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Advances in the Chemistry of Stable Hydrocarbon Radicals

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The current data on the structure of tervalent carbon radicals are examined and their principal spectroscopic characteristics are presented. The latest studies on the synthesis of stable hydrocarbon radicals, including ultrastable perchlorotriarylmethyl radicals, are considered together with classical investigations. In the discussion of chemical properties, much attention has been devoted to the dimerisation of triarylmethyls, since this problem has altered drastically the traditional concept of tervalent carbon radicals. Modern ideas concerning certain hydrocarbon biradicals are presented. The bibliography includes 150 references.

CONTENTS

I.	Introduction	1011
II.	Principal types of stable hydrocarbon radicals	1011
III.	Structure and spectra	1012
IV.	Methods of synthesis	1013
V.	Chemical properties	1014
VI.	Biradicals	1016

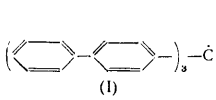
I. INTRODUCTION

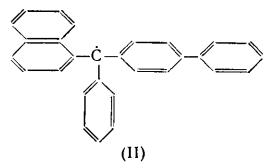
After Gomber's discovery[1] of the triphenylmethyl radical, an enormous number of studies have been published on the chemistry and physics of stable hydrocarbon radicals. Many of them have been analysed in familiar reviews by Soviet and foreign workers[2-4]. However, progress in this field of knowledge has been so great in recent years that many postulates which were believed to be firmly established have become obsolete. Together with classical investigations, the present review deals in detail with the latest studies which have greatly modified the traditional ideas about tervalent carbon radicals.

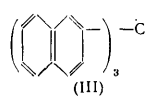
In the literature all stable hydrocarbon radicals are as a rule included under one name — triarylmethyls — which is not altogether correct. It is therefore useful to consider the principal types of stable hydrocarbon radicals before discussing their properties and methods of synthesis.

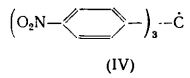
II. PRINCIPAL TYPES OF STABLE HYDROCARBON RADICALS

Gomberg did not synthesise the triphenylmethyl radical but its dimer and it was not until 1909 that Wieland[5] showed that this dimer is in equilibrium with its radical in solution. After establishing the nature of triphenylmethyl, many of its derivatives were synthesised, some of which, namely tri-*p*-biphenylylmethyl (I)[6], *p*-biphenylyl-α-naphthylphenylmethyl (II)[7], tri-β-naphthylmethyl (III)[8], and tri-*p*-nitrophenylmethyl (IV)[9], have been isolated in a crystalline form:

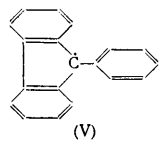

(I)

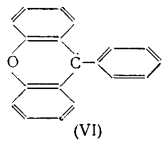

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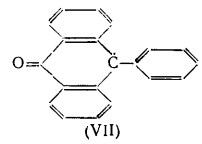

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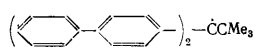

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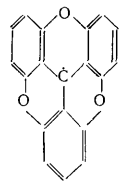
The 9-phenylfluorenyl (V)[6], phenylxanthyl (VI)[10], phenanthronyl (VII)[11], di-*p*-biphenylyl-t-butylmethyl (VIII)[12], and sesquixanthydryl (IX)[13-14] radicals exist in equilibrium with their dimers:


(V)

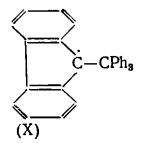

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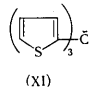

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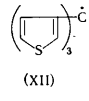

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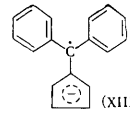
As early as 1922, Schlenk and Mark obtained a higher homologue of triphenylmethyl (pentaphenylmethyl) and its biphenylene analogue (X)[15]:


(X)

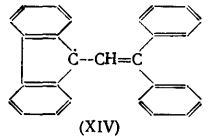
Very stable fluorinated[16-18] and chlorinated[19] derivatives of triphenylmethyl were synthesised recently; analogues of triphenylmethyl radicals were also obtained – trithienylmethyls (XI) and (XII)[20] and the radical-anion of diphenylfulvene (XIII)[21]:

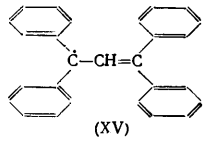

(XI)


(XII)

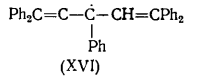

(XIII)

In 1922 Ziegler[22, 23] achieved the synthesis of the allyl radicals (XIV) and (XV), which are examples of a new series of tervalent carbon radicals:


(XIV)

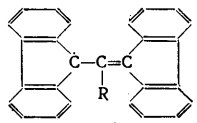

(XV)

Wittig extended this series having synthesised the diallyl and triallyl radicals [(XVI) and (XVII) respectively][24]:

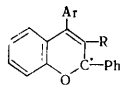

(XVI)

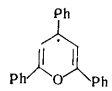

(XVII)

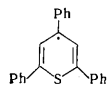
Later Koelsch[25], Solar[26], and Kuhn and coworkers[27, 28] investigated a series of bisbiphenyleneallyl radicals of type (XVIII):

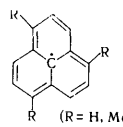

(XVIII) (R=H, Me, Ar)

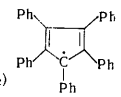
Chromenyl (XIX)[29, 30], pyryl (XX)[31], thiapyryl (XXI)[32], and perinaphthyl (XXII)[33] radicals as well as the highly symmetrical pentaphenylcyclopentadienyl radical (XXIII), which has been isolated in a crystalline form[34], can also be included among radicals of the allyl type:


(XIX) (R = H, Alk, Ar)


(XX)

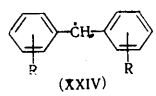

(XXI)


(XXII) (R = H, Me)


(XXIII)

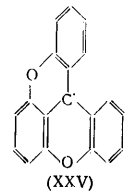
The heterochain radicals $(C_6H_5S)_3C\cdot$ and $CH_3S(C_6H_5S)_2C\cdot$ obtained recently proved to be relatively unstable[35].

Diarylmethyl radicals (XXIV), which have been investigated in detail by Nauta[36, 37] and Theilacker[38], are much less stable than triarylmethyls. Only perchlorodiphenylmethyl has now been isolated in a pure form[39]:


(XXIV)

III. STRUCTURE AND SPECTRA

The electronic spectra of triarylmethyls have two characteristic regions; a region with a very intense absorption at 200 – 400 nm ($\epsilon \simeq 10^4$) and a region of less intense absorption at 500 – 650 nm ($\epsilon \simeq 10^2 - 10^3$)[40]. Triphenylmethyl itself absorbs in the visible region at 484 and 515 nm.[41] Substituents in the *para*-position cause a bathochromic shift of this band, while *ortho*-substituents give rise to a hypsochromic shift owing to the decrease of the coplanarity of the phenyl rings. However, the radical (XXV) absorbs at 490 and 500 nm[42]:


(XXV)

since oxgen bridges prevent the breakdown of coplanarity. The spectrum of 9-phenylfluorenyl (V) is close to that of triphenylmethyl, but the bands are displaced by 800 cm^{-1} towards higher wave-numbers[43]. The electronic spectrum of diphenylmethyl has been interpreted theoretically[44].

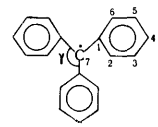
The luminescence spectra of di- and triphenylmethyl radicals were also recorded[45] and showed that diphenylmethyl is more coplanar than triphenylmethyl.

The infrared spectra of tervalent carbon radicals are not characteristic[19, 46].

As expected on symmetry grounds, the dipole moment of triphenylmethyl is close to zero[47].

The earlier quantum-mechanical calculations[48] were based on the hypothesis that the triphenylmethyl molecule is planar. However, it was noted subsequently[49] that account must be taken of the mutual repulsion of the *ortho*-hydrogen atoms. Calculation, taking into account such repulsion, shows that the benzene rings must be rotated relative to the plane of the bonds of the central carbon atom by 30° (the θ angle), i.e. the triphenylmethyl molecule should have the shape of a propeller. In this case the conjugation energy decreases only slightly, while the repulsion energy falls very markedly.

The θ angle in tri-*p*-nitrophenylmethyl, which was determined by X-ray diffraction, proved to be 30°.[50] The value for triphenylmethyl in the gas phase is somethat greater (40 – 45°)[51].



The $C_{(7)} - C_{(1)}$ bond length is 1.48 Å for triphenylmethyl, which is less than in triphenylmethane (1.53 Å). On passing from triphenylmethane to the radical, the angle γ increases from 112° to 118°, which corresponds to a change in the hybridisation of the central atom from sp^3 to sp^2.

The X-ray diffraction patterns of perchlorodiphenylmethyl show that the benzene rings are displaced from the trigonal plane of the central atom[52].

Since di- and triarylmethyls are typical π-electron radicals, their unpaired electron is delocalised over the entire π-bond system, which is clearly reflected in the ESR spectra. The constants for the hyperfine coupling (HFC) with protons, determined from the ESR spectra, are $a_{H(ortho)} = 2.55$ G, $a_{H(meta)} = 1.11$ G, and $a_{H(para)} = 2.78$ G for triphenylmethyl[53]. Similar values were obtained from electron nuclear double resonance (ENOR) spectra[54]. The constant for hyperfine coupling with ^{13}C in the central position is 26 G and the *g*-factor is 2.0026.[55]

More than 50% of the spin density of the unpaired electron is concentrated at the central carbon atom. The spin density is positive in the *ortho*- and *para*-positions of the benzene rings and negative in the *meta*-positions.

para- and *meta*-Substituents have only an insignificant influence on the distribution of spin density, while on introduction of *ortho*-substituents the spin density of the central carbon atom increases and that in the benzene rings decreases[13]. This is due to an increase of the deviation of the benzene rings from coplanarity. An increase of the coplanarity of the rings, as for example in sesquixanthydryl (IX), leads to an increase of $a_{H(para)}$ to 3.17 G.[14]

Table 1. The HFC constants (in gauss) for certain triarylmethyls

Radical	$a_{H(ortho)}$	$a_{H(meta)}$	$a_{H(para)}$	References
$Ph_3\dot{C}$	2.55	1.11	2.78	53
$(p\text{-}FC_6H_4)_3\dot{C}$	2.70	1.13	6.5 (F)	55
$(m\text{-}FC_6H_4)_3\dot{C}$	2.64	1.09 (F)	2.85	55
$(2,6\text{-}F_2C_6H_3)_3\dot{C}$	2.11 (F)	1.06	2.61	57
$(3,5\text{-}F_2C_6H_3)_3\dot{C}$	2.14	1.67 (F)	2.52	57
$(p\text{-}NO_2C_6H_4)_3\dot{C}$	2.50	1.14	0.66 (N)	58
$(p\text{-}MeOC_6H_4)_3\dot{C}$	2.89	1.05	0.34 (Me)	59
$(2,6\text{-}(MeO)_2C_6H_3)_3\dot{C}$	0.14 (Me)	1.06	2.26	13
Sesquixanthydryl(IX)	—	0.39	3.17	14

The unusual ratio $a_{H(ortho)} : a_{H(para)} = 2$ in the 9-phenylthiaxanthyl radical is evidence of the hindered rotation of the phenyl group, the angle of its displacement from the plane of the heterocycle amounting to 72°.[56] Table 1 lists the HFC constants for certain triarylmethyls.

Table 2. The proton HFC constants a_i and spin densities in symmetrical diarylmethyls

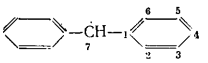
Substituent	a_2	a_3	a_4	a_7	ρ_C^π	References
H	3.05	1.22	3.05	8.36		62
2,6-Me_2	2.15	1.43	3.25	16.27	0.71	63
2,6-Et_2	1.47	1.7	3.17	16.22	0.70	63
2,6-(i-Pr)$_2$	2.22	0.74	2.22	16.69	0.73	63
2-(t-Bu)	3.42	1.37	3.42	15.92	0.69	63
2,5-(t-Bu)$_2$	3.15	1.20	3.50	15.15	0.66	64

The ESR spectrum of perchlorotriphenylmethyl radicals consists of a singlet with satellites due to the ^{13}C nuclei, the *g*-factor amounting to 2.0025. In these radicals, 70% of the spin density is at the central carbon atom, which corresponds to an angle rotation of the benzene rings $\theta \simeq 60°$.[60]

It has been shown[61] that in the radicals (XXVI) and (XXVII) approximately 10% of the spin density is delocalised over remote benzene rings:

$Ph_2\dot{C}-C_6H_4-C\equiv CPh$ (XXVI) $\quad (Ph-C\equiv C-C_6H_4)_3\dot{C}$ (XXVII) .

In broad outline, the distribution of spin density in diarylmethyls differs little from the distribution in triarylmethyls. Table 2 presents the HFC constants and spin densities (ρ_C^π) at the central carbon atom:



The constant for hyperfine coupling with the ^{13}C atom in the central position in the $(C_6Cl_5)\dot{C}Cl$ radical is 39 G, which corresponds to $\rho_C^\pi = 0.9$, and the *g*-factor is 2.0055. The angle of rotation θ is 60°.[60]

Comparison of the ESR spectra of various diarylmethyls led Buchanchenko and Vasserman[65] to the conclusion that, in contrast to its substituted derivatives, the hybridisation of the central carbon atom in the diphenylmethyl radical is not sp^2.

IV. METHODS OF SYNTHESIS

The method of synthesising triarylmethyls by the reduction of halogenotriarylmethanes with metals which Gomberg[1] developed still remains important:

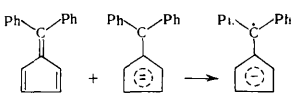
$$Ar_3CX \xrightarrow{M} Ar_3\dot{C} + MX .$$

Silver, mercury, zinc, and various amalgams are most frequently used as reducing agents. Triarylmethyl perchlorates are also employed in place of the halides. The reaction is carried out in an inert medium free from moisture in solvents such as benzene, acetone, ether, petroleum ether, ethyl acetate, and others. In general, triarylmethyl halides and perchlorates are such powerful electron acceptors that they are very readily reduced by a wide range of nucleophilic agents, such as organomagnesium compounds[22, 66], alkoxides and phenoxides[67], sodium diethylphosphite[68], sodium iodide[16], inorganic anions[69], triphenylphosphine and diphenylamine[70], organo-mercury compounds[70], the cyclo-octatetraene dianion[71], and metal ketyls[72].

Diarylmethyls are mainly obtained by Gomberg's method involving the reduction of the corresponding chlorides with metals[64, 73]. Perchlorodiphenylmethyl was obtained for the first time by the reduction of the corresponding chloride with t in (II) chloride[39]:

$$(C_6Cl_5)_2CCl_2 \xrightarrow{SnCl_2} (C_6Cl_5)_2\dot{C}Cl .$$

The diphenylfulvene radical-anion (XIII) was obtained by the reduction of diphenylfulvene by its dianion[21]:



(XIII)

Another general method of synthesising triarylmethyls, involving the reduction of triarylmethyl carbonium ions, was proposed by Conant[74]. Vanadium(II) chloride and sulphate have been used as reducing agents. The carbonium ion was obtained by the dissolution of chlorotriphenylmethane or triphenylmethanol in sulphuric or hydrochloric acid:

$$Ar_3COH \xrightarrow{H^+} Ar_3\overset{+}{C} \xrightarrow{V^{2+}} Ar_3\dot{C} .$$

Chromium[42, 57] and titanium[18] salts have been proposed as reducing agents and trifluoroacetic acid[57] and a mixture of acetic and hydrochloric acids[42] have been suggested as ionising solvents.

The triarylmethyl carbanions formed on dissolution of triarylmethanes in alkalis are readily oxidised to triarylmethyls. The reaction proceeds in an aqueous medium

from which the radical is readily extracted[17]. $KMnO_4$,[17] $K_3Fe(CN)_6$,[28] $AgNO_3$,[8] mercury salts, and bromotriphenylmethane[70] have been used as oxidants:

$$Ar_3CH \xrightarrow{OH^-} Ar_3C^- \xrightarrow{[O]} Ar_3C^{\cdot}$$

Perchlorodiphenylmethyls and perchlorotriphenylmethyls have been obtained by the oxidation of the corresponding carbanions with iodine and oxygen[19].

Zieglar[75, 76] developed a convenient method of synthesising arylalkyl radicals using dibromotetramethylethylene as the electron acceptor:

$$Ar_2RCK + Me_2CBrCBrMe_2 \rightarrow Ar_2RC^{\cdot} + Me_2C{=}CMe_2 + 2KBr$$

Ar_2RCK was obtained by treating the substituted methyl ether with the metal:

$$Ar_2RCOMe + 2K \rightarrow Ar_2RCK + MeOK$$

A modification of Gomberg's method has been proposed by Schmidlin[77], who obtained triphenylmethyl by treating triphenylacetyl chloride with silver:

$$Ph_3CCOCl \xrightarrow{Ag} Ph_3C^{\cdot} + CO$$

Mention may be made of several other methods of synthesising triarylmethyls but these have no preparative value.

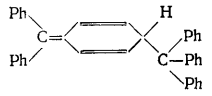
Triphenylmethyl is formed in the decomposition of azo-compounds containing the triphenylmethyl residue[5, 78], t-butyltriphenyl peracetate[79], and *N*-diphenylmethyl-$\alpha\alpha$-diphenylnitrones[80], in the pyrolysis of trityl ethers[81, 82], and in photochemical[83] and certain other reactions[84-87].

The principal method of synthesising the unstable diphenylmethyl radical is photolysis and thermolysis of various diphenylmethane derivatives[45, 62, 88].

V. CHEMICAL PROPERTIES

1. Dimerisation

Tervalent carbon radicals are in thermodynamic equilibrium with their dimers. Since triphenylmethyl was obtained for the first time in an attempt to synthesise hexaphenylethane, the latter was in fact believed to be a dimer of the radical. However, as early as 1905 Jacobson[89] proposed the cyclohexadiene (XXVIII) structure for the dimer:



(XXVIII)

Gomberg[90] also postulated the possibility of several triphenylmethyl dimerisation pathways. The lack of reliable physical methods for the determination of the structure precluded at the time a final solution of this problem and the controversy concerning the structure of triphenylmethyl dimers led to the belief that the only possible structure is that of hexaphenylethane. However, the finding that the dimerisation of tri-(p-*t*-butylphenyl)methyl[91], di-(2,5-di-t-butylphenyl)methyl[92], and di-*p*-substituted diarylmethyls proceeds with extreme difficulty led to the revision by Lankamp et al. of the hypothesis concerning the structure of triarylmethyl and diarylmethyl dimers[93]. The NMR spectra of the diarylmethyl and triarylmethyl dimers which they investigated are consistent with the cyclohexadiene structure and contradict the polyarylethane structure.

The same workers synthesised true tetra-arylethanes by treating diarylmethanols with an excess of vanadium(II) or chromium(II) ions in an acetone solution of hydrochloric acid. True tetra-arylethanes dissociate to diarylmethyl radicals with difficulty and only at a high temperature and the radicals dimerise to cyclohexadienes and not tetra-arylethanes. The melting points of true tetra-arylethanes are much higher than those of the radical dimers. Subsequently the cyclohexadiene structure of the triphenylmethyl dimers was confirmed yet again by ^1H NMR[94] and ^{13}C NMR[95] spectra.

As frequently happens, the fact established not only failed to put an end to the old problems but actually gave rise to new ones. Firstly, not all the radicals dimerised in the "new" way; for example, 9-phenylfluorenyl (V) associates to an ethane derivative[95] and it is probably necessary to determine the structure of the dimer for each radical †. Secondly, it is not clear, for example, why di-(2-t-butylphenyl)methyl dimerises to a cyclohexadiene, while the 2,4- and 2,5-t-butyl derivatives form ethanes[96]. Thirdly, the entire chemistry of polyarylethanes, on which research has been continued for more than 70 years, was suddenly found to be completely unknown.

Other conditions being equal, two main factors influenced the thermodynamic radical – dimer equilibrium: (1) mesomeric stabilisation of the radical and (2) steric interactions in the dimer which promote dissociation.

Estimates of the relative importance of these factors, based on thermochemical data[97], show that the mesomeric effect is approximately twice as effective in promoting dissociation (50 – 55 kcal mole^{-1}) as the steric effect (17 – 22 kcal mole^{-1}).

The heat of dissociation of the triphenylmethyl dimer determined by ESR is 11 kcal mole^{-1}.[98] The activation energy for dissociation, determined by the reaction of this radical with oxygen, is 19 kcal mole^{-1}.[37, 99] A comparison of the thermodynamic data for the recombination and dissociation of diarylmethyls and triarylmethyls has been carried out[37]. While the heats of dissociation of the dimers are almost independent of the solvent, the dissociation constants vary extremely markedly (Table 3).

Table 3. The constants and heats of dissociation of the triphenylmethyl dimer[100]

Solvent	Dissociation constant 10^4K at 20°C	Heat of dissociation, kcal mole^{-1}	Solvent	Dissociation constant 10^4K at 20°C	Heat of dissociation, kcal mole^{-1}
			Ethylene dibromide	3.9	11.4
Propiononitrile	1.2	11.4	Benzene	4.1	11.3
Ethyl benzoate	1.67	12.0	Chloroform	6.9	10.5
Acetophenone	1.70	11.5	Carbon disulphide	19.2	11.0
Dioxan	2.5	11.6			
Bromobenzene	3.7	11.5			

According to Walter's classification[101], triarylmethyl radicals belong to class S, i.e. the degree of dissociation of their dimers increases following the introduction of both electron-donating and electron-accepting substituents.

† A communication was published recently where the literature data on the thermodynamic radical – dimer equilibrium were re-examined in connection with a revision of the structure of the dimers and a correlation equation was successfully applied to the dissociation of the dimers using Taff's steric constants[150].

p-Nitro- and *p*-phenyl substituents have a very marked influence on the dissociation of the dimers (Table 4).

It has been noted that *p*-alkyl-substituted triarylmethyls do not dimerise even at a low temperature. This confirms the cyclohexadiene structure of the dimer. Alkyl substituents in the *meta*- and *para*-positions increase the degree of dissociation but *ortho*-substituents have a particularly marked influence[104]. Thus tri-(2,6-dimethoxyphenyl)-methyl does not dimerise even in the solid state[13]. Coeranthryl (XXV) is also completely dissociated[42]. In contrast, sesquixanthydryl (IX) exists almost entirely as the dimer[13]. This is probably related to the absence of steric hindrance to dimerisation.

Table 4. Dissociation of triarylmethyl dimers[102]

Radical formed	Percentage dissociation in benzene at 5°C	Radical formed	Percentage dissociation in benzene at 5°C
$(C_6H_5)_3\dot{C}$	2—3	$(C_6H_5)_2C{=}CH(C_6H_5)_2\dot{C}$	80
$p\text{-}C_6H_5C_6H_4(C_6H_5)_2\dot{C}$	15	$(CH_3)_3C\,(p\text{-}C_6H_5C_6H_4)_2\dot{C}$	74
$(p\text{-}C_6H_5C_6H_4)_2(C_6H_5)\dot{C}$	79	$\alpha\text{-}C_{10}H_7(C_6H_5)_2\dot{C}$	60
$(p\text{-}C_6H_5C_6H_4)_3\dot{C}$	100	$\beta\text{-}C_{10}H_7(C_6H_5)_2\dot{C}$	33
$(C_6H_5)_3C(C_6H_5)_2\dot{C}$	100	$(\beta\text{-}C_{10}H_7)_3\dot{C}$	24
$(p\text{-}NO_2C_6H_4)_3\dot{C}$	100		

Bisbiphenyleneallyl radicals (XVII) are highly dissociated in solution, although in the solid state they exist mainly as the dimers[27].

Fluorinated triarylmethyls are dissociated in the solid state to the extent of 80 – 90%.[16] Perchlorotriarylmethyls are entirely monomeric both in solution and in the solid state[19].

Table 5. Heats and degrees of dissociation of diarylmethyl dimers[105]

Diarylmethyl dimer	Degree of dissociation, %	Heat of dissociation, kcal mole^{-1}
Di-(2,6-dimethylphenyl) methyl	0.35	22
Di(2-t-butylphenyl)-methyl	0.61	19.7
Di-(2,6-Diethylphenyl)-methyl	1.97	12.0
Triphenylmethyl	12.0	10.9
Di-(2,6-di-isopropyl-phenyl)methyl	100	*

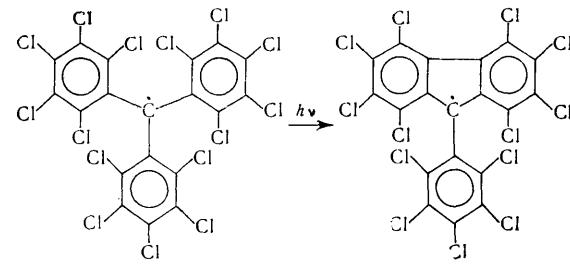
* Not determined owing to the superposition of the disproportionation process

Diarylmethyl radicals dimerise like triarylmethyls, but their dimers are dissociated to a much smaller extent. Diphenylmethyl itself cannot be obtained by the homolytic decomposition of the dimer. Table 5 lists the heats and degrees of dissociation of diarylmethyl dimers in *m*-xylene at 25 °C determined by ESR.

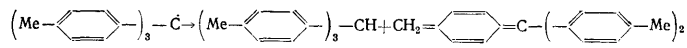
The introduction of alkyl substituents in the *meta*- and *para*-positions does not lead to the dissociation of the dimer. Only the presence of two *ortho*-substituents such as methyl, ethyl, and isopropyl or a single *ortho*-substituent such as t-butyl leads to the dissociation of the dimer. The bis-(2,5-di-t-butylphenyl)methyl dimer dissociates almost completely in solution[64, 96]. Perchlorodiphenylmethyl is the only example of a radical of this type which is fully monomeric even in the crystalline state[39].

2. Disproportionation

Triphenylmethyl solutions in non-polar solvents are decolorised rapidly on standing in the light with formation of triphenylmethane[106] and 1,2-diphenylbisbiphenylenethane[107], i.e. 9-phenylfluorenyl, which is associated more than triphenylmethyl, is formed as an intermediate. Solutions of triphenylmethyl in an ionising solvent such as sulphur dioxide are photochemically stable[108]. The photochemical reaction of perchlorotriphenylmethyl takes place similarly[109]:



p-Alkyl substituents increase the tendency of triarylmethyls towards disproportionation to such an extent that the radical decomposes spontaneously, immediately after formation, into the corresponding triarylmethane and a quinonoid compound which polymerises rapidly[104]:



Di-*p*-t-butyldiphenylmethyl constitutes an exception. It cannot form the quinonoid species by loss of hydrogen. Alkyl substituents in the *meta*- and *ortho*-positions increase the stability of triarylmethyls. Radicals of the allyl type are stable even on heating[27].

In the series of diarylmethyls, 2,4,6,-trialkyl- and 2,5-di-t-butyl-substituted derivatives disproportionate rapidly[36, 91]. The reaction products have not been investigated.

Diarylalkylmethyls disproportionate spontaneously[10] via the reaction

$$2Ar_2\dot{C}Me \rightarrow Ar_2C{=}CH_2 + Ar_2CH{-}Me\,.$$

3. Oxidation and Reduction

Diarylmethyls and triarylmethyls are readily reduced to the corresponding hydrocarbon by sodium amalgam[27], zinc in hydrochloric acid[28], phenylhydrazine[64], and catalytically by activated hydrogen[16]. Bisbiphenyleneallyls are not reduced by reductants such as hydroquinone, sulphite, and ascorbic acid[28].

Alkali metals add reversibly to triphenylmethyl with formation of brick-red salts[111]. Bent et al.[112] used this reaction to determine the electron affinity of triphenylmethyl and found it to be 17.9 kcal mole^{-1}.

Inert perchloro-radicals are reduced by potassium in ether to the corresponding carbanions[19]. Triphenylmethyl can also be reduced by a mixture of magnesium and magnesium bromide with formation of an organomagnesium compound[113].

Iron(III), mercury(II), silver(I), and gold(III) salts readily oxidised triphenylmethyl. In the $SO_2 - O_2$ system triphenylmethyl is oxidised to the carbonium ion[114], while at a rotating platinum electrode perchlorotriphenylmethyl can be reversibly reduced and oxidised to the corresponding ion[115].

4. Reaction with Radicals

Almost all tervalent carbon radicals interact with oxygen forming the colourless peroxide $Ar_3COOCAr_3$. The qualitative detection of triarylmethyls, the so called Schmidlin test[116], depends on this reaction. The coloured solution of the radicals is decolourised on shaking in air but subsequently the colour returns as a result of the dissociation of the dimer. The Schmidlin test can be repeated several times until the quantitative formation of the peroxide takes place. Janzen et al.[117] showed by ESR that the first stage in this reaction is the reversible formation of the peroxy-radical:

$$Ph_3\dot{C} + O_2 \rightleftarrows Ph_3CO\dot{O} \ .$$

Bisbiphenyleneallyls (XVIII, R = Ar) are stable in relation to oxygen[25]. Triarylmethyls combine with nitric oxide[118] forming hyponitrites; it has been suggested that this reaction proceeds via a stage involving the formation of nitrones[119].

The peroxide formed when oxygen acts on diarylmethyls is unstable and decomposes with formation of Ar_2CO, Ar_2CHOH, and $Ar_2CHOCHAr_2$.[120] The same products are formed when diarylmethyls react with NO.

The reactions of diaryl- and triarylmethyls with O_2 and NO have been frequently used to obtain thermodynamic data for the dissociation of radical dimers.

Nitrogen dioxide reacts with triphenylmethyl both via the nitrogen and via the oxygen with formation of two products — nitrotriphenylmethane and triphenylmethyl nitrite[118]:

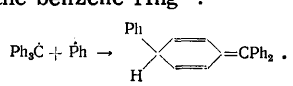
$$Ph_3\dot{C} + O{=}N{-}\dot{O} \leftrightarrow O{=}\overset{+}{\dot{N}}{-}O^- \rightarrow Ph_3C{-}N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O} + Ph_3C{-}O{-}N{=}O \ .$$

On heating, triarylmethyls can abstract hydrogen from certain hydrocarbons, for example from toluene with formation of triarylmethane and triarylbenzylmethane via the mechanism[121]:

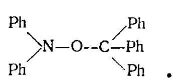
$$Ar_3\dot{C} + PhCH_3 \rightarrow Ar_3CH + Ph\dot{C}H_2 \ ,$$

$$Ar_3\dot{C} + Ph\dot{C}H_2 \rightarrow Ar_3CCH_2Ph \ .$$

Active radicals interact with triarylmethyls, adding to the p-position of the benzene ring[83]:



Aromatic nitroxy-radicals react with triphenylmethyl[122] forming compound (XXIX), while non-aromatic radicals do not[123].



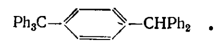
(XXIX)

5. Other Reactions

When dry hydrogen chloride acts on triphenylmethyl in the light, the latter disproportionates to chlorotriphenylmethane and triphenylmethane[9]:

$$2Ph_3\dot{C} + HCl \rightarrow Ph_3CCl + Ph_3CH \ .$$

The reaction with hydrochloric acid yields the so called Ullmann-Barsum hydrocarbon (XXX)[124]. The structure of this compound, initially assumed to be that of hexaphenylethane, was established by Chichibabin[125]:



(XXX)

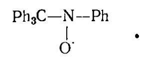
Triarylmethyls react rapidly with halogens, forming triarylchloromethanes[1]. The reaction with iodine is reversible. Bisbiphenyleneallyls react with chlorine and bromine but not with iodine[27]. The reaction of triarylmethyls with sulphur gives rise to triarylmethyl polysulphides[126].

Triarylmethyls can add to a double bond[127], for example 1,4-addition to isoprene takes place[128]:

$$2Ph_3\dot{C} + CH_2{=}C(CH_3){-}CH{=}CH_2 \rightarrow Ph_3CCH_2C(CH_3){=}CH{-}CH_2CPh_3 \ .$$

By adding to benzoquinone, triphenylmethyl forms the bistriphenylmethyl ether of hydroquinone[82].

The reaction of nitrosobenzene with triphenylmethyl yields the stable nitroxy-radical (XXXI)[129]:



(XXXI)

The reaction of triphenylmethyl with benzoyl peroxide results in the formation of tetraphenylmethane, benzoic acid, and its trityl ester[130]. The kinetics of this reaction, which has an ionic mechanism, have been investigated[131].

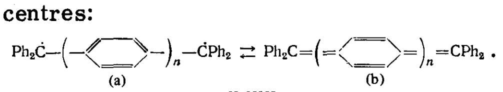
When triphenylmethyl reacts with diazomethane, the main product is hexaphenylpropane[132]:

$$Ph_3\dot{C} + CH_2N_2 \rightarrow Ph_3CCH_2CPh_3 + N_2 \ .$$

In conclusion of the discussion of the chemical properties of triarylmethyls, we shall consider the unusual inertness of the perchloro-derivatives of diarylmethyls and triarylmethyls. These radicals, which were obtained and investigated by Ballester and coworkers[19,39], differ sharply in their properties from other tervalent carbon radicals. As already mentioned above, Ballester's radicals are entirely monomeric in solution and in the solid state. Perchlorotriphenylmethyls do not react with oxygen, nitric oxide, active radicals, benzoquinone, acids (even concentrated acids), alkalis, halogens, phosphines, and phosphites[133]. Perchlorodiphenylmethyl is somewhat less stable, but even this radical surpasses in this respect almost all known triarylmethyls. Perchlorodiphenylmethyl reacts with concentrated nitric acid, forming the corresponding benzophenone, and, on refluxing in toluene, hydrogen is abstracted from the solvent with formation of $(C_6Cl_5)_2CHCl$. The inertness of these radicals can be accounted for by the screening of the reaction centres.

VI. BIRADICALS

Soon after the discovery of triphenylmethyl, attempts were made to synthesise triarylmethyls containing several radical centres:

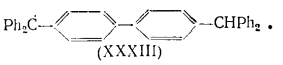


(XXXII)

Compounds of this type can exist both in the triplet biradical form (a) and in the singlet quinonoid form (b). The amount of the biradical form depends on the energy difference between the singlet and triplet levels. For Thiele's hydrocarbon[134] (XXXII, $n = 1$), this energy difference is high (5.3 kcal)[135], as a result of which the compound is diamagnetic[136].

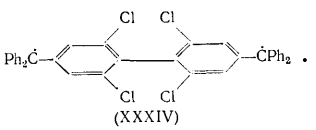
The situation is more complicated with Chichibabin's hydrocarbon[137] (XXXII, $n = 2$). The excitation energy for this compound is 2.5 kcal, i.e. even at room temperature there is a possibility of a thermodynamic equilibrium involving a small amount (1 – 3%) of paramagnetic species. Such a small admixture of paramagnetic species cannot be detected by magnetic methods[138], but has been detected by ESR.[136] However, a new problem arises, which enabled McConnell to formulate the so-called "biradical paradox"[139]. The point is that theory predicts $J = 15 \times 10^6$ MHz for electron – electron interaction in biradicals of the type of Chichibabin's hydrocarbon, while the experimental value is only 70 MHz. The problem was solved by analysing the ENDOR spectra[140].

It was found that the ESR spectra of solutions of Chichibabin's hydrocarbon are due to the presence of the monoradical (XXXIII), which is formed from (XXXII, $n = 2$) following the abstraction of a hydrogen atom from the solvent:



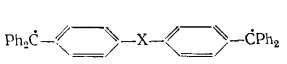
(XXXIII)

The breakdown of the coplanarity of the benzene rings due to the presence of *ortho*-substituents can stabilise the biradical form[141, 142]. Although (XXXIV) does give an ESR spectrum in the solid state, it too is not a biradical[143]:



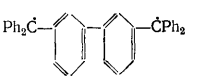
(XXXIV)

The introduction of non-conducting bridges such as O and CH_2 makes it possible to obtain stable hydrocarbon biradicals (XXXV)[136]:



X=O, $(CH_2)_n$

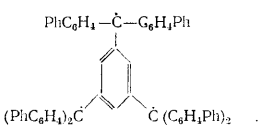
(XXXV)



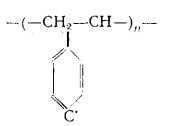
(XXXVI)

Schlenk's hydrocarbon (XXXVI), which is incapable of giving rise to quinonoid forms, also has a triplet ground state[144]. In solution (XXXVI) is largely associated[145] and its ESR spectrum is additionally complicated by the presence of monoradicals[146].

Triradicals (XXXVII)[147] and polyradicals (XXXVIII)[148] of the triarylmethyl series were obtained. In solution these radicals are probably associated:

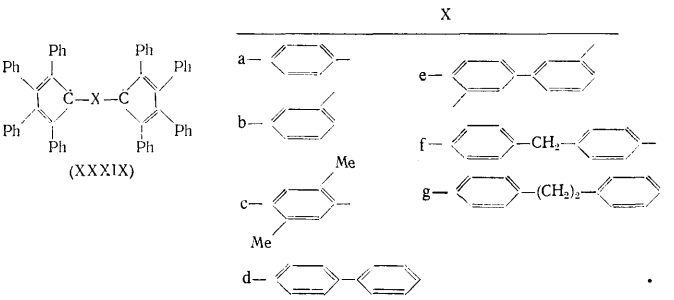


(XXXVII)



(XXXVIII)

In contrast to the compounds described above, the biradicals (XXXIX, $a-g$ are not associated[149]. All these, with the exception of (XXXIXa), have a triplet ground state; although (XXXIXa) is in fact paramagnetic, it is not a biradical:



(XXXIX)

The chemical properties of biradicals and polyradicals differ little from those of the monoradicals.

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