maleate (10%, 8% yield). The last two fractions were essentially pure exo ester, bp 123° (22 mm), $n^{24}D$ 1.4675 (lit.[37] bp 109–110° (18 mm)).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 71.39; H, 9.59. Found: C, 71.41; H, 9.62.

The endo ester was isolated by gas chromatography and purified by short-path distillation.

Anal. Calcd for $C_{10}H_{16}N_2$: C, 71.39; H, 9.59. Found: C, 71.39; H, 9.74.

The infrared spectrum of the endo ester is very similar to that of the exo isomer with slight differences in the fingerprint region. Thus, a single band at 950 cm^{-1} in the endo isomer is split into a doublet in the exo compound; a band at 840 cm^{-1}, present in the exo isomer, is absent in the endo isomer, which in turn shows a band at 815 cm^{-1}, absent in the exo isomer. The two isomers, however, are well separated by gas chromatography on a silicone XF-1150 column at 135°; relative retention times: endo, 15.9 min; exo, 20.9 min.

Inert Carbon Free Radicals. I. Perchlorodiphenylmethyl and Perchlorotriphenylmethyl Radical Series[1,2]

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Abstract: A number of extremely stable chlorocarbon free radicals derived from diphenylmethyl and triphenylmethyl are here described and examined. They are obtained either by dechlorination of alkaromatic chlorocarbons or oxidation of the corresponding perchlorocarbanions. Perchlorodiphenylmethyl (PDM), perchloro-4-phenyldiphenylmethyl (PPDM), perchloro-4,4′-diphenyldiphenylmethyl (PDDM), perchlorotriphenylmethyl (PTM), perchloro-4-phenyltriphenylmethyl (PPTM), perchloro-4,4′-diphenyltriphenylmethyl (PDTM), and perchloro-4,4′,4′′-triphenyltriphenylmethyl (PTTM) have been obtained. Perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-ylene (PTBT), a biradical, has also been synthesized. Some of these radicals (PTM series) have in the air half-lives of decades, and withstand typical radical reagents (nitric oxide, hydroquinone, quinone) and even highly aggressive chemical species (concentrated sulfuric and nitric acids, sodium hydroxide, halogens) with little or no alteration. Also, they possess a remarkably high thermal stability (up to 300°). They are all completely disassociated both in solid form and in solution. The epr, uv-visible, and ir spectra of these radicals and related quasi-perchloro compounds are examined. Application of Ballester, Riera, and Spialter spectral correlation for benzene derivatives shows that in these radicals the band found in the vicinity of 300 nm corresponds to the ^1L_b electronic transition (secondary band). Evidence is presented showing the steric nature of these radicals' inertness. The synthesis of a number of related new compounds is here described.

Since Gomberg reported in 1900 the detection of the first free radical a great number of stable radicals have been detected and even isolated.[3]

The carbon free radicals are highly reactive species. Nevertheless, some of them show a remarkable stability, the best example being, possibly, Kuhn's 2-(*p*-biphenylyl)bisbiphenylenylallyl[4] that in solution has a half-life of 10 hr, does not react under mild conditions with some typical radical traps (hydroquinone or iodine), and withstands temperatures close to 100°.

Thermal and chemical stabilities of free radicals are governed by two main factors: resonance and steric hindrance.[3] Since the alkaromatic chlorocarbons show great steric effects (inhibition of resonance, shielding, strain, and distortion),[5,6] which frequently cause high thermal stability and chemical inertness,[7] it seemed promising to attempt the synthesis of certain alkaromatic chlorocarbon free radicals.

Evidence for the simplest radical of this type—the perchlorobenzyl radical—was reported by Ballester and coworkers in the chemistry of perchlorotoluene (reaction with iodide[8] or stannous ions,[9] pyrolysis,[10] photolysis[11]).

The preparation—although in a very low yield—of perchlorodiphenylmethane (I) by perchlorination of benzophenone chloride with reagent BMC[12,13] allowed, under conditions similar to those leading to the formation of transient perchlorobenzyl, the synthesis of radical perchlorodiphenylmethyl (PDM).[14]

$$\underset{\text{I}}{(C_6Cl_5)_2CCl_2} \xrightarrow{SnCl_2} \underset{\text{PDM}}{(C_6Cl_5)_2\dot{C}Cl}$$

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(1) This research has been sponsored by the Aerospace Research Laboratories (Wright-Patterson A. F. B., Ohio) through the European Office of Aerospace Research, under Contract AF 61 (052)-749.

(2) Some results here reported have been presented before the IUPAC Symposium on "Free Radicals in Solution" (Gomberg Symposium), University of Michigan, Ann Arbor, Mich., Aug 1966.

(3) M. Ballester, *Pure Appl. Chem.*, **15**, 123 (1967).

(4) R. Kuhn and F. A. Neugebauer, *Monatsh. Chem.*, **95**, 3 (1964).

(5) M. Ballester, *Bull. Soc. Chim. Fr.*, 7 (1966).

(6) M. Ballester, *et al.*, "The Chlorocarbons. Anthology I," L. Spialter, Ed., Aerospace Research Laboratories (USAF), ARL-67-0167, 1967.

(7) M. Ballester, J. Castañer, and J. Riera, *J. Amer. Chem. Soc.*, **88**, 957 (1966).

(8) M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, **6**, 109 (1959).

(9) J. Riera-Figueras, Doctoral Thesis, Universidad de Barcelona, April 12, 1962.

(10) M. Ballester, C. Molinet, and J. Rosa, *An. Real. Soc. Espan. Fis. Quim., Ser. B*, **57**, 393 (1961).

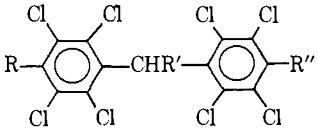
(11) M. Ballester and J. Castañer, *ibid., Ser. B*, **62**, 397 (1966).

(12) M. Ballester, C. Molinet, and J. Castañer, *J. Amer. Chem. Soc.*, **82**, 4254 (1960).

(13) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1131.

(14) M. Ballester and J. Riera, *J. Amer. Chem. Soc.*, **86**, 4505 (1964), preliminary communication.

Table I



Compd	R	R′	R″	Calcd, % C	Calcd, % Cl	Found, % C	Found, % Cl	Mp, °C	Nmr, τ	Yield, %
II	Cl	Cl	Cl	28.5	71.3	28.5	71.0	231–233	2.85[a]	81.6
III	C_6Cl_5	Cl	Cl	29.9	70.0	29.8	70.1	295–298	2.75[a]	71.8
IV	C_6Cl_5	Cl	C_6Cl_5	30.8	69.1	30.8	68.8	310–316	2.65[a]	90.6
V	Cl	C_6Cl_5	Cl	29.9	70.0	30.0	69.9	320 dec	3.00[b]	92.7
VI	C_6Cl_5	C_6Cl_5	Cl	30.8	69.1	30.8	69.3	410 dec	2.70[b]	75.8
VII	C_6Cl_5	C_6Cl_5	C_6Cl_5	31.3	68.6	31.4	68.8	400 dec	2.80[a]	54.0
VIII	C_6Cl_5	$C_6Cl_5C_6Cl_4$	C_6Cl_5	31.6	68.3	31.9	68.2	280–285		64.4
IX				35.9	63.7	35.9	63.8	360 dec		88.2
X				31.5	68.4	31.7	68.4	400 dec		49.3

[a] In carbon tetrachloride. [b] In deuteriochloroform.

This result prompted us to attempt the preparation of other perchlorinated radicals related to diphenylmethyl and triphenylmethyl by alternative, more convenient paths, *i.e.*, through α*H*-quasi-perchlorodi- and -triphenylmethanes.[15] These compounds do not possess any significant molecular strain and, therefore, the relevant ring perchlorination is not subjected to steric hindrance, as that leading to the perchlorinated precursors.

Results

α*H*-Quasi-perchlorodi- and -triphenylmethanes. Ring perchlorination of diphenylmethanes and triphenylmethanes with reagent BMC[12,13] has resulted in the synthesis of α*H*-undecachlorodiphenylmethane (II), α*H*-pentadecachloro-4-phenyldiphenylmethane (III), α*H*-nonadecachloro-4,4′-diphenyldiphenylmethane (IV) (see Scheme I), and α*H*-pentadecachlorotriphenylmethane (V), α*H*-nonadecachloro-4-phenyltriphenylmethane (VI), α*H*-tricosachloro-4,4′-diphenyltriphenylmethane (VII), and α*H*-heptacosachloro-4,4′,4″-triphenyltriphenylmethane (VIII) (see Scheme II). Similarly, α*H*,α′*H*-dodecachlorotriptycene (IX) and α*H*,α′*H*-octaicosachloro-α,α,α′,α′-tetraphenylbi-*p*-tolyl (X) have been obtained by chlorination of triptycene and α,α,α′,α′-tetraphenylbi-*p*-tolyl, respectively. The characterization of these α*H*-quasi-perchloro compounds has been carried out by carbon–hydrogen and chlorine analyses, and spectra (Table I).

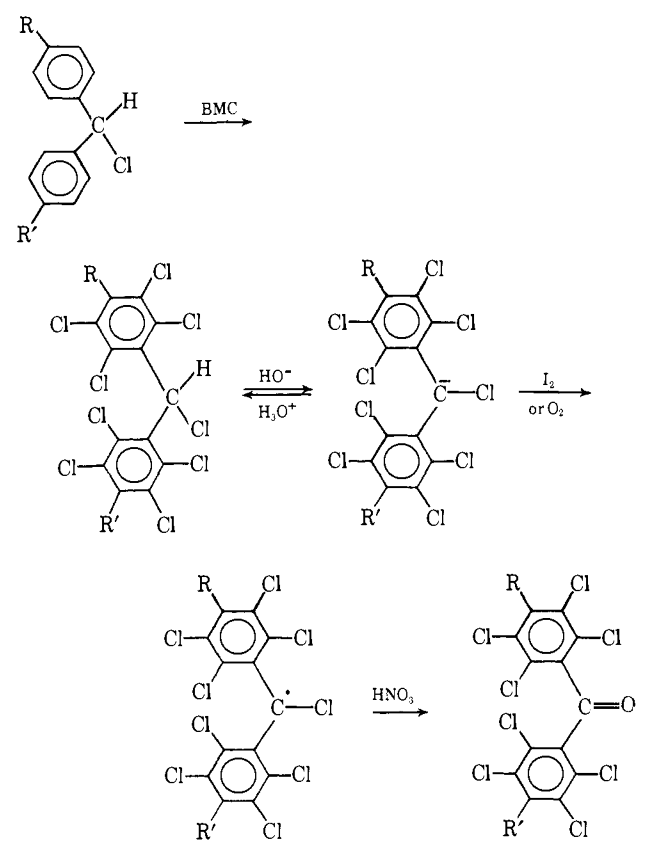
α*H*-Undecachlorodiphenylmethane has been converted with oleum into bispentachlorophenylcarbinol and with diglyme into α*H*,α*H*-decachlorodiphenylmethane.

Perchlorodi- and -triphenylcarbanions. All α*H*-quasi-perchlorodi- and -triphenylmethanes react almost quantitatively with sodium or potassium hydroxide in ethyl ether–DMSO giving their perchlorocarbanions. The solutions of perchlorodiphenylcarbanions are intense blue while those of perchlorotriphenylcarbanions are wine red in color. Their visible spectra present intense band maxima at 600 and 510 nm, respectively.

Both types of carbanions show remarkable features. The perchlorodiarylcarbanions are by far the most stable α-chlorocarbanions known.[3] In solvents containing DMSO they withstand room temperature and above without chloride ion elimination, although they oxidize readily. The perchlorotriphenylcarbanions possess a good stability toward oxygen.

A solution of a perchlorotriphenylcarbanion in ether–DMSO can be diluted with water without being hydrolyzed completely (color). This indicates that the corresponding α*H*-quasi-perchloro compounds are remarkably strong acids (see Discussion). Treatment with diluted aqueous hydrochloric acid yields the latter

Scheme I



αH compounds: II, R = R′ = Cl; III, R = Cl, R′ = C_6Cl_5; IV, R = R′ = C_6Cl_5
radicals: PDM, R = R′ = Cl; PPDM, R = Cl, R′ = C_6Cl_5; PDDM, R = R′ = C_6Cl_5
ketones: XIII, R = R′ = Cl; XVI, R = Cl, R′ = C_6Cl_5; XVII, R = R′ = C_6Cl_5

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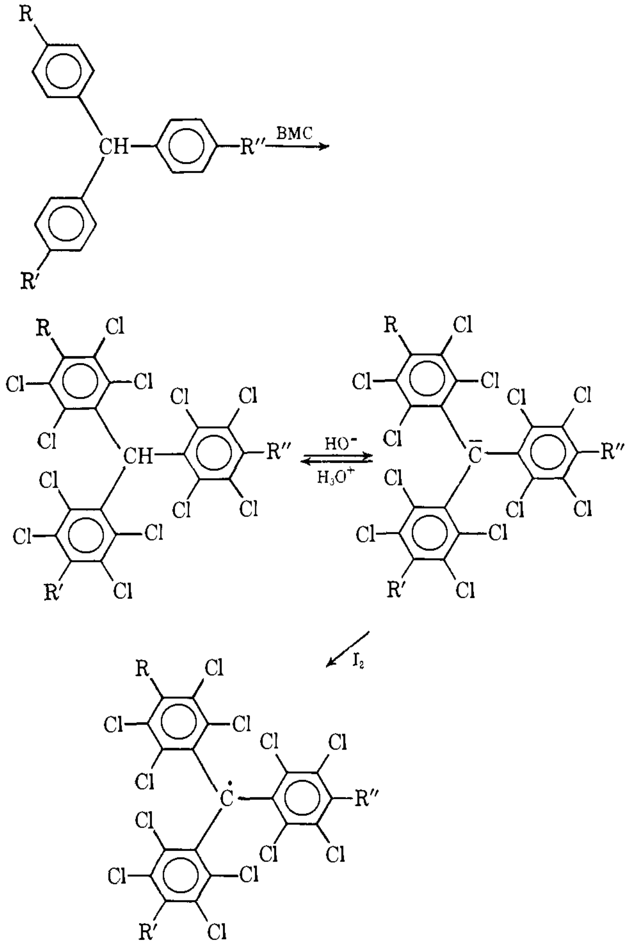
(15) Quasi-perchloro indicates substitution of all hydrogens by chlorines *except* those indicated by the preceding term (here αH). See also ref 16.

(16) *Chem. Soc., Spec. Publ.*, No. 14, 191 (1961).

immediately and quantitatively. In this connection it should be mentioned, however, that triptycene IX (Scheme III) is not attacked by strong bases in warm ethyl ether–DMSO or THF–DMSO.

Scheme II



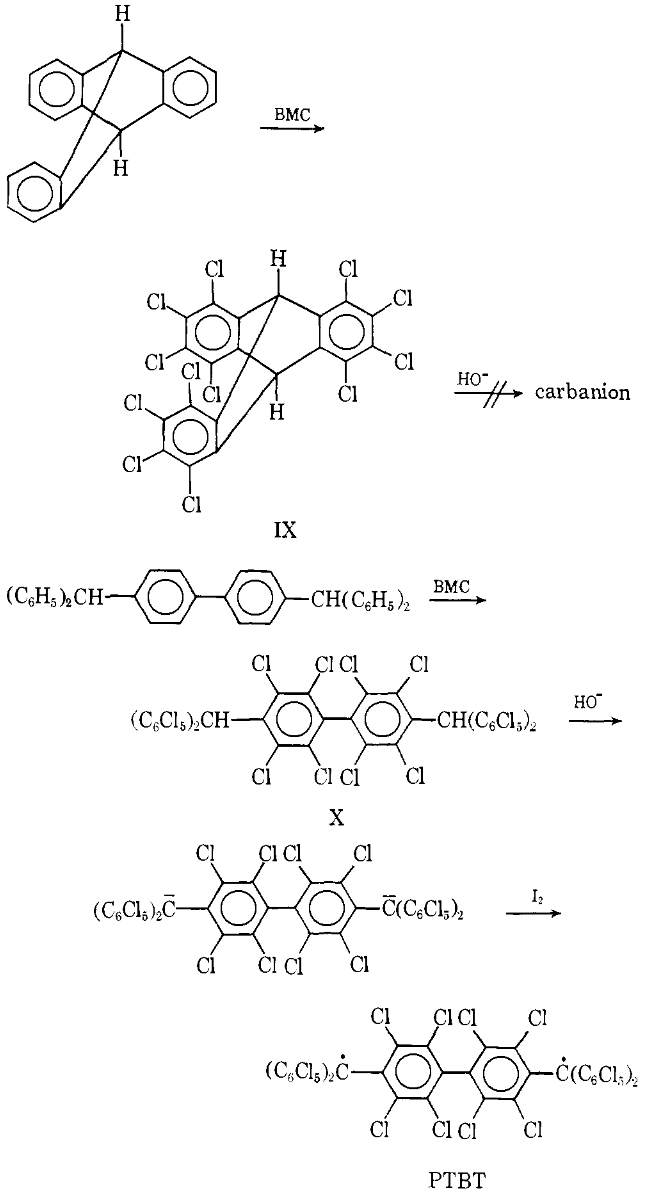
αH compounds: V, R = R' = R'' = Cl; VI, R = R' = Cl; R'' = C_6Cl_5; VII, R = Cl, R' = R'' = C_6Cl_5; VIII, R = R' = R'' = C_6Cl_5
radicals: PTM, R = R' = R'' = Cl; PPTM, R = R' = Cl; R'' = C_6Cl_5; PDTM, R = Cl, R' = R'' = C_6Cl_5; PTTM, R = R' = R'' = C_6Cl_5

Perchlorodi- and -triphenylmethyl Radicals. The perchlorodiarylcarbanions react rapidly with iodine or oxygen to give the perchlorodiphenylmethyl radicals. In this way perchlorodiphenylmethyl (PDM), perchloro-4-phenyldiphenylmethyl (PPDM), and perchloro-4,4'-diphenyldiphenylmethyl (PDDM) have been synthesized. Some data on these radicals are listed in Table II.

The perchlorotriphenylcarbanions oxidize with iodine to the corresponding radicals, although at a much lower rate than the perchlorodiphenylcarbanions. In this fashion perchlorotriphenylmethyl (PTM), perchloro-4-phenyltriphenylmethyl (PPTM), perchloro-4,4'-diphenyltriphenylmethyl (PDTM), and perchloro-4,4',4''-triphenyltriphenylmethyl (PTTM) have been prepared (Table II). X gives perchloro-α,α,α',α'-tetraphenylbi-*p*-tolyl-α,α'-ylene (PTBT), a biradical.

The number of spins per mole in the solid state, calculated from magnetic susceptibility data, indicates that these radicals are completely disassociated (Table II). Data obtained from osmometry and electronic absorption spectrum (Beer's law) in solution has led to the same conclusion.

Scheme III



The synthesis of PDM has also been effected starting from perchlorodiphenylmethane (I) by reduction with stannous chloride in ethyl ether (48% yield),[14] ferrous chloride in ethyl ether (95%) or in chloroform–DMSO (85%), or mercury in ethyl ether–DMSO and ultrasonics (46%).

I has been obtained in a 9.1% yield by ring chlorination of benzophenone chloride with reagent BMC,[12,13] along with perchlorofluorene (XI) and 2*H*,2'*H*-decachlorodiphenylmethane (XII) in comparable yields (6.9 and 8.6%, respectively). I, XI, and XII have been characterized as usual, and by conversion with oleum into perchlorobenzophenone (XIII, ~100%), perchlorofluorenone (XIV, 77%), and *oH*,*o'H*-octachlorobenzophenone (XV, 56%), respectively (Scheme IV).

The stability of the free radicals here described is much higher than that of any carbon free radical reported previously. PDM, the least stable of them all, in solution, in the air, and at room temperature has a half-life of 2–3 days (10 hr for Kuhn's radical[4]). Under

Table II

Radical	Color	Mp, °C (dec)	Molecular weight[a] Found	Calcd	Spins per mole ($\times 10^{23}$)[b]	*Anal.* Calcd, % C	Cl	Found, % C	Cl	Yield, %
PDM	Orange-red	190	563	546	5.0	28.6	71.4	28.7	71.4	74
PPDM	Orange-yellow	255–260	792	760	6.3	30.0	70.0	29.9	69.7	76
PDDM	Orange-yellow	280–300	1018	973.5	5.9	30.8	69.2	30.9	69.1	73
PTM	Deep red	305	771	760	6.0	30.0	70.0	30.6	70.1	87
PPTM	Crimson	340–346	*c*	974	5.0	30.8	69.2	31.0	69.4	77
PDTM	Crimson	338–342	1278	1188	6.4	31.3	68.7	31.4	68.7	91
PTTM	Purple	316–322	*c*	1401	5.6	31.7	68.3	31.8	68.6	65
PTBT	Purple	250	*c*	1449.5	11.0	31.5	68.5	31.5	68.5	65

[a] Estimated error, 4%. [b] Magnetic susceptibility measurements in solid state. [c] Lack of solubility in suitable media precluded measurement.

Scheme IV

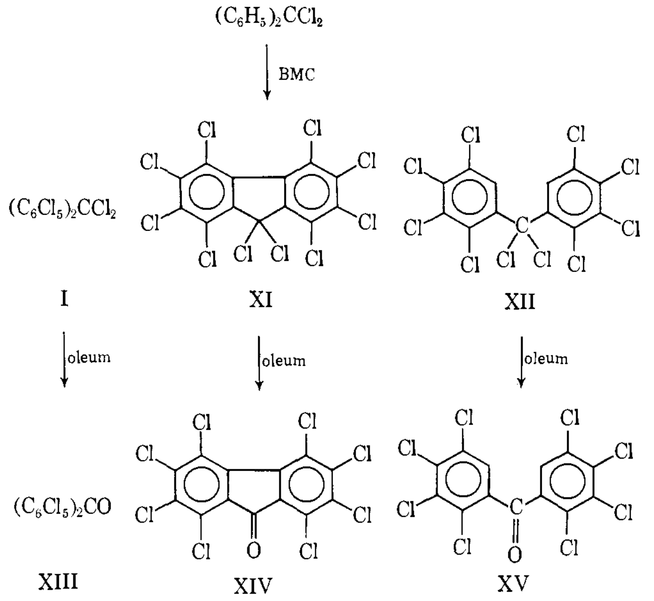


Table III. Chemical Stabilities of the PDM Radicals in the Dark and under Argon

Reagent	Radical	Solvent	Reaction times, days	Recovery,[c] % (half-life, days)
Br_2[a]	PDM	CCl_4	3.5	83.5
	PPDM	CCl_4	2	55.4
	PDDM	CCl_4	6	84.4
Cl_2[a]	PDM	CCl_4	1	87.7
	PPDM	CCl_4	1	89.8
	PDDM	CCl_4	1	84.4
HNO_3[a] (concd)	PDM		2	84.1
	PPDM		4	35
	PDDM		2	26
Toluene[b]	PDM		1	0
	PPDM		1	0
	PDDM		1	0
O_2 (air)	PDM	C_6H_{12} or CCl_4	Slow	(3)
	PPDM	CCl_4	Very slow	(13)
	PDDM	CCl_4	Very slow	(14)

[a] Room temperature. [b] Reflux temperature. [c] The yields have been ascertained by combining weight and absorptivity for bands C or D in a suitable solvent. Considering the size of the sample (~0.1 g), at least a loss of 1–5% should be allowed for product isolation and handling.

the same conditions, the half-lives for PPDM and PDDM are, respectively, 13 and 14 days, as ascertained by quantitative spectral measurements. Precision spectral measurements in dilute solution, in the air, and at room temperature on the radicals of PTM series for periods of months have failed to detect any alteration. It is concluded, therefore, that *the half-lives of these radicals are of the order of decades*. In solid state, they can be kept for years in the air with little (PDMs) or no (PTMs) alteration.

The stabilities of these radicals toward a variety of chemical agents have been tested. Thus, it has been found that the PDMs and the PTMs are perfectly stable (room temperature, dark, and argon) *vs.* water (2–4 days), cyclohexane (4–16 days), carbon tetrachloride (1 day–2 months), chloroform (6 days–2 months), hydroquinone (6 days–2 months; CCl_4), *p*-quinone (7–14 days; CCl_4), nitric oxide (2.5 hr; CCl_4), powdered sodium hydroxide (2–14 days; ether or CCl_4), and concentrated sulfuric acid (2 days–2 months).

While the PTMs are also inert toward bromine (3 days–2 months; CCl_4), chlorine (2–7 days; CCl_4), boiling toluene (8–40 hr), or concentrated nitric acid (2 days), the PDMs, although very stable, under the same conditions are slowly attacked by these reagents (Table III). The reaction with boiling toluene gives, among other products, the αH-quasi-perchlorodiphenylmethanes (PDM, 56%; PPDM, 64%; PDDM, 54%). The reaction with concentrated nitric acid yields the corresponding ketones, *i.e.*, perchlorobenzophenone (XIII, 58%), perchloro-4-phenylbenzophenone (XVI, 77%), and perchloro-4,4′-diphenylbenzophenone (XVII, 52%). It must be pointed out that although biradical PTBT belongs structurally to the PTM series it is, nevertheless, sensitive to concentrated nitric acid.

Therefore, the radicals of the PTM series are extremely stable or completely inert toward aggressive chemical species and typical radical reagents. It has also been found that there are no scavengers for short-lived free radicals.[17] Their thermal stability in solid form is also remarkable; they decompose in the air around or beyond 300°.

Consequently, *the stability of the radicals of the PTM series is, in the broadest sense, clearly greater than that of the majority of "normal" tetravalent carbon compounds*. For this reason, various correspondents and the authors of this paper prefer to call them *inert free radicals* rather than just stable free radicals. However, the perchloro radicals react with potassium in ethyl ether and with hydroxide ion in mixtures *containing DMSO* giving a high yield of the corresponding perchlorocarbanions.

[17] P. D. Bartlett, private communication.

Discussion

Electronic Absorption Spectra. Examination of the relevant electronic absorption spectra shows that the αH-quasi-perchlorodi- and -triphenylmethanes are nondistorted benzene derivatives. They consist of a medium-intensity secondary (^1L_b) band ~300 nm, with two maxima 10 nm apart, and an intense primary band group ~210–225 nm.[18,19]

These results indicate, first of all, that in compounds III, IV, VI, VII, VIII, and X no biphenyl chromophore exists, since it would cause a high-intensity (conjugation) band to appear near 300 nm. Consequently, there occurs strong inhibition of resonance due to steric interaction among the four central *o*-chlorines causing the benzene rings in the biphenyl system to be almost perpendicular to each other. These rings are, therefore, spectroscopically independent.[7,20]

The conjugation moment for the constellation[19] 1,3,2-$Cl_2(CHClC_6Cl_5)$ and 1,3,2-$Cl_2[CH(C_6Cl_5)_2]$ can be easily ascertained from the maximum absorptivities of the secondary band for II ($\bar{\epsilon}$ 1270). Their values are −21.7 and −16.8, respectively.[21,22]

On the other side, from perchlorobiphenyl ($\bar{\epsilon}$ 1080) a constellation migration moment of −19.7 for 1,3,2-$Cl_2(C_6Cl_5)$ is obtained. From the above three moments, it is possible to calculate, by vector addition, the absorptivities of the remaining six αH-quasi-perchloro compounds. The perchlorophenyl ring is regarded not only as substituent in a benzene ring but also as a chromophore possessing, therefore, its own absorption.[23]

Table IV. Absorptivities $\bar{\epsilon}$ for the Secondary (^1L_b) Band of the αH-Quasi-perchloro Compounds

Compd	Obsd	Calcd	Error, %
II[a]	1240	(1240)	(0.0)
III[a]	2450	2566	4.1
IV[a]	3900	3892	−0.2
V[a]	1270	(1270)	(0.0)
VI[a]	2900	2596	−11
VII[a]	3790	3923	3.5
VIII[a]	4840	5250	8.5
X[b]	4250	4112	−3.2

[a] In cyclohexane. [b] In chloroform.

The electronic absorption spectrum of *the radicals* shows four bands (A, B, C, and D) found around 215, 290, 380, and 500 nm (Table V, Figure 1).

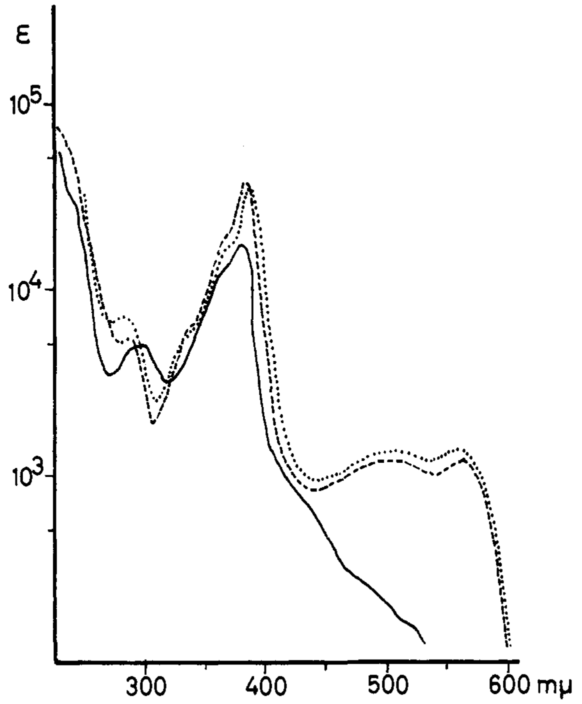


Figure 1. Electronic absorption spectra of radicals: ——, PDM; – – – – – –, PTM; · · · · · ·, PTBT.

Notice that within each series both wavelength and absorptivity of bands C and D vary little with substitution. This is regarded, consequently, as due to the radical character and shows, once more, the absence of biphenyl delocalization. This fact is particularly evident in the case of biradical PTBT, the whole spectrum ($\epsilon/2$) of which is almost coincident with that of PTM (Figure 1).

Bands C and D correspond to those of triphenylmethyl radical[24,25] found at 340 and 510 nm. Although substituents displace them bathochromically, however, the existence of steric inhibition of resonance due to ortho substitution shifts them in the opposite direction. Accordingly, they are found not far from those of unsubstituted trityl radical. In this connection, it is mentioned that in tri-*o*-tolylmethyl radical band B is just a shoulder at about 450 nm.[25]

Conversely, band B varies much with substitution. Since this band is riding on a slope of band A its true maximum absorptivity can only be ascertained approximately. The values are given in Table V, in parentheses. The maximum relative error of this estimation is, nevertheless, not significantly greater than 10%.

The position and substitution changes for band B suggest the possibility of its being the "secondary" (^1L_b) band of benzene derivatives. The constellation migration moments of 1,3,2-$Cl_2(\dot{C}ClC_6Cl_5)$ and 1,3,2-$Cl_2[\dot{C}(C_6Cl_5)_2]$, calculated from PDM and PTM, are −50.0 and −39.6, respectively. From these values, the following absorptivities for band B are obtained: PDM (3500); PPDM, 4828; PDDM, 6156; PTM (4000); PPTM, 5330; PDTM, 6657;.PTTM, 7986; PTBT, 4788 (compare with Table V). Since the agreement with the observed values is excellent the assignment is, therefore, well established.

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(18) M. Ballester and J. Castañer, *J. Amer. Chem. Soc.*, **82**, 4259 (1960).

(19) M. Ballester, J. Riera, and L. Spialter, *ibid.*, **86**, 4276 (1964).

(20) M. Ballester and J. Riera, unpublished.

(21) The constellation moment "*m*" is obtained from the expression

$$\frac{1}{n}\bar{\epsilon} = 40\,m - 250$$

This is so because no contribution is expected from the constellation formed by the chlorines in the 4, 5, and 6 positions of the benzene rings. Factor $1/n$ takes care of the fact that "*n*" equivalent rings are involved.

(22) The sign for these moments is usually ascertained from derivatives having substituents with well-established signs.[19] A negative sign corresponds in general to an electron-attracting substituent.

(23) In these calculations III is regarded as a 1-phenyl-4-benzylbenzene. Therefore, the resultant moment (38.4) corresponding to the central benzene ring is obtained by adding the moments of constellations 1,3,2-$Cl_2(C_6Cl_5)$ and 1,3,2-$Cl_2[CHCl(C_6H_5)]$. The absorptivity, calculated from expression in ref 19 (n = 1), is therefore 1406. Since the absorptivities of these constellations are, respectively, one-half that of perchlorobiphenyl (540) and one-half that of II (620), the total absorptivity ϵ should be 2566 (Table IV).

(24) T. L. Chu and S. I. Weissman, *J. Chem. Phys.*, **22**, 21 (1954).

(25) W. Theilacker and M. L. Wessel-Ewald, *Justus Liebigs Ann. Chem.*, **594**, 214 (1955).

Table V. Electronic Absorption Maxima of the Radicals

Radical	Band A λ, nm	Band A $\epsilon \times 10^{-3}$	Band B λ, nm	Band B $\epsilon \times 10^{-3}$ [c]	Band C λ, nm	Band C $\epsilon \times 10^{-3}$	Band D λ, nm	Band D $\epsilon \times 10^{-3}$
PDM[d]	225		300	5.29 (3.5)	380	17.5	500	0.20
PPDM[d]	215	100	300	6.39 (4.5)	381	17.1	500	0.29
PDDM[d]	213	140	297	7.85 (6.0)	381	17.1	500	0.39
PTM[d]	220	72.8	283	5.46 (4.0)	382	37.2	510, 562	1.19, 1.20
PPTM[a,e]			280	6.85 (5.0)	384	36.3	500, 560	1.20, 1.17
PDTM[a,e]			280	7.98 (6.0)	384	36.4	500, 560	1.22, 1.13
PTTM[a,e]			286	10.00 (8.0)	382	44.4	500, 550	1.36, 1.20
PTBT[a,b,e]			282	6.92 (4.5)	386	37.4	510, 560	1.33, 1.35

[a] The insolubility of this compound in solvents which are transparent in the 200–250-nm region has prevented us from taking its band A data. [b] The absorptivity is referred to here as 0.5 mol. [c] The figures in parentheses are values obtained by subtracting an estimated absorption contribution from the neighboring bands. [d] In cyclohexane. [e] In chloroform.

The rather high moment moduli for those constellations is accountable in terms of lone-electron delocalization.[19] Steric interaction is probably not a major factor since the moment moduli for the more strained constellations 1,3,2-$Cl_2(CHClC_6Cl_5)$ and 1,3,2-$Cl_2[CH(C_6Cl_5)_2]$ are moderate, about one-half as great (21.7 and 16.8). It is mentioned that the moment modulus for constellation 1,3,2-$Cl_2(CHCl_2)$ is 31.2. Notice that 50/39.6 = 1.26 (moduli ratio for radicals), and 21.7/16.8 = 1.29 (moduli ratio for the α*H*-quasi-perchloro compounds) are about the same.

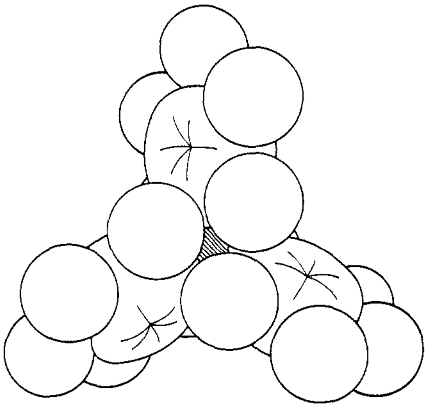


Figure 2. Space-filling model of perchlorotriphenylmethyl radical.

Band A is tentatively regarded as the "primary band" of benzene derivatives.[18,19]

Comparison of absorptivities in the PDM and PTM series concerning bands, B, C, and D leads to the following conclusions.

(1) The constellation migration moment modulus is greater in the PDMs (50.0 *vs.* 39.6). This indicates that perchlorophenylmethyl group is a stronger electron-attracting substituent than the perchlorodiphenylmethyl.

(2) The absorptivities of bands C and D for the PDMs are, respectively, about one-half and one-fourth as high as those for the PTMs. These facts are probably due to the extent of lone-electron delocalization (number of active benzene rings) which is higher in the latter series, lone-electron delocalization per active ring being assumed roughly constant (see epr discussion).

(3) Since the wavelength for the maximum of band C in both series is the same the separation between the relevant ground and excited states should also be the same. In very general terms, it is assumed that the main factor here is lone-electron delocalization per ring.

Infrared Spectra. The α*H*-quasi-perchloro compounds present infrared spectra which appear to be normal among perchlorobenzene derivatives. In the diphenyl- and triphenylmethanes the C–H stretching peaks are found around 2960 and 2920 cm^{-1} (very weak). Benzenoid peaks show around 1525 (weak) and 1330 cm^{-1} (strong), corresponding to those found at 1600 and 1500 cm^{-1} in oligosubstituted benzenes.

Apparently the infrared spectra of the radicals have no special features that can be traced to their radical (trivalent carbon) character. The only noticeable difference is a slight bathrochromic shift of the first (weak) benzenoid peak which is found here around 1500 cm^{-1}. (In PPDM and PDDM it is not detected.)

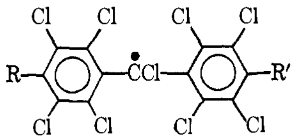
The α*H*-quasi-perchloro compounds and the perchloro radicals of both series containing the biphenyl system show a peak at 13.2 μ (758 cm^{-1}) which is also found in related derivatives.[7] As expected, its intensity increases in both the α*H* compounds and radicals with the number of 4-perchlorobiphenyl groups.

The simplicity of the spectrum of PTM is remarkable. This is due to the high symmetry (one threefold axis and three twofold axes; point group D_3) of its helicoidal configuration. Figure 2 shows a top view (along the threefold axis of symmetry) of the PTM propeller-shaped model.

Electron Paramagnetic Resonance. For the purpose of spin counting the magnetic susceptibility measurements have been preferred to the epr technique—which compares absorption intensities with standard samples—since the latter involves, in the present cases, a much higher error. However, both techniques have also been used for PDM and PTM, and their results are in agreement.

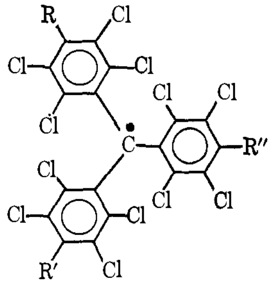
The epr data at room temperature in carbon tetrachloride solution for all radicals here described are pre-

Table VI. Epr Data on Radicals



Radical	R	R′	g value	α-Cl splitting No. of lines	α-Cl splitting a, MHz	^{13}C splittings, MHz α	^{13}C splittings, MHz Aromatic
PDM	Cl	Cl	2.0055	4	6.1	102.5	36.5
PPDM	C_6Cl_5	Cl	2.0055	4	6.2	104	32
PDDM	C_6Cl_5	C_6Cl_5	2.0050	4	6.1	100	31

Table VII. Epr Data on Radicals



Radical	R	R′	R″	g value	Line width, MHz	^{13}C splittings, MHz α	^{13}C splittings, MHz Aromatic
PTM	Cl	Cl	Cl	2.0026	4.0	82.5	30, 35.5 (sh)
PPTM	C_6Cl_5	Cl	Cl	2.0025	3.7	82.5	29.5, 34 (sh)
PDTM	C_6Cl_5	C_6Cl_5	Cl	2.0027	3.2	83.5	29.5, 34.5 (sh)
PTTM	C_6Cl_5	C_6Cl_5	C_6Cl_5	2.0026	2.5	83.5	28.0, 34.5,
PTBT				2.0028	3.6	81.5	26.5 (sh), 37

sented in Tables VI and VII, along with those for PDM and PTM which have recently been examined.[26]

The radicals of the PDM series present a quadruplet which originates from coupling with the α-chlorine nucleus (spin $^3/_2$). The g value is around 2.0050, higher than that for the free electron, a fact that is interpreted as due to interaction with the α-chlorine which has a significant spin-orbit coupling.

The hyperfine splitting caused by the α-chlorine is around 6 MHz. There is no evidence of interaction with the aromatic chlorines other than, possibly, band broadening (~5 MHz).

As for the PTM series, including PTBT, only one peak is found as expected. Factor g is here ~2.0025, a normal value for trivalent carbon radicals.

With a much higher gain pairs of symmetrical satellite bands appear. In the case of the PDMs two pairs of quadruplets with hyperfine splittings of about 100 and 35 MHz are found. These two pairs have the same internal splitting as the central quadruplet which is about 200 times as intense as the 100-MHz quadruplets. The latter should therefore be assigned to spin coupling of the lone electron with the α-^{13}C nucleus.[26]

The 35-MHz quadruplets are more intense and, consequently, they are regarded as due to aromatic ^{13}C nuclei. The ratios of intensities between these and the α quadruplets (see later) are PDM, 7; PPDM, 13; PDDM,—. Because of overlapping with the central quadruplet, the intensity corresponding to the aromatic carbons cannot be ascertained accurately.

In the PTM series, two pairs of weak, symmetrical satellite peaks around 80 and 30 MHz are found. Also, on the basis of its intensity and coupling constants they are assigned to the α and aromatic ^{13}C's respectively.

Three facts prevent, however, calculation of reliable ^{13}C absorption intensity ratios: (a) some overlapping of the aromatic ^{13}C with the main peak; (b) partial cancellation within the aromatic ^{13}C signal because of the presence of two overlapping (about 5 MHz apart) peaks; (c) the width of the peaks to be compared can be considerably different; for example, while that for the α-^{13}C grows gradually larger going from PTM to PTTM (4.2–5.9 MHz) that of the main peak decreases (4.0–3.6 MHz) (Table VII).

As for the ratio I (aromatic ^{13}C)/I(α-^{13}C), because of (a) and (b) the apparent values should be smaller than the actual ones. However, on account of (c) they should be larger. Some tentative calculations trying to incorporate such factors indicate that in all cases the ratio is of the order of 10. This value is consistent with the assumption that the 30-MHz signal is due to coupling with three ^{13}C per ring bonded to the trivalent carbon, probably the two ortho and the bridgehead carbons.[26]

The gradual narrowing of the main peak is found also in the aromatic ^{13}C peaks. Consequently, in PTTM the two 30-MHz components are *almost* completely resolved (Figure 3) into two peaks, corresponding to 28.0 and 34.5 MHz (Table VII), which could be regarded as due to the bridgehead and the ortho ^{13}C absorptions, respectively. Accordingly, the intensity ratio between them is 2.5, approximately.

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[26] M. R. Falle, G. R. Luckhurst, A. Horsfield, and M. Ballester, *J. Chem. Phys.*, 50, 258 (1969).

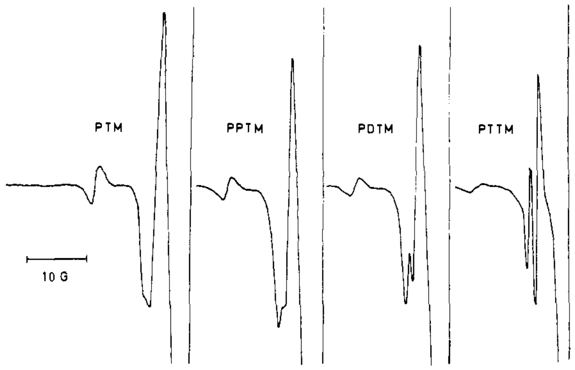

Figure 3. Epr spectra.

(If the peaks were completely resolved it should be equal to two.)

The smaller coupling (~80 MHz) with the α-^{13}C in the PTM series as compared with the PDM series (~100 MHz) is attributed to a smaller spin density at this carbon due to a greater lone-electron delocalization.

Notice that in both series coupling with aromatic ^{13}C diminishes somewhat when para substitution by pentachlorophenyl increases. This indicates that in spite of the quasi-perpendicularity of the benzene rings in the biphenyl systems lone-electron delocalization slightly increases without changing significantly the spin density at the α carbon.

The Acidity of the αH-Quasi-perchlorodiphenyl- and -triphenylmethanes. The quantitative conversion of the αH-quasi-perchloro compounds into their perchlorocarbanions in ethers containing DMSO, using a relatively mild base such as sodium hydroxide, shows their high acidity. Accordingly, their nmr spectrum presents a peak within an unusually low-field region (τ 2.6–3.0) (Table I).

The easy heterolysis of the carbon–hydrogen bond is traced to three intramolecular causes: (a) accumulated electron-attracting effects of the chlorines, (b) B-strain is released when the α-carbon goes from sp^3 to sp^2 hybridization, (c) some resonance in the carbanion.

Factors (b) and (c) cannot operate in triptycene IX and, accordingly, it failed to give any carbanion. In this connection it should also be mentioned that the most effective steric shielding of hydrogen in an αH-quasi-perchloro compound is found precisely in IX, where the rings are parallel to its threefold symmetry axis and, consequently, one triad of o-chlorines is tightly packed about each hydrogen, protecting the front side while the back side is shielded by the triptycene framework.

Stability of the Radicals. A number of factors contribute to the exceptional chemical inertness and high thermal stability of the radicals here described. However, steric shielding of the α- (tricovalent) carbon is by far predominant. Notice in the space-filling model shown in Figure 2 that that atom is buried in a crowd of substituents possessing high-shielding capacity. The chlorine shield is almost impregnable on account of being a single substituent and also because it forms a strong bond with sp^2 carbons.

The approach of an attacking species to the α-carbon is so hindered in the PTM series that, apparently, the intermolecular distance, where effective bond formation begins to occur, cannot be reached.

These radicals owe, therefore, their unique behavior to their being invulnerable at both the α-carbon and the rings. The invulnerability of the latter is also due to low spin delocalization on them caused by their high-angle tilting with respect to the plane of the α-carbon sp^3 bonds.

Stabilization by resonance plays, therefore, a minor role. Polar effects should also be relatively unimportant since salts of the related perchlorocarbonium ions and perchlorocarbanions have recently been synthesized and they both are remarkably stable.[27]

PDM radicals are not so inert because of their lesser shielding at the α-carbon. Accordingly, they react—although slowly—with oxygen, nitric acid, or boiling toluene, while the PTMs do not.

If these overcrowded radicals would react at the α-carbon forming a bond the hybridization of the latter would change from sp^2 to sp^3 thus creating a B strain. This is, therefore, an additional reason for inertness. Consequently, both F and B strain in the normal reaction products cause their chemical passivity.

Doubtless, these effects also play a role in the stability of the carbanions toward oxygen or iodine. In fact, while the perchlorodiphenylcarbanions react smoothly with these reagents the perchlorotriphenylcarbanions do not react with the former and react slowly with the latter.

Reactivity of the Radicals. The reaction of the PDMs with toluene giving the corresponding αH-quasi-perchloro compounds occurs, among other reasons, because of the small size of hydrogen. This reaction is interpreted as

$$\mathrm{Ar_2\dot{C}Cl + C_6H_5CH_3 \longrightarrow Ar_2CHCl + C_6H_5\dot{C}H_2}$$

$$\mathrm{Ar_2\dot{C}Cl + C_6H_5\dot{C}H_2 \longrightarrow Ar_2CClCH_2C_6H_5 \xrightarrow{-HCl} Ar_2C{=}CHC_6H_5}$$

In the case of PDM, the triarylethylene has been isolated in the reaction mixture.

The reactions of the perchloro radicals with alkaline metals or hydroxide ion in DMSO mixtures, giving the perchlorocarbanions, are electron-transfer processes and, consequently, do not require formation of a new bond with the α-carbon. Therefore, steric shielding is here not effective in preventing reaction.

Another electron-transfer process of these radicals, giving perchlorocarbonium ions, has recently been found.[27]

The mechanism of reaction with hydroxide ion is not clearly understood. Possibly stabilization of the perchlorocarbanion and formation of DMSO carbanion play essential roles.

While in solution the PDMs are insensitive to light; the PTMs undergo changes. In forthcoming papers the authors shall describe and examine some aspects of the chemical and photochemical reactivities of these and other related free radicals.

Experimental Section

Apparatus. Molecular weights have been determined with a Mechrolab Model 301a vapor pressure osmometer. Infrared spectra have been recorded on Perkin-Elmer Infracord Model 137 and Model 457 spectrophotometers. Electronic absorption spectra have been obtained with Perkin-Elmer Models 137 UV and 350

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[27] M. Ballester, J. Riera-Figueras, and J. Rodriquez-Siurana, *Tetrahedron Lett.*, 3615 (1970); M. Ballester and G. de la Fuente, *ibid.*, 4509 (1970).

spectrophotometers. All nmr spectra have been recorded on a Perkin-Elmer Model R-10 spectrometer. Magnetic susceptibility data have been taken by Dr. J. F. Weiher (du Pont de Nemours and Co.) using a constant gradient Varian magnet and a Cahn Model RG electronic balance. Electron paramagnetic resonance spectra have been taken with a Varian Model E-4 spectrometer. Melting points have been obtained with a Reichert Kofler microscope and with a Berl-type copper block, the latter for temperatures above 300°.

Starting Materials. The diphenylmethyl chlorides (diphenyl, 4-phenyldiphenyl, and 4,4′-diphenyldiphenyl) have been prepared by the reaction of hydrogen chloride on the diphenylcarbinols.[28] The triphenylmethanes (4-phenyltriphenyl, 4,4′-diphenyltriphenyl, and 4,4′,4′′-triphenyltriphenyl) except the triphenylmethane[29] have been prepared by reaction of the triphenylcarbinols with formic acid by the method of Guyot and Kovache.[30]

The $\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl[31] has been similarly obtained from the corresponding glycol. Triptycene has been obtained following Friedman and Logullo.[32]

αH-Quasi-perchlorodiphenyl- and -triphenylmethanes. These compounds have been obtained from the corresponding α-chlorodiphenylmethanes or hydrocarbons by ring perchlorination with reagent BMC.[12,13]

General Procedure. To a boiling solution of anhydrous aluminum chloride in sulfuryl chloride another of the starting aromatic compound and sulfur monochloride in sulfuryl chloride was added gradually (15–30 min). The resulting mixture was then distilled gently (20 min–4 hr) until it was down to one-third to one-twentieth the initial volume[33] and then it was refluxed for a time (45 min–5 hr), keeping its volume constant through eventual small additions of sulfuryl chloride.

The weight ratio sulfur monochloride–aluminum chloride was, in all cases, equal to 2. The initial weight concentration of aluminum chloride was about 0.25 g/100 ml of sulfuryl chloride. That for the substrate had been about 1%.

The resulting reaction mixture was treated as usual.[12] In some cases substantial chlorinolysis occurred with formation of perchlorobenzene and less-arylated αH-quasi-perchloro compounds.

In most cases, the resulting solid was dissolved in carbon tetrachloride and then passed through silica gel or alumina of maximum activity. When the solubility of the product was very low (PPTM and PTTM) the passage was performed with continuous extraction in a modified Soxhlet apparatus.

Tables I and IV present some data concerning the preparation and characterization of these αH-quasi-perchloro compounds.

Infrared spectra (KBr)[34] were as follows: II 2960 (vw), 1530 (m), 1360 (s), 1335 (s), 1255 (m), 1115 (m), 930 (m), 785 (s), 670 (s), 640 (m), 520 cm^{-1} (s); III 2960 (vw), 1527 (w), 1353 (m), 1330 (s), 1255 (m), 1095 (m), 945 (m), 820 (m), 790 (s), 760 (s), 685 (s), 660 (m), 590 (m), 530 cm^{-1} (s); IV 2950 (vw), 1530–1520 (vw), 1350 (m), 1330 (s), 1260 (m), 1145 (m), 1095 (m), 810 (m), 760 (s), 695 (m), 645 (m), 575 (m), 520 cm^{-1} (s); V 2920 (vw), 1530–1515 (w), 1370 (m), 1340 (s), 1295 (s), 810 (s), 690 (m), 680 (m), 645 (m), 530 cm^{-1} (s); VI 2920 (vw), 1530–1515 (vw), 1360 (m), 1335 (s), 1295 (m), 805 (s), 750 (m), 685 (s), 645 (m), 510 cm^{-1} (m); VII 2920 (vw), 1530–1515 (vw), 1360 (m), 1335 (s), 1295 (m), 1095 (m), 805 (m), 750 (s), 685 (s), 505 cm^{-1} (m); VIII 2910 (vw?), 1530–1515 (vw), 1355 (m), 1335 (s), 1295 (m), 1095 (m), 750 (s), 685 (s), 505 cm^{-1} (s); IX 2910 (vw), 1510 (vw), 1370 (s), 1350 (s), 1210 (s), 1165 (s), 1000 (m), 855 (s), 810 (m), 650 (s), 635 (s), 545 (s), 510 cm^{-1} (m); X 2910 (vw?), 1525 (w), 1355 (m), 1330 (s), 1295 (m), 1100 (m), 810 (s), 760 (m), 705 (m), 685 (m), 650 (m), 550 (m), 520 cm^{-1} (m).

Hydrolysis of αH-Undecachlorodiphenylmethane (II). A mixture of II (1.01 g) and 20% oleum (60 ml) was treated at 100° (24 hr). The resulting deep blue mixture was poured over cracked ice, and the solid formed was filtered, washed, dried, and recrystallized from carbon tetrachloride, giving bispentachlorophenylcarbinol (0.367 g), mp 281–289° dec. *Anal.* Calcd for $C_{13}H_2Cl_{10}O$: C, 29.5; H, 0.4; Cl, 67.1. Found: C, 29.5; H, 0.6; Cl, 66.9. Ir (KBr) showed ν 3571 (w), 1527 (w), 1410 (w), 1370 (s), 1290 (m), 1245 (m), 1122 (s), 1075 (m), 800 (m), 793 (m), 685 cm^{-1} (m); uv (dioxane) λ (ϵ) 242 (24,850) (sh), 277 (413) (min), 293 (814) (max), 297 (770) (min), 303 (900) nm (max).

A comparable amount (0.475 g) of starting material was recovered. The conversion yield was 71.0% of theory.

Ring Chlorination of α,α-Dichlorodiphenylmethane. To a boiling solution of anhydrous aluminum chloride (3.00 g) in freshly distilled sulfuryl chloride (1200 ml), another one of α,α-dichlorodiphenylmethane (10.00 g) and sulfur monochloride (5.00 g) in the same solvent (400 ml) was added gradually (15 min). The mixture was then concentrated slowly (2 hr) down to a small fraction of its original volume, and then refluxed extendedly (32 hr) keeping its volume constant (50 ml) with eventual small additions of sulfuryl chloride. Most of the latter was distilled at room temperature under vacuum, and the residue treated as usual[12] with boiling water, sodium bicarbonate, and then concentrated hydrochloric acid. The solid obtained (20.48 g) was digested with hexane and the insoluble fraction (4.46 g) was recrystallized from carbon tetrachloride, giving perchlorofluorene (XI) (1.49 g) [mp 256–258°. *Anal.* Calcd for $C_{13}Cl_{10}$: C, 30.6; Cl, 69.4. Found: C, 30.6; Cl, 69.2. Ir (KBr) showed 1545 (vw), 1520 (w), 1380 (m), 1335 (m), 1325 (s), 1240 (m), 1190 (m), 1160 (s), 805 (s), 708 (m), 650 (s), 570 (m), 500 cm^{-1} (s); uv (cyclohexane) λ (ϵ) 243 (47,000), 266 (27,900), 276 (28,600), 310 (16,000), 350 (2195) nm] and perchlorodiphenylmethane (I) (1.79 g) [mp 213–216°. *Anal.* Calcd for $C_{13}Cl_{12}$: C, 26.9; Cl, 73.2. Found: C, 27.2; Cl, 73.4. Ir (KBr) showed ν 1510 (w), 1355 (m), 1335 (m), 1325 (s), 1305 (s), 1110 (m), 815 (s), 690 (s), 610 (m), 565 cm^{-1} (s); uv (cyclohexane) λ (ϵ) 223 (72,500) (max), 296 (900) (min), 305 (1250) (sh), 315 (1600) nm (max)].

The fraction soluble in hexane (16.2 g), by recrystallization from this solvent, gave some more I (0.45 g) and 2*H*,2′*H*-decachlorodiphenylmethane (XII) (1.87 g), mp 174–176°. *Anal.* Calcd for $C_{13}H_2Cl_{10}$: C, 30.4; Cl, 69.2. Found: C, 30.4; Cl, 69.2. Ir (KBr) showed ν 3080 (vw), 1525 (w), 1405 (s), 1345 (s), 1225 (m), 1195 (m), 1090 (m), 870 (m), 790 (m), 760 (s), 620 (m), 550 (m), 510 cm^{-1} (m); uv (cyclohexane) λ (ϵ) 221 (59,500) (max), 240 (25,500) (sh), 277 (700) (min), 292 (1075) (max), 298 (900) (min), 302 (1025) (max) nm; nmr (CCl_4) τ 1.4 (s, aromatic H).

The total yields of I, XI, and XII were, respectively, 9.1, 6.9, and 8.6%.

The remaining fractions were very complex mixtures containing the isolated compounds and unknown products.

Shorter reaction times did not improve the yield of I but permitted the isolation of a new compound (chlorine adduct) melting at 146–150°. *Anal.* Calcd for $C_{13}HCl_{13}$: C, 25.3; H, 0.2; Cl, 74.3. Found: C, 25.4; H, 0.4; Cl, 74.3. Ir (KBr) showed ν 3040 (vw?), 1610 (m), 1530 (m), 1350 (s), 1290 (m), 1270 (m), 1130 (m), 950 (m), 865 (m), 825 (m), 790 (m), 770 (m), 745 (m), 735 (m), 725 (s), 714 cm^{-1} (m).

Hydrolyses. XII (0.288 g) was shaken (66 hr) with 20% oleum (20 ml) at room temperature. The mixture, which had turned deep violet, was poured over cracked ice, and gave a solid (0.260 g), which was dissolved in carbon tetrachloride and passed through activated alumina. The resulting substance (0.255 g) was recrystallized from hexane giving 2*H*,2′*H*-octachlorobenzophenone (XV) (0.147 g, 56% yield), mp 164–166°. *Anal.* Calcd for $C_{13}H_2Cl_8O$: C, 34.1; H, 0.4; Cl, 62.0. Found: C, 34.3; H, 0.4; Cl, 62.1. Ir (CS_2, C_2Cl_4) showed ν 3040 (vw), 1685 (s), 1665 (m), 1560 (m), 1520 (w), 1400 (m), 1350 (s), 1330 (s), 1255 (s), 1235 (m), 1025 (s), 875 (m), 825 (m), 770 cm^{-1} (m); uv (cyclohexane) λ (ϵ) 217 (41,000) (max), 230 (32,000) (sh), 257 (10,200) (min), 271 (11,800) (max), 300 (2300) (min), 308 (2380) (max) nm; nmr (CCl_4) τ 2.32 (s, aromatic H). Some more XV and XII remained in the mother liquors.

I (0.264 g) was shaken (48 hr) with 20% oleum (20 ml), at room temperature. The deep-green mixture was treated as before. The solid obtained (0.239 g) was recrystallized from chloroform giving a high yield of pure perchlorobenzophenone (XIII), mp 333–334°. Since it melted about 15° above the value in the literature,[35] it was characterized as if it were a new compound. *Anal.* Calcd for $C_{13}Cl_{10}O$: C, 29.6; Cl, 67.3. Found: C, 29.7; Cl, 67.3. Ir (KBr) showed ν 1715 (s), 1360 (s), 1350 (s), 1315 (w), 1240 (s), 1145 (m), 1015 (m), 800 (s), 755 (m), 695 (m), 680 (s),

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(28) R. Stewart, *J. Amer. Chem. Soc.*, **79**, 3098 (1957).

(29) E. Fischer and O. Fischer, *Justus Liebigs Ann. Chem.*, **194**, 252 (1884).

(30) A. Guyot and K. Kovache, *C. R. Acad. Sci., Paris*, **155**, 838 (1912).

(31) A. E. Chichibabin, *Ber. Deut. Chem. Ges.*, **40**, 1817 (1907).

(32) L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **88**, 907 (1966).

(33) The triphenylmethane's reacting mixture could not be concentrated as much as those of α-chlorodiphenylmethanes. In the case of Chichibabin hydrocarbon the mixture was not concentrated at all.

(34) Below 1300 cm^{-1}, peaks s and m only.

(35) K. Steiner, *Monatsh. Chem.*, **36**, 825 (1915).

645 (s), 565 cm^{-1} (s); uv (dioxane) λ (ε) 270 (8400) (sh), 303 (2040) (min), 316 (2460) nm (max).

XI (0.251 g) was shaken (48 hr) with 20% oleum (24 ml) at room temperature. The deep-green mixture was treated as before. The resulting solid (0.209 g) by recrystallization yielded yellow needles (0.170 g, 77% yield) of perchlorofluorenone (XIV) melting at 294–295°. *Anal.* Calcd for $C_{13}Cl_8O$: C, 34.3; Cl, 62.2. Found: C, 33.9; Cl, 62.0. Ir (KBr) showed 1725 (s), 1550 (m), 1525 (m), 1385 (m), 1360 (m), 1340 (w), 1325 (s), 1295 (m), 1245 (m), 1160 (s), 1005 (m), 910 (m), 850 (m), 785 (m), 765 (s), 670 (m), 660 (m), 525 cm^{-1} (m); uv (cyclohexane) λ (ε) 244 (24,000) (max), 257 (10,000) (min), 284 (39,000) (sh), 290 (56,000) (max), 310 (2450) (sh), 320 (2250) (min), 328 (2520) (max), 334 (2400) (min), 341 (2700) (max), 355 (1650) (min), 363 (1910) (max), 373 (1230) (min), 403 (1800) nm (max).

Dechlorination of *αH*-Undecachlorodiphenylmethane (II). A solution of II (6.0 g) in diglyme (250 ml) was refluxed (48 hr) in argon. Treatment with water gave a solid which was washed and dried (6.0 g). Recrystallization from carbon tetrachloride yielded *αH*,*αH*-decachlorodiphenylmethane (2.8 g), mp 299–302°. *Anal.* Calcd for $C_{13}H_2Cl_{10}$: C, 30.5; H, 0.4; Cl, 69.2; mol wt, 512.6. Found: C, 30.2; H, 0.6; Cl, 69.3; mol wt, 526. Ir (KBr) showed ν 2950 (vw), 1530 (w), 1425 (w), 1365 (m), 1350 (s), 1285 (m), 925 (s), 765 (m), 675 (s), 505 cm^{-1} (m); uv (cyclohexane) λ (ε) 216 (84,000) (max), 230 (44,000) (sh), 276 (375) (min), 288 (525) (max), 295 (477) (min), 298 (480) nm (max).

Synthesis of Perchlorodiphenyl- and Perchlorotriphenylmethyls. These radicals have been obtained from the corresponding *αH*-quasi-perchloro compounds by treatment with sodium hydroxide followed by oxidation with iodine. In one case the oxidation was performed with oxygen. For analyses and other data concerning these radicals, see also Tables II, III, V, VI, and VII.

General Procedure. PDMs. In the exclusion of air (argon), a mixture of similar weights of *αH*-quasi-perchloro compound and finely powdered sodium hydroxide was shaken for 1–2 days with a 15% solution of DMSO in ethyl ether (250 ml/g of *αH* compound). The mixture was filtered through a sintered glass over a threefold excess of iodine in ethyl ether. It was washed immediately with aqueous sodium bisulfite (to destroy iodine), aqueous sodium chloride, and water (to eliminate DMSO). By evaporation a solid residue was obtained, the hexane–carbon tetrachloride (10:1) solution of which was passed through activated silica gel. The second solid residue obtained was finally recrystallized from ethyl ether.

Use of oxygen instead of iodine gave a mixture containing perchlorodiphenylmethyl and perchlorobenzophenone, the yield of the former being 42% of theory. Infrared spectra (KBr)[34] showed PDM, 1510 (w), 1370 (w), 1335 (s), 1310 (m), 1265 (m), 1005 (m), 800 (m), 700 (s), 660 (m), 535 cm^{-1} (s); PPDM, 1510 (vw?), 1350 (m), 1330 (s), 1325 (s), 1305 (w), 835 (m), 760 (m), 700 (s), 520 cm^{-1} (s); PDDM, 1510 (vw?), 1350 (m), 1330 (s), 1320 (s), 1100 (m), 760 (s), 700 (s), 690 (m), 665 (m), 655 (m), 510 cm^{-1} (m).

PTMs. The procedure was analogous to the one given for the PDMs. A 17% solution of DMSO in ethyl ether was used (in the case of biradical PTBT it was 25%) in the proportion of 250–1500 ml/g of αH compound. The anion forming mixture was refluxed 0.5–3 hr, allowed to stand for an additional 12–48 hr at room temperature, oxygen was bubbled through for a while,[36] and, as usual, it was filtered over iodine and ethyl ether. In this series the mixture was left undisturbed for 14–48 hr in the dark. In some cases, part of the radical separates and it is collected apart. Purification of the soluble part is effected with silica gel, except in PDTM, which was simply recrystallized from ethyl ether. However, depending upon the solubility, hexane (PTM), carbon tetrachloride (PPTM) and PTBT), or benzene (PTTM) was used as the eluent. Infrared spectra (KBr)[34] showed PTM, 1500 (w), 1335 (s), 1260 (s), 815 (s), 735 (m), 710 (m), 650 (s), 525 cm^{-1} (s); PPTM, 1510 (vw), 1360 (m), 1335 (s), 1275 (m), 1260 (m), 865 (m), 810 (m), 750 (m), 730 (m), 700 (m), 690 (m), 645 (m), 520 (m), 510 cm^{-1} (m); PDTM, 1510 (vw), 1360 (m), 1335 (s), 1275 (m), 1030 (m), 850 (m), 750 (m), 690 (s), 510 cm^{-1} (m); PTTM, 1520 (?) (vw), 1360 (m), 1335 (s), 1275 (m), 1030 (m), 750 (s), 690 (s), 505 cm^{-1} (m); PTBT, 1505 (w), 1330 (s), 1255 (m), 810 (m), 730 (m), 700 (m), 650 (m), 530 (m), 505 cm^{-1} (m).

Preparation of Perchlorodiphenylmethyl from Perchlorodiphenylmethane. (a) An argon-blanketed mixture of perchlorodiphenylmethane (I, 4.07 g), anhydrous stannous chloride (6.7 g), and anhydrous ethyl ether (800 ml) was refluxed (4 hr) and then poured over cold diluted aqueous hydrochloric acid. Elimination of the volatile parts of the ethereal layer gave a residue (3.84 g) which was extracted with hexane (800 ml) (the insoluble part was perchlorobenzophenone), and the resulting solution was passed through acid alumina grade I, yielding perchlorodiphenylmethyl (PDM) (1.93 g, 50.5%) which was identified by analysis and ultraviolet-visible and infrared spectra.

(b) An argon-blanketed mixture of perchlorodiphenylmethane (I, 0.100 g), anhydrous ferrous chloride (0.218 g), and anhydrous ethyl ether (75 ml) was first refluxed (24 hr), and then poured over diluted aqueous hydrochloric acid. Treatment of the residue obtained from the ethereal layer yielded PDM (0.090 g, 95%).

(c) A mixture containing anhydrous ethyl ether (40 ml), DMSO (10 ml), mercury (2.5 g), and powdered perchlorodiphenylmethane (0.247 g) was shaken at room temperature and in argon with ultrasonics (2.5 hr). The suspended mercury was filtered off, and the resulting solution was washed with water and evaporated, yielding PDM (45.7%).

Reaction of the PDMs with Toluene. A solution of PDM (1.636 g) in anhydrous toluene (200 ml) was heated during 24.5 hr at 100° in the dark and in argon. Evaporation of the volatile parts gave a semisolid residue which was digested in hexane giving a solid (0.621 g) and a viscous oil (1.137 g). By recrystallization from hexane–carbon tetrachloride, the solid gave *αH*-undecachlorodiphenylmethane (II, 0.200 g), mp 224–229°. Chromatography of the oil on silica gel, using cyclohexane as an eluent, gave, first, more II (0.286 g), mp 227–230°, and then an impure white solid, which was recrystallized from cyclohexane giving 1,1-bispentachlorophenyl-2-phenylethylene (0.231 g), mp 211.5–215.0°. *Anal.* Calcd for $C_{20}H_6Cl_{10}$: C, 40.0; H, 1.0; Cl, 59.0. Found: C, 40.1; H, 0.8; Cl, 59.0.

Ir (KBr)[37] showed 3010 (vw), 1620 (w), 1570[37] (vw), 1525 (vw), 1485 (w), 1445 (w), 1390 (w), 1330 (s), 1235 (m), 805 (m), 760 (s), 750 (m), 745 (s), 715 (m), 690 cm^{-1} (s); uv (cyclohexane)[38] λ (ε) 218 (69,900) (max), 274 (15,800) (min), 294 (17,150) nm (max); nmr (CCl_4) τ 2.7–3.1 (m, aromatic H), 2.9[39] (s, ethylene H).

PPDM and PDDM gave 64 and 54% yields of III and IV, respectively, referred to initial radical.

Attempted Reaction of the PTMs with Toluene. In an argon atmosphere and in the dark, a sample (30–90 mg) of radical was dissolved in anhydrous boiling toluene (20–50 ml) and the resulting solution refluxed extendedly (8–40 hr). Elimination of the solvent gave back the radical (infrared).

The per cent recoveries were PTM, 98.5; PPTM, 97.9; PDTM, 95.8; PTTM, 98.5; PTBT, 99.2. They were ascertained by combining weight and absorptivities at 500 nm (or 560 nm).

Reaction of the PDMs with Nitric Acid. A mixture of finely powdered radical (0.3–0.4 g) and concentrated nitric acid (10 ml) was shaken extendedly (60–260 hr) in the dark, under argon, at room temperature. The resulting solid was filtered off, washed with water, and dried, and either recrystallized directly from a suitable solvent or after chromatography to eliminate nonpolar impurities. The perchloro ketones XIII, XVI, and XVII were obtained: mp 333–334, 303–310, 345–348°; yields 58, 77, and 52%. *Anal.* Calcd for $C_{19}Cl_{14}O$ (XVI): C, 30.8; Cl, 67.0. Found: C, 30.8; Cl, 67.2. Ir (KBr) showed ν 1705 (s), 1520 (m), 1415 (w), 1335 (s), 1255 (m), 1220 (m), 1150 (m), 1100 (m), 1020 (m), 795 (m), 765 (m), 760 (m), 695 cm^{-1} (m); uv (cyclohexane) λ (ε) 215 (140,000) (max), 242 (62,800) (sh), 270 (12,650) (sh), 292 (2658) (min), 310 (3230) nm (max).

Anal. Calcd for $C_{25}Cl_{18}O$ (XVII): C, 31.5; Cl, 66.9. Found: C, 31.5; Cl, 66.9. Ir (KBr) showed ν 1695 (m), 1560–1535 (w), 1420 (w), 1350 (m), 1335 (s), 1260 (m), 1160 (m), 1110 (m), 785 (m), 760 (s), 710 (m), 695 (m), 675 cm^{-1} (m); uv (cyclohexane) λ (ε) 215 (140,000) (max), 241 (65,000) (sh), 270 (12,700) (sh), 292 (2650) (min), 302 (3300) (max), 306 (3250) (min), 312 (3350) nm (max).

Attempted Reaction of the PTMs with Nitric Acid. In a sealed glass tube a mixture of finely ground radical (0.5 g) and concentrated

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(36) To destroy carbanions resulting from chlorolytical impurities in the starting *αH* compound.

(37) The "stretching" aromatic peaks due to the phenyl and perchlorophenyl groups are located between 1625 and 1400 cm^{-1}. The identification of the ethylene stretching peak—which should be between 1625 and 1520 cm^{-1}—is, therefore, uncertain.

(38) Absorption and 294 nm corresponds to the so-called "conjugation band."[9]

(39) This exceptionally low-field value is traced to the chlorine overcrowding.

nitric acid (15 ml) was shaken in the dark (48 hr). The mixture was poured over water and filtered. The solid residue was unaltered radical. The per cent recoveries of PTM, PPTM, PDTM, and PPTM were 98.8, 97.4, 98.9, and 99.2, respectively, as ascertained by combining weight and absorptivity at 500 nm.

Reaction of the PDMs with Sodium Hydroxide in DMSO. In the dark, under argon, and at room temperature, a mixture of radical (0.100 g), powdered sodium hydroxide (~0.5 g), ethyl ether (30–50 ml), and DMSO (7–12 ml) was shaken (2–5 hr). The resulting blue mixture was poured over diluted aqueous hydrochloric acid and the ethereal layer separated. By evaporation a solid was obtained which was purified (recrystallization, chromatography). The product was identified by infrared and mixture melting point with the corresponding αH-quasi-perchloro compound. The yields of II, III, and IV were 70, 57, and 78%, respectively.

Reaction of the PTMs with Sodium Hydroxide in DMSO. The reaction was performed as in the preceding case. However, on account of the low solubility of the radicals—except for PTBT—THF was replaced for ethyl ether, and the contact extended (up to 2 days) after having refluxed the mixture for a time (2 hr). The corresponding αH-quasi-perchloro compounds were obtained. They were characterized by infrared and CH analysis. The yields of V, VI, VII, and X were 94, 86, 84, and 70%, respectively.

Reaction of PDM with Potassium. A mixture of PDM (0.302 g), anhydrous ethyl ether (100 ml), and one chunk of potassium metal (~0.5 g) was shaken vigorously (1 hr) at room temperature and under argon. The remaining potassium was separated and the resulting violet solution poured over water. The ethereal layer gave a solid mixture (0.303 g) which was chromatographed with alumina grade 1 (hexane) giving a mixture of αH-undecachlorodiphenylmethane (II, 0.253 g, 83.5%) and $\alpha H,\alpha H$-decachlorodiphenylmethane (0.016 g, 5.6%), which were identified by mixture melting point and infrared spectra.

Reaction of PTM with Potassium. A mixture of PTM (0.085 g), anhydrous ethyl ether (50 ml), and chunks of potassium, metal was shaken vigorously (8 hr) at room temperature, under argon, and in the dark. The potassium was filtered off, the red solution was poured over diluted aqueous hydrochloric acid, and the ethereal layer was decanted, washed with water, and dried. Elimination of the solvent gave a solid (0.078 g) that was dissolved in hexane–carbon tetrachloride (1:1) and passed through silica gel. The white residue obtained consisted of αH-pentadecachlorotriphenylmethane (V, 0.067 g, 79%) which was identified by infrared and carbon–hydrogen analysis.

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Electrophilic Substitution at Saturated Carbon. XLV. Dissection of Mechanisms of Base-Catalyzed Hydrogen–Deuterium Exchange of Carbon Acids into Inversion, Isoinversion, and Racemization Pathways[1]

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Abstract: The stereochemical course of base-catalyzed hydrogen–deuterium exchange between carbon acids and hydroxylic solvents has been studied by the technique of reresolution of partially racemized mixtures. Partial racemization of (+)-2-methyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide ((+)-I-*h*) in methanol-*O-d* containing potassium methoxide at 75° gave material that was reresolved and analyzed for deuterium. The data provided the following second-order rate constants: net inversion with exchange, $6.1 \pm 1 \times 10^{-5}$ l. mol^{-1} sec^{-1}; isoinversion (inversion without exchange), $1.4 \pm 0.2 \times 10^{-5}$ l. mol^{-1} sec^{-1}; racemization with exchange, $11.7 \pm 1 \times 10^{-5}$ l. mol^{-1} sec.$^{-1}$ A parallel experiment with (+)-2-deuterio-2-methyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide ((+)-I-*d*) in methanol-*O-h* containing potassium methoxide at 75° gave rate constants: net inversion with exchange, $3.5 \pm 0.3 \times 10^{-5}$ l. mol^{-1} sec^{-1}; isoinversion, $3.1 \pm 0.4 \times 10^{-6}$ l. mol^{-1} sec^{-1}; racemization with exchange, $3.9 \pm 0.3 \times 10^{-5}$ l. mol^{-1} sec^{-1}. These data provided substrate and solvent isotope effects for racemization that agreed well with independently measured values. Mechanisms are proposed which rationalize the simultaneous occurrence of simple inversion and isoinversion in which solvation of the sulfone's oxygens plays a key role. Similar experiments with (−)-4-biphenylylphenylmethoxydeuteriomethane ((−)-II-*d*) at 150° in methanol-*O-h* containing potassium methoxide gave only racemization. The methoxyl group of (−)-II-*d* appeared unable to play the solvent organizational role assumed by the sulfone group in (+)-I-*d*.

In the early work on base-catalyzed hydrogen–deuterium exchange between optically active carbon acids and hydroxylic solvents,[3] k_e/k_α values (k_e is the rate constant for isotopic exchange and k_α that for racemization) were employed as criteria of the stereochemical pathway for reaction. This method identified reactions that occurred with high retention, complete racemization, or with high isoinversion, but failed to separate these from one another and from inversion with isotopic exchange when the rates of the possible

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