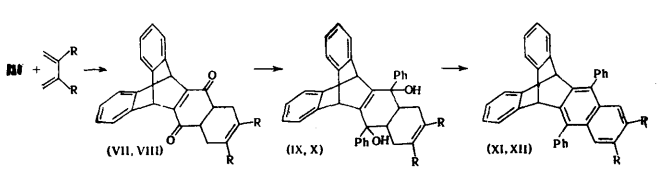
from which, however, he was unable to obtain triptycene. Bartlett et al.[1,15] extended Clar's scheme, and were the first to accomplish the multistage synthesis of triptycene:

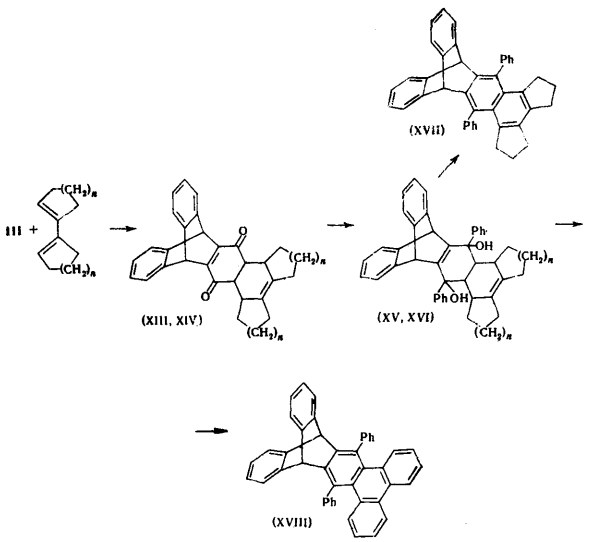


Triptycene was obtained also by dehydration of the dion (VI) (by boiling with alcoholic hydrogen chloride[16] or with a mixture of phosphorus trichloride and phosphoryl chloride), which is readily formed by direct reduction of the adduct (II) with lithium tetrahydroaluminate[16] or with aluminium isopropoxide in propan-2-ol:[11]

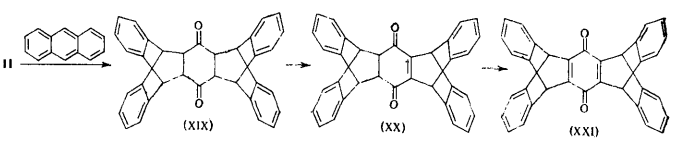


Triptycenequinone (III), which was used by Bartlett in the preparation of triptycene (I),[1,15] later served as the starting compound for the synthesis of several more complicated structures containing a triptycene fragment. Thus a detailed study was made of the dienophilic reactivity of triptycenequinone (III) with aliphatic dienes (butadiene, 2,3-dimethylbutadiene) and bicyclic dienes (1,1′-bicyclohexenyl, 1,1′-bicyclopentenyl) (an adduct of triptycenequinone (III) with acecyclone had been described earlier)[17]. The action of phenyl-lithium on the adducts obtained (VII, VIII, XIII, XIV) gave the corresponding diols (IX, X, XV, XVI), whose dehydration produced quantitative yields of 5,12-diphenyltetrahydro-6,11-benzonaphthacenes, which on subsequent dehydrogenation are converted into hydrocarbons of complicated structure—1,4-diphenyl-2,3-benzotriptycenes (XI, XII, XVII, XVIII):[18-20]



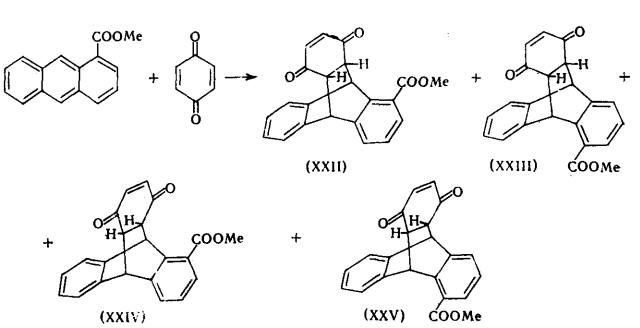


Other dienophiles which have been made to react with anthracene are derivatives of *p*-benzoquinone[21-27] and 1,4-naphthaquinone[28-31], 1,4-anthraquinone[32], quinones of the triptycene series[33-35] and bicyclo[2,2,1]heptadiene-2,3-dicarboxylic anhydride[36], but no attempts were made to obtain from these adducts the corresponding hydrocarbons having a triptycene structure. Depending on the conditions the reaction between anthracene and *p*-benzoquinone yields not only the adduct (II) but also other compounds. Thus with excess of anthracene the double adduct (XIX) is formed; at 140–165°C this is dehydrogenated first to the diketone (XX), and at 165°C to the quinone (XXI):[11]

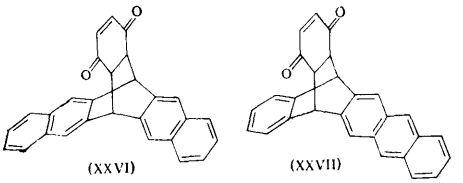


In the presence of aluminium chloride the adduct (II) is formed in high yield even at room temperature, and with excess of anthracene the double adduct (XIX).[37]

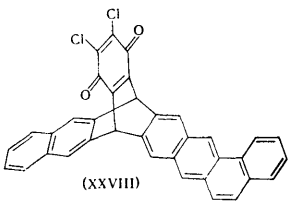
With substituted anthracenes *p*-benzoquinone forms isomeric compounds. Thus with methyl 1-anthroate adducts of *exo*- and *endo*-configuration are obtained, each of which in turn is a racemic mixture of stereoisomers (XXII–XXV):[13]



Other acenes react similarly to anthracene with *p*-benzoquinone. Thus pentacene undergoes diene synthesis with the formation of two adducts, of symmetrical (XXVI) and unsymmetrical (XXVII) structure[38].



(XXVI) (XXVII)

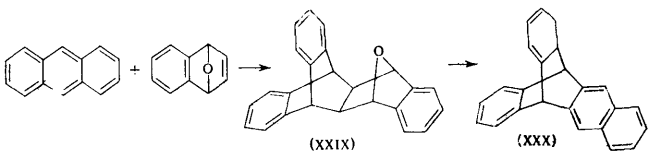


(XXVIII)

Pentacene reacts similarly with chloranil[14], and the latter has been reported to react with 7,14-dihydro-1,2-benzohexacene to yield the adduct (XXVIII).[39]

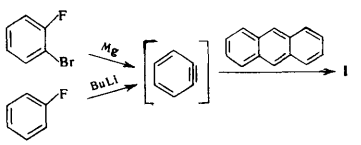
Hydrocarbons having a partly hydrogenated triptycene structure are obtained by diene synthesis between anthracene and cyclohexene[40], 1,4-dihydronaphthalene[28], 1,4-dihydro-1,4-methanonaphthalene[41], and bicyclo[2,2,1]-heptadiene[42,43].

An original route to 2,3-benzotriptycene (XXX) was suggested by Wittig et al.[41], who applied the Diels–Alder reaction to anthracene and 1,4-epoxy-1,4-dihydronaphthalene (in turn obtained by diene synthesis from furan and dehydrobenzene), and heated the resulting adduct (XXIX) in acetic acid[44]:



(XXIX) (XXX)

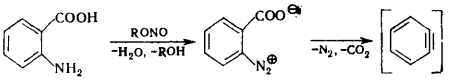
The direct method of preparing triptycene by diene synthesis from anthracene and dehydrobenzene, proposed by Wittig in 1956,[2] is at present time the simplest and the most convenient. Its development has made triptycene readily available as a subject for many interesting investigations. Various processes have been described for generating dehydrobenzene from numerous monosubstituted and *ortho*-disubstituted benzene derivatives‡, as well as procedures for conducting the diene synthesis. Triptycene is obtained in various yields depending on the method of producing dehydrobenzene and on the conditions of its reaction with anthracene. Thus Wittig et al. obtained a 30% yield by the action of magnesium on *o*-bromofluorobenzene (in oxolan or ether) in the presence of anthracene[2,3,6]; reaction of anthracene with dehydrobenzene generated by treating fluorobenzene with *n*-butyllithium in oxolan gave only a 10% yield of triptycene[5]:



‡ A special monograph[45] was devoted to dehydrobenzene and arynes.

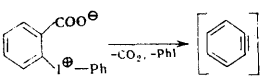
Triptycene has been obtained also from dehydrobenzene generated from fluorobenzene by the action of lithium hexaphenylantimonate[7], from halogenobenzenes by the action of potassium t-butoxide[46,47], by the decomposition of *N*-nitrosoacetanilides[47-52], by the oxidation of 1-aminobenzotriazole[53], by the decomposition of *N*-*o*-carboxyphenyl-*N'*-toluene-*p*-sulphonyldi-imide *N*-oxide[54], by heating benzo-1,2,2-thiadiazole dioxide in oxolan[8,9], and by decomposing *o*-diiodobenzene with zinc in the gas phase (at 550°C).[55]

The most convenient mode of generating dehydrobenzene for the preparation of triptycene is to decompose *o*-diazonium benzoate (a betaine obtained by diazotising anthranilic acid) by heating in an aprotic solvent[56,57]:



In the improved method of Friedman and Logullo[58,59] anthranilic acid dissolved in acetone (oxolan, butan-2-one, or diglyme) is added to a boiling solution of anthracene and pentyl (or butyl) nitrite in dichloromethane (chloroform or 1,2-dichloroethane). The yield of triptycene is 50–60%, but with simultaneous mixing of the reactants it sometimes falls to 10%; use of a molar excess of anthracene or anthranilic acid tends to raise the yield to 70–80%. With difficulty accessible substituted anthracenes it is sometimes better to use a modified method involving intermediate isolation of *o*-diazonium benzoate[60]. Dioxan[61] and *p*-xylene[62] have also been used as high-boiling solvents in the preparation of substituted triptycenes.

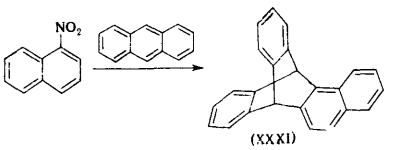
The use in certain cases of dehydrobenzene formed by the decomposition of iodonium *o*-benzoate (in boiling diglyme[63] or triglyme[64], sometimes in the presence of catalytic additions of iodine or copper sulphate or acetate[65])



has no significant advantages over the above method[58,59].

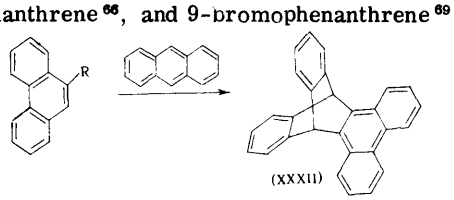
Not only dehydrobenzene and its substituted derivatives but also other arynes—2,3-dehydronaphthalene[58], 9,10-dehydrophenanthrene[66], 2,3-dehydro-9,10-anthraquinone[67], and dehydro[2,2]paracyclophane[68]—have been used in diene syntheses with anthracene.

Many reactions yielding benzotriptycenes (XXX–XXXII) also involve the intermediate formation of arynes—e.g. the reaction of anthracene (at 300°C) with 1-nitronaphthalene[28]



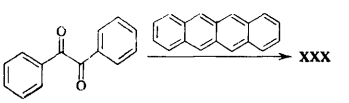
(XXXI)

9-nitrophenanthrene[66], and 9-bromophenanthrene[69]

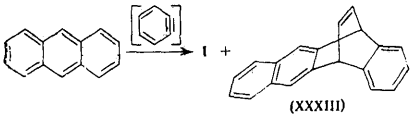


(XXXII)

and the pyrolysis of benzil in the presence of naphthacene[70].

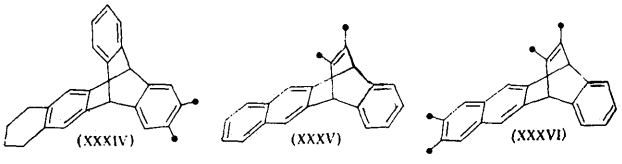


Dehydrobenzene adds to anthracene not only at the *meso*(9,10)-positions but also partly at the 1,4-positions, so that triptycene is accompanied by traces of 5,12-dihydro-5,12-ethenonaphthacene (XXXIII):[71]



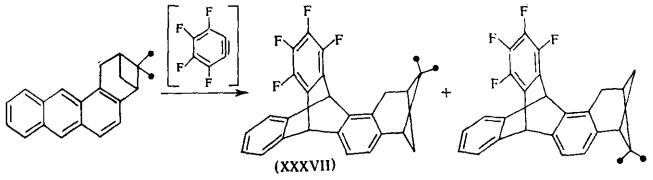
(XXXIII)

Substituted anthracenes react similarly, with the nature of the substituents and their positions in the anthracene molecule determining the proportions of isomeric adducts formed. Electron-accepting or sufficiently bulky substituents diminish appreciably the diene activity of the anthracene system towards dehydrobenzene and orient its addition predominantly to the unsubstituted rings[53,72]. Thus the presence of two *meso*-nitrile groups deactivates both the middle and the outer rings, so that isomeric adducts are obtained in equal quantities but with a very low total yield (4%).[71] The activity of 9,10-diphenylanthracene is only 20% of that of anthracene, while the ratio of products of addition at positions 9,10 and 1,4 falls to 8%.[53] Electron-donating substituents direct the addition of dehydrobenzene predominantly to the substituted ring, at the same time increasing the diene activity of the anthracene system[72]. Depending on the structure of the initial methylanthracenes the addition of dehydrobenzene takes place either solely at the 9,10-positions with formation of a triptycene compound (XXXIV from 1,2,3,4-tetrahydro-8,9-dimethylnaphthacene) or also at the 1,4-positions with the formation of substituted ethenonaphthacenes (XXXV and XXXVI from 2,3-di- and 2,3,6,7-tetra-methylanthracenes).



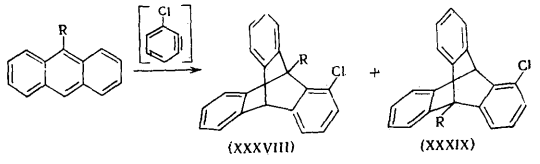
(XXXIV) (XXXV) (XXXVI)

Reaction between dehydrotetrafluorobenzene[74] and 1,2,3,4-tetrahydro-3,3-dimethyl-2,4-methanobenz[*a*]-anthracene yields a mixture of two isomeric compounds:



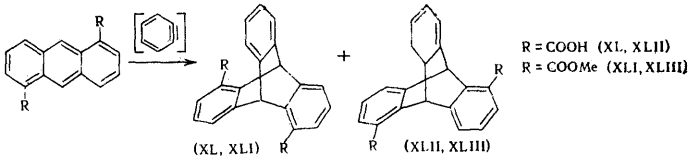
(XXXVII)

where the products (XXXVII) of addition on the sterically most hindered side of the initial anthracene molecule predominates[75]. Several substituted anthracenes form mixtures of *quasi-cis*- and *quasi-trans*-isomers (XXXVIII and XXXIX) by diene synthesis with substituted dehydrobenzenes:



(XXXVIII) (XXXIX)

The reactions of 9-substituted anthracenes with 3-chloro-dehydrobenzene show that the ratio of the isomers formed depends mainly on the inductive effect of the substituent R, not on its size[76]. Anthracene derivatives substituted in the outer rings give with dehydrobenzene racemic mixtures of optical enantiomers. Thus stereoisomeric disubstituted triptycenes (XL–XLIII) have been obtained from 1,5-disubstituted anthracenes[77]:

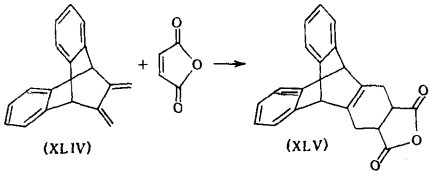


R = COOH (XL, XLII)
R = COOMe (XLI, XLIII)

(XL, XLI) (XLII, XLIII)

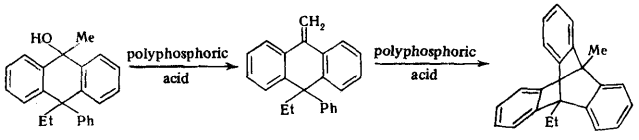
Other reactions of substituted dehydrobenzenes with substituted anthracenes have also been reported[78–80].

A specific method for building a partly hydrogenated triptycene system by diene synthesis is the action of maleic anhydride on the compound (XLIV), which gives 1,2,3,4-tetrahydrotriptycene-2,3-dicarboxylic anhydride (XLV):[81]



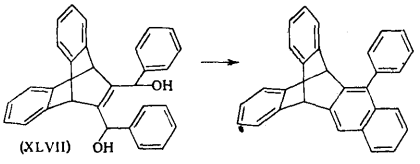
(XLIV) (XLV)

Cyclisation has been used to synthesise certain substituted triptycenes. For example, 9-ethyl-10-methyl-triptycene (XLVI) was obtained in theoretical yield by the action of polyphosphoric acid on 10-ethyl-9,10-dihydro-9-methyl-10-phenyl-9-anthrol:[82]



(XLVI)

1-Phenyl-2,3-benzotriptycene has been obtained by the cyclodehydration of (XLVII):[44]



(XLVII)

III. STRUCTURE AND PHYSICAL PROPERTIES OF TRIPTYCENE COMPOUNDS

Triptycene is a colourless substance, melting at 254.03°C when 99.999 mole % pure and readily soluble in the usual organic solvents[83]. It crystallises in the orthorhombic system with a unit cell belonging to the $P2_12_12_1$ space group and having the parameters 0.822, 2.064, and 0.816 nm, number of formula units $z = 4$, and volume 1.384 nm^3; the crystallographic density is 1.227 g cm^{-3}, and the symmetry of the molecule $\bar{6}m2$.[84,85]

Changes in the enthalpy of triptycene correspond to the integral of heat capacity with respect to temperature between 429° and 519°K, and the temperature dependence of heat obeys Debye's law. The large difference in heat

capacity between solid and liquid triptycene (11.48 cal deg^{-1} $mole^{-1}$) indicates strong bonding of the molecules in the crystal lattice; movement of the molecules is restricted at temperatures somewhat above the melting point. The heat capacity of triptycene is well approximated by that of a model in which three benzene rings are superposed on bicyclo[2,2,2]octane.[83]

The highly symmetrical structure of the triptycene molecule is confirmed by infrared, ultraviolet, and proton magnetic resonance spectroscopy. The infrared spectrum is characterised by absorption bands having wavenumbers (νmax, cm^{-1}) of 3040 (stretching vibrations of aromatic carbon–hydrogen bonds), 2960 (aliphatic carbon–hydrogen bonds of bridging methine groups), 1470 to 1450 (aromatic carbon–carbon bonds), and 755–740 (deformation vibrations of carbon–hydrogen bonds in *ortho*-disubstituted benzenes)[65,86,87]. The ultraviolet spectra of triptycene and its 9,10-substituted derivatives are characterised by bands having λmax (in nm) (and $\lg\epsilon$)—263 (3.25), 271 (3.56), and 278 (3.66)[87-92]—and can be interpreted[89] by the superposition of three benzene chromophores, which is supported by calculation of the intensities of the bands of longest wavelength for several chlorinated triptycenes[76] and benzo-derivatives[67]. The ultraviolet spectra reveal only an inductive effect of substituents in the bridges, since their conjugation with the aromatic rings is impossible[87].

The ^{1}H n.m.r. spectrum of triptycene contains a multiplet of aromatic protons (with its centre δ = 7.05 ppm) and a singlet of bridge protons (δ = 5.21 ppm).[93,94] The measured transition frequencies in the multiplet agree well with those calculated for the four-spin system AA'BB'.[93,95] A certain broadening of the AA' part of the spectrum is due to interaction between α-protons and bridge protons[95].

The ^{1}H n.m.r. spectra of triptycenes substituted in an aromatic ring differ markedly depending on the position of the substituent. Thus β-substituents have almost the same effect on the chemical shifts of the two bridge protons, since their signals appear in the spectrum as one singlet. Probably the only exception is provided by the nitro-group: the signal due to one bridge proton in 2-nitrotriptycene is displaced 3 Hz from that due to the other[96], and with 2,7-dinitrotriptycene the separation is 5 Hz.[97] The ^{1}H n.m.r. spectra of α-monosubstituted triptycenes always contain two singlets due to the bridge protons (because of the non-equivalence of the latter relative to the α-substituent)[44]. Analysis of the spectra has shown that the signal due to the bridge proton adjacent to the substituent is usually displaced down-field[44,62,76,96,98].

In the series—1-chloro-, 1,8-dichloro-, and 1,8,14-trichloro-triptycenes—the average increase in the difference between the chemical shifts of the signals due to the bridge protons is 0.43 ppm. This quantity is the sum of the contributions by magnetic anisotropy, the electrical field, and the van der Waals effect, among which the field effect makes the main contribution (0.29 ppm).[76] Triptycene derivatives are thus convenient compounds for the study of magnetic anisotropy[76].

In 1,4-diphenyltriptycene steric factors hinder a coplanar arrangement of the phenyl substituents, which is also apparent in their spectra[98].

The isomeric vinyltriptycenes have been the simplest convenient models for studying several structural features of differently substituted unsaturated triptycene derivatives. Thus the ^{1}H n.m.r. spectra indicate that the protons of a 2-vinyl group in triptycene are less shielded than are those of a vinyl group in position 1 and of course 9. The coplanarity of vinyl group and benzene ring in 1- and 2-vinyltriptycenes is confirmed by an analysis of spectroscopic results (ultraviolet and n.m.r.).[99]

The structure of triptycene has been reliably confirmed by X-ray diffraction[84,85,100-102]. The molecule possesses a threefold axis of symmetry and a plane of symmetry perpendicular to this axis. The aliphatic carbon–carbon bonds in the bicyclo[2,2,2]octane system and also the carbon–carbon bonds in the aromatic rings have the normal length, but the $C_{(4a)}-C_{(9a)}$ bond, which is common to the bicyclic system, is somewhat elongated. The presence of a strained bicyclic system is evident also in the variation in the bond angles. Thus the angles between the aliphatic carbon–carbon bonds are 105° (instead of 109°47′), and those between aliphatic and aromatic carbon–carbon bonds common to the bicyclic system are 113° (instead of the usual 120°). The distortion of the angles produces corresponding changes in hybridisation of the orbitals bonding atoms of the bicyclic system and the neighbouring atoms of the aromatic rings.

Certain distortions are observed in triptycene derivatives with substituents at positions 9 and 10. Thus internuclear distances are somewhat increased for atoms in the vicinity of the bridge substituents in 9-bromotriptycene[100] and 9-2′-chloroethyltriptycene[101]; the angles between the aliphatic carbon–carbon bonds in the former molecule are 107°. Rotation of the chloroethyl group in the latter molecule is retarded by the spatial proximity of α-hydrogen atoms of the aromatic rings, which in turn causes a general distortion of structure and non-equivalence of the aromatic rings[101]. Retarded rotation of a chloromethyl group attached to a bridging carbon atom is also definitely revealed in the ^{1}H n.m.r. spectra of 9-chloromethyl- and 9,10-bischloromethyl-triptycenes. The activation energy of rotation of such a chloromethyl group determined from the spectroscopic results (~16 kcal $mole^{-1}$) was about treble that for an ordinary σ-bond.[103]

The ^{1}H n.m.r. spectra of several other 9-substituted triptycenes have been studied[104]. The spectrum of the adduct of *p*-benzoquinone with 9,10-di-t-butylanthracene reveals the methyl protons as three separate singlets[105]. Stable rotational isomers may be formed in the presence of sufficiently bulky bridge substituents. Thus two conformers have been isolated and characterised in the reaction of dehydrobenzene with anthracene-9,10-bis-$\alpha\alpha$-dimethylacetonitrile; their equilibrium interconversion occurs at 200°C.[106]

Certain features of the chemical behaviour of 9-substituted triptycenes are due to the steric hindrance of substituents in this position. Examples are the stability of triptycen-9-yl iodoformate, the impossibility of obtaining ditriptycen-9-yl oxalate, the low reactivity of triptycen-9-ol towards alkali metals[107], and the difficulty of the formation of 9,9′-bitriptycenyl[15] (although ditriptycen-9-ylmercury has been obtained in good yield by the mercuration of triptycen-9-yl-lithium[108]). The low yield of α-nitrotriptycene obtained by the nitration of triptycene has been attributed[97] to steric hindrance of the α-positions in the aromatic rings. The difficulty of the solvolysis of compounds containing halogenomethyl bridge groups is also explained by peculiarities of the three-dimensional structure of the triptycene system[109,110].

The mass spectra of triptycene have been discussed in several papers[111-113], but the interpretation of the experimental results is ambiguous.

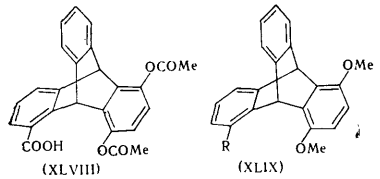
Studies have been made also of the electron spin resonance spectra of triptycene[12,114-121], its substituted derivatives[121-125], and semiquinones[126-130]. The absence

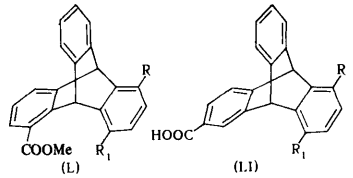
of fine structure from the e.s.r. spectrum in the last case indicates that the bridge carbon atoms completely interrupt conjugation of electrons between the benzene rings and the quinonoid portion of the molecule [129].

The hypothesis that transannular interactions may occur between the aromatic rings in the triptycene molecule, which appeared in several publications [88,95,98], was not subsequently confirmed [67,97,131].

Thus the factors responsible for the peculiarities of chemical behaviour are probably the strain in the bicyclic structural fragment and the three-dimensional structure of the triptycene system.

The molecule of a substituted triptycene having three non-equivalent rings is chiral, which leads to the appearance of optical isomers. Such a system is an ideal model for studying the effect of substituents on optical activity, since the rigid structure of the molecule excludes the possibility of interaction between its various parts, and conversions can be accomplished without racemisation or inversion of configuration [13].



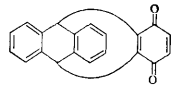
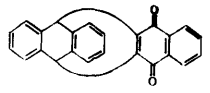
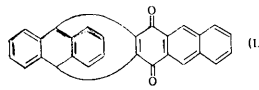
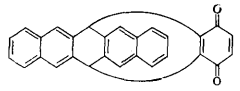
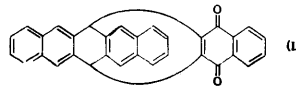
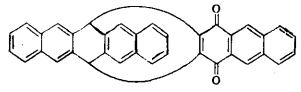
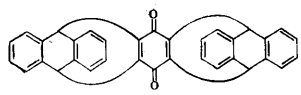
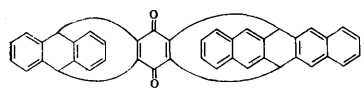


Optical activity in the triptycene series was first shown for 5,8-diacetoxytriptycene-1-carboxylic acid (XLVIII), obtained by conversion of the isomeric compounds (XXII–XXV) and resolved into enantiomers [13]. A series of 5-substituted (+)-1,4-dimethoxytriptycenes (XLIX) were obtained [77,132–134] from (+)-(XLVIII), and from these the the absolute configuration 9*R*, 10*S* was established for (+)-5-*NN*-dimethylamino-1,4-dimethoxytriptycene hydrobromide [XLIX: R = $N(CH_3)_2$.HBr] by X-ray structural analysis by Bijvoet's method [102]. This configuration is possessed by other members of the (XLIX) series, as well as by 5,8-disubstituted methyl triptycene-1-carboxylates (L), [135] for which the optical rotatory dispersion was also studied [132]. The structure of the isomeric methyl 5-hydroxy-8-methoxy- and 8-hydroxy-5-methoxytriptycene-1-carboxylates was established from the measured dipole moments [136]; in the latter ester infrared spectroscopy reveals an intramolecular hydrogen bond between the spatially contiguous methoxycarbonyl and hydroxyl groups.

Other optically active triptycene derivatives have been obtained from enantiomeric 5- and 8-substituted triptycene-1-carboxylic acids [137]. The absolute configuration of the chiral centres (9*R*, 10*R*) has been determined by chemical correlation with (+)-(XLIX) in (+)-5-methoxytriptycene-1-carboxylic acid, and confirmed by comparison of the circular dichroic spectrum with that of (+)-methyl 5-acetoxy-8-methoxytriptycene-1-carboxylate (L). The absolute configuration of (−)-5-methoxytriptycene-1-carboxylic acid (9*S*, 10*S*) was established by X-ray structural analysis and chemical correlation; the configuration of (+)-5-chlorotriptycene-1-carboxylic acid was also determined. The chiral 5,8-disubstituted triptycene-2-carboxylic acids (LI) and esters have been studied; the absolute configuration (9*R*, 10*S*) has been determined by chemical correlation for the dextrorotatory enantiomers [138]. Chiral 1,5- and 1,8-disubstituted triptycenes have also been obtained. Chemical correlation has established the absolute configuration 9*R*, 10*R* for the dextrorotatory enantiomer of 8-methoxytriptycene-1-carboxylic acid, and the inverse configuration for the laevorotatory enantiomer [77,139].

Determination of the absolute configuration of 1,5-disubstituted triptycenes by means of circular dichroism gave results [140] directly opposite to those obtained earlier by X-ray and chemical methods. However, these conclusions [140] were revised a little later [141].

Polorgraphic characteristics of quinones of the triptycene series (in 0.1 *N* KNO_3 in dimethylformamide).

Quinone	First wave K'	First wave $-E'_{1/2}$, mV	Second wave K''	Second wave $-E''_{1/2}$, mV	$\overline{E}_1$, mV	E^0, mV	$\lg K_{sq}$
 (III)	1.55	644	1.34	1248	946	666	10.237
 (LII)	1.62	877	1.33	1473	1175	437	10.169
 (LIII)	1.53	944	1.28	1400	1172	440	7.728
 (LIV)	1.09	673	1.14	1280	977	635	10.305
 (LV)	1.11	806	0.92	1352	1079	533	9.254
 (LVI)	1.06	819	0.91	1350	1085	527	8.983
 (XXI)	1.57	665	1.56	1342	1004	608	11.592
 (LVII)	1.42	633	1.31	1260	947	667	10.644

A study has been made of the polarographic reduction of triptycenequinone (III) and benzotriptycenequinones (XXI and LII–LVII) containing different numbers of annelated benzene rings in the quinonoid and triptycene moieties [32,34,142–148]. Quinones are characterised by two one-electron polarographic waves on reduction in dimethylformamide. Reduction occurs reversibly, with

intermediate formation of the semiquinone to yield the dianion of the quinol (or the quinol itself at sufficient hydrogen-ion concentrations):

$$Q + e^- \underset{}{\overset{K_{sqn}}{\rightleftarrows}} S; \quad S + e^- \rightleftarrows Q^{-2} .$$

The Table[148] illustrates the effect of annelation on the redox potentials of the quinones E°, the constants of the diffusion currents K, the half-wave potentials, and the effective formation constants of the semiquinone

$$K_{sqn} = \left[10^{\frac{0.5(E'_{1/2} - E''_{1/2})F}{RT}} - 3 \cdot 10^{-\frac{0.5(E'_{1/2} - E''_{1/2})F}{RT}} \right]^2,$$

where $E'_{1/2}$ and $E''_{1/2}$ are the first and second half-wave potentials. The constant of the diffusion current seemed to vary little for the triptycenequinones (III, LII, LIII) and also for the dibenzotriptycenequinones (LIV–LVI). The ratio of these constants K''/K' is about 0.85 for all quinones, indicating partial protonation of the semiquinone, which is further reduced at the same potential. On annelation in the quinonoid part of the molecule the negative potentials $E'_{1/2}$ and $E''_{1/2}$ increase in all these compounds, while K_{sqn} decreases and reduction is hindered only at the first stage. Annelation in the hydrocarbon part of the quinone molecules produces negative shifts in $E'_{1/2}$, $E''_{1/2}$, and $1/2(E'_{1/2} - E''_{1/2})$, accompanied by increase in K_{sqn} and in the hindrance to catalytic hydrogenation (cf. quinones III and LIV). With the quinones (LII) and (LV), as well as with (LIII) and (LVI), annelation displaces $E'_{1/2}$ and $E''_{1/2}$ to more positive potentials; the former pair of quinones show a decrease in K_{sqn} with increase in annelation, whereas the latter pair shown an increase. With the quinones (XXI) and (LVII) annelation makes the half-wave potentials more positive and diminishes both the constant of the diffusion current and K_{sqn}: i.e. in this case reduction occurs more easily as the structure becomes more complicated. Comparison of quinones (III) and (XXI), however, shows that reduction becomes more difficult with complication of the structure. This effect is almost completely absent with the quinones (III) and (LVII).

IV. REACTIVITY OF BRIDGE ATOMS

The early work on the chemistry of triptycene showed that the halogen at the bridgehead in 9-halogenated triptycenes is inert towards various nucleophilic reagents. Thus Bartlett and his coworkers were unable to make 9-bromotriptycene[88,149] or 9-iodotriptycene[15] react with sodium ethoxide, tin(II) chloride, sodium sulphide, or silver nitrite even under severe conditions. Nucleophilic substitution at a bridging carbon atom in the triptycene molecule is difficult for structural reasons. Reactions having an S_N1 mechanism are improbable, since intermediate formation of a carbonium cation would have required transition of the bridging carbon to an sp^2-hybridised state and a coplanar arrangement of the aliphatic carbon–carbon bonds§ in the already strained bicyclic fragment of triptycene; furthermore, such a carbonium ion could not have been stabilised by conjugation with the aromatic rings but, on the contrary, would have been destabilised by the negative inductive effect of the three *o*-phenylene substituents[88,152]. An unsuccessful attempt to generate a bridging carbonium ion from triptycen-9-yl iodoformate by the action of silver tetrafluoroborate has been reported[107]: only triptycen-9-yl fluoroformate was isolated from the reaction products.

Reactions occurring by an S_N2 mechanism are also impossible, since carbon atoms at a bridgehead are shielded from attack by nucleophilic reagents[88,152]. This confirmed the S_N2 rule, according to which substitution by an S_N2 mechanism always involves inversion of configuration[153].

As already remarked above[84–86], distortion of the tetrahedral angle at a bridging carbon atom in the triptycene molecule produces a change in hybridisation of the corresponding orbitals, and the carbon–carbon bonds acquire a greater p-character, while the bridge carbon–hydrogen bond is enriched with the s-component, approximating in character to bonds having sp^2-hybridisation of the carbon orbitals. This is accompanied by an increase in electronegativity of the bridging carbon atom, while the hydrogen atom becomes the positive pole of the dipole of the carbon–hydrogen bond, thereby becoming more acidic (in comparison with the methine hydrogen atoms in alkanes[86]). These structural peculiarities of triptycene find confirmation in its infrared spectrum[86,87]: the frequency of the absorption band due to the bridge carbon–hydrogen bond approaches that of a carbon–hydrogen bond in an alkene (3000 cm^{-1}). X-Ray examination shows that the bridge carbon atom has $sp^{2.26}$-hybridisation (the $J_{^{13}C-H}$ interaction constant gives $sp^{2.45}$-hybridisation). The smaller hybridisation calculated from crystallographic data was attributed[154] to curvature of the aliphatic carbon–carbon bonds in the triptycene molecule.

Nevertheless, halogenated triptycenes react with organometallic compounds under conditions under which nucleophilic attack at a bridging carbon atom is impossible. For example, 9-bromotriptycene reacts with n-butyllithium to give triptycen-9-yl-lithium[4,108,155]; 9-bromo- and 9,10-dibromo-2,3-benzotriptycenes react similarly[41]. The transition state leading to triptycen-9-yl-lithium may be four-membered with little carbanion character, and the lithium compound itself largely covalent[152]. Triptycen-9-yl-lithium undergoes substitution with intermediate formation of a carbanion bridge, and reacts in the usual way with carbon dioxide, benzophenone, triphenylboron, benzenediazonium tetrafluoroborate, mercury(II) chloride, and selenium chloride; it can be hydrolysed to triptycene[108].

Formation of a tetrahedral carbanion bridge, in contrast to a carbonium ion bridge, does not obstruct the structural peculiarities of the triptycene molecule. The straining of the bond angles at the carbon bridge should destabilise the carbanion, but this effect may be balanced by increase in the electronegativity of the bridging carbon atom. The stability of the carbanions would also be increased by the $-I$ effect of the three *o*-phenylene groups (although stabilisation by conjugation is excluded).

The comparatively ready formation of a bridging carbanion in triptycene is confirmed by a study of the kinetic acidity of the attached hydrogen atom[154,156]. Triptycene is similar to aromatic hydrocarbons in its ability to split off a bridge proton: the acidity of the hydrogen atom is closely similar to that of an *o*-hydrogen in toluene, and

§ The adamantyl cation with a tertiary carbonium atom at the bridgehead, for which a planar configuration is also impossible because of the three-dimensional structure, nevertheless is formed and exists in SbF_5-SO_2 solution[150]. In this case stabilisation is attributed to polarisation of the electrons of the carbon–hydrogen bonds of the tertiary carbon atoms (at positions 3, 5, and 7), which are attracted to the cationoid centre inside the adamantane skeleton[151].

far higher than in cyclohexane. According to Streitwieser and Ziegler [154] the enhanced acidity of the bridge hydrogen in triptycene is two-thirds due to the $-I$ effect of the three o-phenylene groups and only one-third due to strengthening of the s-character of the bridge carbon–hydrogen bond. This conclusion is consistent with the kinetic acidities of the bridge hydrogen atoms in triptycene and in 2,3-benzotriptycene [157]. Furthermore, the acidity of the 9-hydrogen atom in 2-methyltriptycene, in which the bicyclic part of the molecule has remained unchanged, is one-half, and that of the 10-hydrogen one-third, of the acidity of the hydrogen atoms in triptycene [154].

9-Bromotriptycene reacts with magnesium in ether [88] or oxolan [158], but the triptycen-9-ylmagnesium bromide formed, which can be hydrolysed to triptycene, cannot be carbonylated [88]. 9-Bromotriptycene is unaffected by sodium in boiling toluene, but reacts with the metal when heated in mineral oil to 140°C (even in an atmosphere of carbon dioxide), being converted almost quantitatively into triptycene [88]. This reaction probably involves intermediate formation of the triptycen-9-yl radical.

Barlett et al. showed [15] that the thermal decomposition of triptycen-9-ylcarbonyl peroxide was about two-thirds due to homolytic rupture of the oxygen–oxygen bond. Free-radical breakdown was accompanied by inversion of the carboxyl, yielding on subsequent hydrolysis triptycen-9-ol and triptycene-9-carboxylic acid:

$$\mathrm{Tr{-}COO{-}OOC{-}Tr \rightarrow 2\,Tr{-}COO\cdot;\ Tr{-}COO\cdot \rightarrow Tr\cdot + CO_2;}$$

$$\mathrm{2\,Tr\cdot \rightarrow Tr{-}Tr;\ Tr\cdot + C_6H_6 \rightarrow TrH + Ph\cdot;\ 2\,Ph\cdot \rightarrow Ph{-}Ph;}$$

$$\mathrm{Tr{-}CO{-}O{-}O{-}CO{-}Tr \rightarrow Tr{-}CO{-}O{-}CO{-}O{-}Tr \rightarrow TrOH + TrCOOH + CO_2.}$$

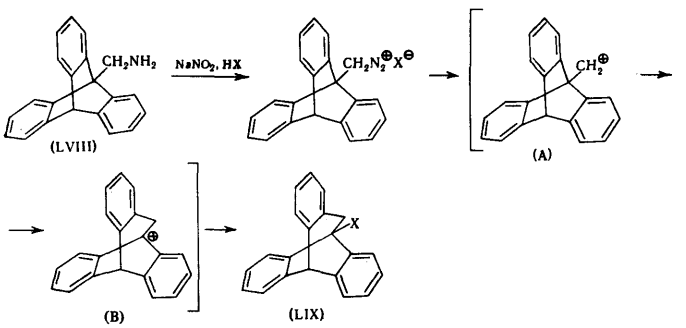
The free radical formed by decomposition of the peroxide possessed great affinity for hydrogen and iodine. The formation of triptycene in the reactions of triptycen-9-yllithium with halides of transition metals (silver, copper, cobalt, nickel) and of 9-bromotriptycene with metallic silver probably involves the triptycen-9-yl radical as an intermediate stage [108]. A small yield of a substance of high melting point, regarded as 9,9′-bitriptycenyl in view of its infrared spectrum, was isolated on decomposition of the peroxide. (9,9′-Bitriptycenyl obtained by addition of dehydrobenzene to 9,9′-bianthryl melted at 577°C and had a similar infrared spectrum [159].) In other reactions in which the radical occurred as an intermediate stage formation of a dimer was not observed (e.g. in the decomposition of ditriptycen-9-ylmercury of ditriptycen-9-yl diselenide in the presence of metallic silver or copper) [108].

Thermal decomposition of t-butyl triptycene-9-peroxycarboxylate gave triptycene in the high yield of 92%, attributable to the fact that the t-butyl groups in the original ester and in the decomposition products of the t-butoxyl radical are active donors of hydrogen. Decomposition of the same ester in chlorobenzene gave an 80% yield of triptycene (with traces of triptycene-9-carboxylic acid) [160].

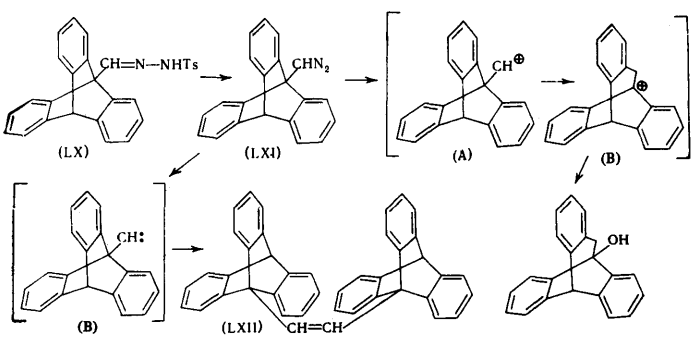
Decomposition of triptycen-9-al in the presence of t-butyl peroxide in carbon tetrachloride led to the isolation, after treatment with methanol, of 9-chlorotriptycene and methyl triptycene-9-carboxylate [160]. The results established that detachment of a chlorine atom from the solvent greatly predominated over decarbonylation. The thermal decomposition of triptycen-9-yl iodoformate to give 9-iodotriptycene (in 52% yield) is a peculiar substitution of the bridge oxygen function by homolysis of the carbon–oxygen bond [107]. 9-Iodotriptycene has been obtained also by irradiation of triptycene-9-carboxylic acid in the presence of iodine and lead tetra-acetate [155].

The ability of the bridge positions in triptycene to undergo radical substitution is thus a well established fact. The radical formed obviously has a tetrahedral configuration and is not stabilised by conjugation with the aromatic rings. Triptycen-9-yl is closely similar to the 1-norbornyl radical in stability [160], which supports Bartlett's suggested analogy [15] in the properties of the bicyclo[2,2,1]-heptane and triptycene bicyclic systems, which exhibit closely similar angular strains. It is also obvious that destabilisation of the triptycenyl radical due to the negative inductive effect of the three aromatic rings is slight [150].

The enhanced acidity of hydrogen atoms and the reactivity of halogen atoms at a bridgehead in the triptycene molecule make the bridging carbon atoms like aromatic carbon atoms. Among other reactions of 9-substituted triptycenes several transformations have been reported of the 9-nitro, [161] 9-nitroso, [161,162] and 9-bromo [163–165] derivatives, as well as reactions of 9-aminotriptycene-1,4-quinone [166], triptycene-9-carboxylic acid [167], and triptycen-9-ylmethylamine [168]. Diazotisation of this amine (LVIII) yields derivatives of a homologue of triptycene—homotriptycene (tribenzobicyclo[3,2,2]nonatriene (LIX)—formed by a Dem'yanov rearrangement involving expansion of the ring [168]:



Studies have been made [169] of the reactions of 9-diazomethyltriptycene (LXI), obtained by treating triptycen-9-al toluene-p-sulphonylhydrazone (LX) with sodium methoxide in pyridine. Decomposition of the hydrazone (LX) at 80° to 90°C involved intermediate formation of the carbonium ions (A) and (B) together with the carbene (C); decomposition of the dry sodium derivative of the hydrazone in a vacuum at 170–200°C involved preferential formation of the carbene (C), which was converted into a high yield of the hydrocarbon (LXII):



Unsuccessful attempts have been made to prepare a bridge iodonium salt of triptycene [155] and also to solvolyse a chloromethyl group located at a bridgehead in triptycene [109]. The bromine atom in 9-bromomethyltriptycene is also unreactive [110].

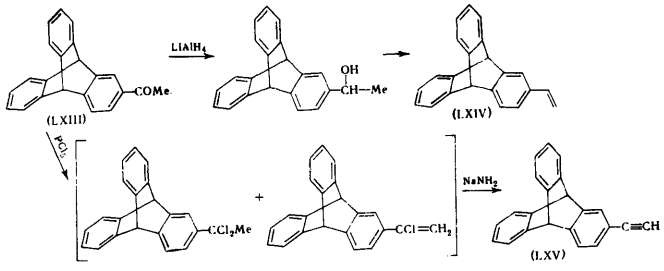
Functional substituents distant two or more methylene units from the bridging carbon atoms develop their normal reactivity [61].

Results obtained for the dissociation constants of several 10-substituted triptycene-9-carboxylic acids and for their esterification with diazodiphenylmethane were analysed by means of the linear free-energy equation. As was to be expected, the acidity and the rate of esterification of these acids are determined mainly by the inductive effect of the substituent [170].

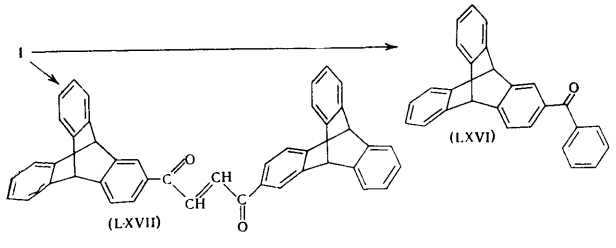
9-Vinyltriptycene [99,171] and 9-ethynyltriptycene [172] have been prepared, and their properties studied. Many 9- and 9,10-substituted triptycenes have been obtained with the aim of studying their physiological activity [61,173,174]. Certain amines of this series possess anti-inflammatory activity [61]; triptycene itself binds nucleosides weakly [175]. Several 9,10-disubstituted triptycenes have been subjected to polycondensation; the resulting polyesters were thermostable, in several cases also plastic, and could be processed into films and fibres [42,43,60]. A film based on a polyamide containing triptycene fragments enables hydrogen and helium to be separated from methane [176].

V. REACTIVITY OF AROMATIC RINGS

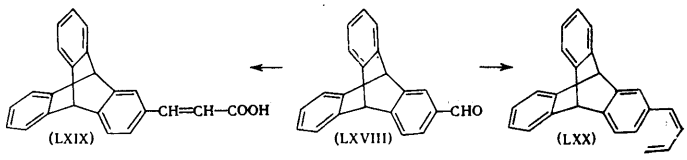
Electrophilic substitution usually occurs preferentially at the β-position in the aromatic rings of triptycene. Thus treatment of triptycene with acetyl chloride in the presence of aluminium chloride (at $-20°C$) gives a high yield of 2-acetyltriptycene (LXIII). [96] This compound has been used as a readily accessible starting material for the preparation of unsaturated hydrocarbons of the triptycene series—the 2-vinyl (LXIV) [99] and 2-ethynyl (LXV) [177] derivatives:



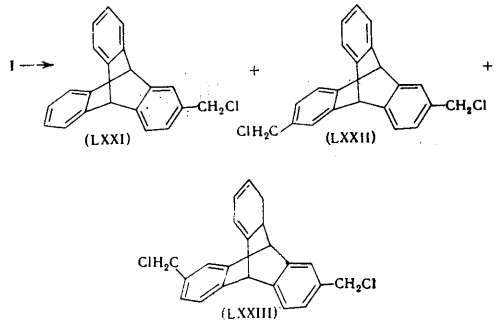
Triptycene is acylated by benzoyl and fumaroyl chlorides also exclusively at position 2 to form the corresponding ketones (LXVI and LXVII): [178]



The direct formylation of triptycene with excess of dichloromethyl methyl ether in the presence of aluminium chloride (at $-20°C$) gives a 51% yield of triptycen-2-al (LXVIII). [179] This aldehyde had previously been obtained from 2-acetyltriptycene (LXIII) in several stages [180]. Triptycen-2-al (LXVIII) has been used for the preparation of 2-butadienyltriptycene (LXX) [179] and β-triptycen-2-ylacrylic acid (LXIX): [180]



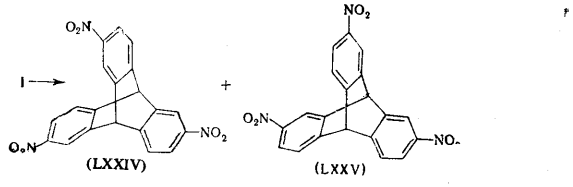
Triptycene undergoes chloromethylation under comparatively severe conditions with the formation of three products—the 2-chloromethyl (LXXI, 15%), 2,6-bischloromethyl (LXXII, 52%), and 2,7-bischloromethyl (LXXIII, 16%) [181] derivatives:



Treatment of triptycene with concentrated nitric acid in acetic anhydride led to isolation of the 2-nitro (44%), 2,6- and 2,7-dinitro, and traces of the 1-nitro (2.3%, identified from the ^1H n.m.r. spectrum) compounds [97].

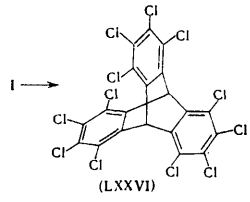
The formation of isomeric dinitro- and bischloromethyl-triptycenes and the presence of unchanged triptycene in the reaction mixture indicate that a substituent in one aromatic ring has little effect on the reactivity of unsubstituted rings towards sufficiently active electrophilic reagents.

A mixture of isomeric 2,6,12- and 2,7,13-trinitrotriptycenes (LXXIV and LXXV) containing no α-substituted isomers is formed when triptycene is treated with fuming nitric acid [182]:



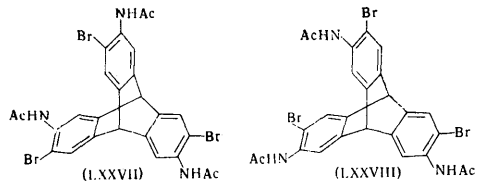
Preparation of a hexanitrotriptycene of undetermined structure has been reported in the patent literature [183].

The action of a combined chlorinating agent (sulphuryl chloride in the presence of sulphur monochloride and aluminium chloride) gave dodecachlorotriptycene (LXXXVI) in high yield [184]:

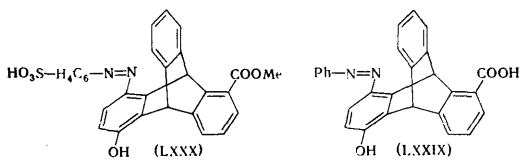


Among other compounds of the series 9,10-dimethyltriptycene has been most thoroughly studied in relation to

electrophilic substitution[185]; β-monosubstituted derivatives are obtained on bromination, acylation, and nitration[186]. Monosubstituted derivatives of undetermined structure were obtained by the nitration and acylation of 1,2-benzotriptycene, but this hydrocarbon could not be brominated[28]. The chloromethylation of 2-chloromethyltriptycene (LXXI) gives the 2,6-bischloromethyl derivative (LXXII) in theoretical yield[181]. The bromination of isomeric triacetamidotriptycenes (obtained by reducing a mixture of trinitrotriptycenes in acetic acid) gives a mixture of isomeric triacetamidotribromotriptycenes



in high yield[182]. The reaction of 5-hydroxytriptycene-1-carboxylic acid with benzenediazonium chloride and that of its methyl ester with diazotised sulphanilic acid yield the corresponding azo-compounds (LXXIX and LXXX).[137]



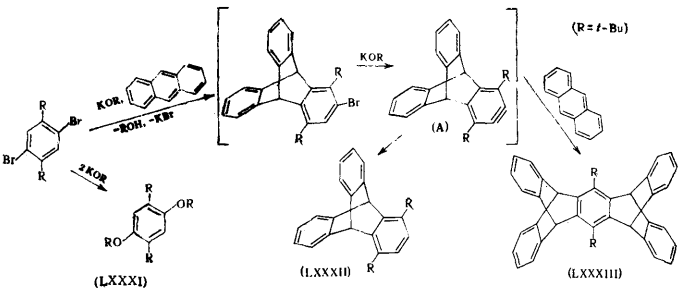
The reactivity of α- and β-positions in the aromatic rings of the triptycene molecule towards electrophilic and nucleophilic reagents has been studied quantitatively by deuterium exchange in the presence of trifluoroacetic acid[187,188] and caesium cyclohexylamide[188] respectively. In the former case exchange of a hydrogen atom was more rapid in the β- than in the α-position by factors of 7–8; but isotopic exchange in the presence of the amide was more rapid in the α- than in the β-position by factors of 7.3–7.5. Under conditions of electrophilic isotope exchange a hydrogen atom in either position was less mobile than in *o*-xylene or 9,10-dihydroanthracene[187]; but under conditions of nucleophilic isotope exchange it was more mobile than in benzene[154].

Differences in reactivity between α- and β-positions in the aromatic rings of the triptycene molecule are attributed to strain in the bicyclo[2,2,2]octane system[188], which distorts the angles between aromatic and aliphatic carbon–carbon bonds[84,85]. This results in changes in the hybridisation of the orbitals and the lengths of the carbon–carbon bonds in the aromatic ring. The bond common to the bicyclic system and the aromatic ring acquires an enhanced *p*-character like an aliphatic carbon–carbon bond, and the remaining orbitals of the bounding carbon atoms acquires a greater *s*-character, while becoming more electronegative. Therefore the α-carbon atom attached by the electronegative orbital is less reactive towards electrophilic substitution than is the β-carbon atom (which remains unaffected by the strained ring); as a consequence the α-hydrogen atom develops enhanced acidity.

An attempt was made to explain the preferential β-substitution on electrophilic attack also by the Mills–Nixon effect[189]—by the fixation of multiple bonds at the 1–9a, 2–3, and 4–4a positions in the aromatic rings of triptycene because of the strain in the bicyclic system—indirect support for which was obtained by comparing the oxidation potential of triptycenequinone with those of other *p*-quinones[38]. Dynamic factors may also determine the final results of electrophilic substitution and the differently strained σ-complexes formed on α- and β-substitution[190].

Nucleophilic substitution in an activated aromatic ring in triptycene has been accomplished with 2,3-dichlorotriptycene-1,4-quinone, which is analogous to 2,3-dichloro-1,4-naphthaquinone in chemical behaviour. This triptycene derivative reacted with amines to form quinonoid compounds, but the latter did not dye cellulose acetate fibre, probably owing to non-coplanarity of the structure[191,192].

Nucleophilic substitution in an unactivated aromatic ring of triptycene involves intermediate formation of 1,2-dehydrotriptycene, indicated by the reactions of 2-bromotriptycene with potassamide and lithium piperidide, as well as that of 1-chlorotriptycene with the latter, which yield mixtures (~1 : 3) of 1- and 2-substituted triptycenes. Phenyl-lithium reacts similarly with 2-fluoro- and 2-chloro-triptycenes, but with 2-bromotriptycene under these conditions the bromine atom is exchanged for lithium[193]¶. The intermediate formation of 1,2-dehydrotriptycene appears at first glance to be inconsistent with the distribution of bond lengths in the aromatic ring[84,85], since it should have been more strained than 2,3-dehydrotriptycene. For this reason, however, 1,2-dehydrotriptycene is obviously the more reactive, which probably explains the composition of the reaction products[193]. Formation of an *sp*-hybridised $C_{(2)}-C_{(3)}$ bond in triptycene compounds (2,3-dehydrotriptycene, A) has been postulated[47] only for the action of potassium t-butoxide on 1,4-dibromo-2,5-di-t-butylbenzene in the presence of anthracene, when 1,4-di-t-butoxy-2,5-di-t-butylbenzene in the presence of anthracene, when 1,4-di-t-butoxy-2,5-di-t-butylbenzene (LXXXI), 1,4-di-t-butyltriptycene (LXXXII), and the adduct (LXXXIII) were isolated, which suggested the reaction scheme.



Homolytic substitution in an aromatic ring of triptycene has not been studied. A substance containing a little chlorine and of undetermined structure was isolated from the products of the radical chlorination of triptycene[1].

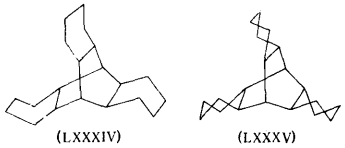
Triptycene derivatives containing functional substituents in the aromatic rings exhibit no significant difference in properties from other aromatic compounds[1,96,99,133,135,137,139,178–182,193–195]. Thus 2-chloromethyltriptycene (LXXI) is comparable in reactivity with benzyl chloride: it undergoes nucleophilic substitution (solvolysis, cyanolysis) and reduction and also forms an organomagnesium compound, under the same conditions as benzyl chloride.

¶ Triptycen-2-yl-lithium was formed also by the reaction of 2-bromotriptycene with n-butyl-lithium[96]. Triptycene was obtained on hydrolysis of this compound[193], but treatment with acetonitrile gave 2-acetyltriptycene[96].

The hydrolysis rate constant of 2-chloromethyltriptycene (LXXI) (in 40% aqueous acetone) exceeds that of benzyl chloride by a factor of 2.73, which indicates that the dihydroanthrylene fragment of triptycene exerts a positive inductive effect [109].

More severe conditions are required for the nucleophilic substitution of 1-chloromethyltriptycene. Its hydrolysis rate constant is smaller than that of 2-chloromethyltriptycene by a factor of 5.8. [194] Isomeric α- and β-carboxylic acids differ in acidity: triptycene-1-carboxylic acid is stronger than the 2-isomer, which is weaker than benzoic acid (as established by potentiometric titration in non-aqueous solvents—acetonitrile and dimethylformamide) [196]. This is also consistent with the general rule that substituents in α- and β-positions in the aromatic rings of triptycene differ in behaviour and with the change in hybridisation of the orbitals of the corresponding carbon atoms.

Triptycene is hydrogenated over palladium or ruthenium on carbon (under 30–100 atm at 100–200°C), either partly or completely depending on the conditions [197]. Exhaustive hydrogenation gives iso-*cis*-perhydrotriptycene (LXXXIV) rapidly and iso-*trans*-perhydrotriptycene (LXXXV) far more slowly (in 60% yield after 1 month).



(LXXXIV) (LXXXV)

In triptycenequinol (IV) either the substituted or an unsubstituted ring is reduced depending on the conditions [1]. Variously annelated quinones of the triptycene series undergo very rapid catalytic hydrogenation by an electronic mechanism [198–205]. Steric factors have a slight effect on the rate of hydrogenation. The rate usually increases with the degree of annelation of the quinones. Comparison of results for the catalytic hydrogenation of quinones over nickel and palladium on carbon with those for polarographic reduction (see Table in Section III) revealed the linear relation $\lg k_1 - \lg k_2 = \chi(E_1^\circ - E_2^\circ)$, where k_1 and k_2 are the hydrogenation rate constants for two members of the series, E_1° and E_2° are their standard potentials, and it was found that $\chi = 1.7\ V^{-1}$. The rate of catalytic hydrogenation should thus increase as the standard potential of the quinone falls (as a result of the diminished stability of the intermediate semiquinone). On hydrogenation over nickel, furthermore, the first-order rate constant increases with the activation energy owing to an increase in the entropy factor.

The hydrogenation of adducts of anthracene and pentacene with *p*-benzoquinone was investigated on the basis of the multiplet theory of catalysis [206–214]. Since successive complication of the structure of the non-reacting part of the molecule (II, XXVI, XXVII) has no significant effect on the rate or the extent of the process, it was deduced that the catalyst (nickel) surface contained projecting active centres, on which the indicial group of the reactant molecule was superposed (hydrogenation of the $C_{(2)}-C_{(3)}$ bond). The results enabled a model of the active complex to be constructed and permitted determination of the number of active centres (1.20^{20} [sic] g^{-1} Ni) and their optimum dimensions (height not exceeding 3.9 Å).

Hydroaromatic compounds of the triptycene series are dehydrogenated by sulphur or palladium on carbon with the formation of substituted triptycenes [18,19,28,215].

A high-melting complex of triptycene with tricarbonylchromium was obtained and found to be soluble in organic solvents and to decompose on fusion, sublimation, or illumination. Its proton magnetic resonance spectrum indicated that the chromium atom was coordinated with one of the aromatic rings [216].

Several substituted triptycenes readily form clathrates [30,34,35,38,98,139]. For example, 1,4-diphenyltriptycene gives with carbon tetrachloride and cyclohexane stable clathrates containing one solvent molecule per two hydrocarbon molecules [98].

It has been reported that quinols of the triptycene series can be used as photographic developers [217,218] and stabilisers for synthetic elastomers [219,220]. The reactivity of 2-vinyltriptycene (LXIV) is close to that of styrene under conditions of radical homo- and co-polymerisation, whereas 9-vinyltriptycene, in which the vinyl group is sterically hindered and is not conjugated with the ring system, is inert under these conditions and does not polymerise. Polymerisation of 2-vinyltriptycene (LXIV) occurs at the vinyl bond to give a linear polymer containing the triptycene fragment in the side-chain, which is less thermostable than polymers containing a triptycene residue in the main chain [220].

VI. REACTIONS INVOLVING OPENING OF THE BRIDGE SYSTEM

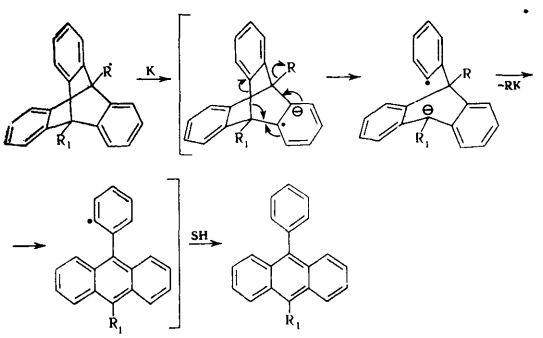
Triptycene is comparatively readily oxidised by strong oxidants such as chromium trioxide or potassium permanganate in acetic acid with the formation of anthraquinone, which resists further oxidation under these conditions [1]. Formally oxidation involves cleavage of the bicyclic system, but initial attack by the oxidant on one of the aromatic rings is not excluded. Intermediate oxidation products could not be isolated (probably because of their enhanced activity under the reaction conditions).

Triptycenequinone (III) is also oxidised to anthraquinone [14]. The latter compound and 1,4-diphenylanthraquinone (2 : 1) have been isolated from the oxidation of 1,4-diphenyltriptycene, the ratio of the products being obviously determined not only by statistical factors (otherwise the inverse ratio would have been obtained) [98]. The oxidation of 1,2-benzotriptycene [28] and 9,10-dibromo-2,3-benzotriptycene [41] also yielded anthraquinone, and no other reaction products could be identified. Thus derivatives of anthraquinone are the most usual oxidation products of compounds of the triptycene series. Nevertheless, the oxidation of substituted triptycenequinones with ammonium persulphate leads to cleavage of the quinonoid ring with the formation of substituted 9,10-dihydro-9,10-ethenoanthracenes [134].

Under milder conditions functional groups can be oxidised while the triptycene structure is preserved. Thus triptycenequinol (IV) can be oxidised to triptycenequinone (III), [1] 9,10-bishydroxymethyltriptycene to triptycene-9,10-dicarboxylic acid [60], 2-acetyltriptycene (LXIII) to triptycene-2-carboxylic acid [178], and triptycen-2-ylmethanol to triptycen-2-al (LXVIII). [180] Triptycene compounds with substituents containing multiple bonds can be ozonised without affecting the triptycene structure [178,222].

The bridging system of triptycene is opened up by reduction under severe conditions. Thus triptycene-1,4-quinol (IV) and triptycenequinone (III) give 9,10-dihydroanthracene when distilled with zinc dust [14]; 1,2-benzotriptycene breaks down into naphthalene and 9,10-dihydroanthracene [28].

Triptycene hydrocarbons undergo an interesting cleavage reaction under the influence of potassium in oxolan [223] or a potassium–sodium alloy in ether [224]. The electron spin resonance spectra of the reaction products indicate intermediate formation of a radical-anion of anthracene. Study of the effect of a substituent group on the stability of the intermediate radical-anion suggested the reaction mechanism. [223]



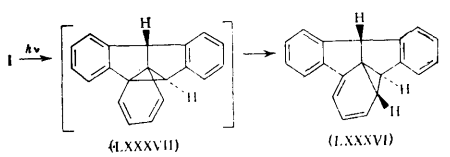
The detachment of 9,10-substituents accelerates in the sequence

$$CH_3 > C_6H_5 < H, C_6H_5CH_2$$

which confirms that one of the substituents leaves as an anion. Metallic sodium has a slight effect on the cleavage of 9-phenyltriptycene, and does not interact at all with other hydrocarbons of the series [223].

The previously mentioned diazotisation of triptycen-9-ylmethylamine (LVIII) [168] and decomposition of 9-diazomethyltriptycene (LXI) [169] also involve cleavage of the bicyclic system.

The product of the photochemical isomerisation of triptycene, in contrast to the related barrelene and benzobarrelene (which are converted into a mixture of semibullvalenes and cyclo-octatetraenes) [225], is the hydrocarbon (LXXXVI), which has been regarded [226] as formed by the sigmatropic rearrangement of the intermediate semibullvalene (LXXXVII):



(LXXXVII) (LXXXVI)

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Papers have appeared recently on the chemistry of triptycene. Thus it has been synthesised from dehydrobenzene generated from 1,1-dimethyl-3-phenyltriazen in the presence of sodium trichloroacetate and trichloroacetic acid [227], and the preparation of deuterotriptycene has been reported [228]. The enthalpy of formation and the energy of strain of triptycene have been determined [229]. The high-resolution ^1H n.m.r. spectrum of triptycen-2-amine exhibits signals due to non-equivalent bridge protons [230]. The electron spin resonance and optical spectra of the radical-ions of certain derivatives have been studied [231]. Hindered rotation of the methyl group has been detected in tetra- and octa-chloro-9-methyltriptycenes [232,233]. The optical activity of 5-substituted 1,4-dimethoxytriptycenes has been investigated [234]. 9-Butadienyltriptycene has been prepared [235], and several reactions of 9-bromo- and 9,10-dibromo-triptycenes have been accomplished [236]. β-Substituted mono-, di-, and tri-nitrotriptycenes are formed by the action of acetyl nitrate [237], and the bromination of triptycen-2-amine gives 3-bromotriptycen-2-amine [238].

Tetrahydrodi-*o*-benzopentacene has been obtained by the reaction of 2-bromo-3-fluorotriptycene with magnesium in the presence of anthracene in oxolan, which indicates the intermediate formation of 2,3-dehydrotriptycene [238]. The photoisomerisation of triptycene in methanol involves an intermediate carbene stage [239]. Other publications have also appeared [240–247].

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