Inert Carbon Free Radicals. 5. Perchloro-9-phenylfluorenyl Radical Series

M. Ballester,* J. Castañer, J. Riera, J. Pujadas, O. Armet, C. Onrubia, and J. A. Rio

Instituto de Química Orgánica Aplicada (C.S.I.C.), C. Jorge Girona Salgado, Barcelona 34, Spain

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The synthesis of the perchloro-9-phenylfluorenyl radical (PPF) from 9-phenylfluorene (1) has been accomplished through a chlorolytic aromatic perchlorination to αH -pentadecachloro-2-biphenylylphenylmethane (2) with BMC reagent, followed by a cyclization at 300 °C (91%). The radical PPF is also obtained by cyclization at 320 °C of the perchlorotriphenylmethyl radical (PTM). Other syntheses of the radical PPF are described. PPF is chlorinated to perchloro-9-phenylfluorene (7), oxidized to perchloro-9-phenyl-3-fluorenone (9) and perchloro-4-(9-fluorenylidene)cyclohexadienone (10), and reduced to 9H-tridecachloro-9-phenylfluorene (6). Other radicals related to PPF have also been synthesized: perchloro-9-(2-biphenylyl)fluorenyl (34), perchloro-9-(4-biphenylyl)fluorenyl (22), 3-methyldodecachloro-9-phenylfluorenyl (28), and dodecachloro-3-methoxy-9-phenylfluorenyl (17). In total, 19 highly chlorinated diphenylmethane and fluorene derivatives have been obtained for the first time, including chlorocarbons 7 and perchlorospiro-9,9'-bifluorene (32). Some unusual reactions have been interpreted. The intermediacy of ionic species such as the perchloro-2-biphenylylphenylmethyl anion (3), perchloro-9-phenylfluorenyl anion (4), and perchloro-9-phenylfluorenylium (5) has been established. The IR, UV-vis, and ESR spectra of the compounds synthesized are reported and discussed. The variation of the magnetic susceptibility of the radicals with temperature indicates antiferromagnetism at low temperatures and, except for radical 34, purities of near 100%. The unusual inertness of radicals PPF, 17, 22, and 28 is traced to steric shielding of the trivalent carbon by the neighboring chlorines. However, such shielding and chemical inertness are not as great as in the radicals of the PTM series. Nevertheless, the thermal stability of radicals PPF and 22 is significantly higher.

Introduction

We have previously reported the first known "inert carbon free radicals". $^{1-4}\,$ They are insensitive to oxygen and highly reactive reagents, and they resist temperatures up to 300 °C in air. Typical of these species is the perchlorotriphenvlmethyl radical (PTM), a propeller-like molecule, in which the blades are the three pentachlorophenyl groups. The stability of the radicals of the PTM series is essentially due to steric shielding of the central trivalent carbon atom by the six ortho chlorines and the three benzene rings attached to it.¹

This paper deals with the synthesis and properties of the perchloro-9-phenylfluorenyl radical (PPF) and other related radicals and compounds. Structurally these radicals may be regarded as the result of the substitution of two tilted phenyl rings in radicals of the PTM series by an essentially planar ortho biphenylene group. In such a structural change spin delocalization must increase significantly, while steric shielding of the 9-carbon (where most of the spin density should reside), mainly by the two ortho chlorines of the pentachlorophenyl group and chlorines 1 and 8 of the fluorene system, presumably decreases. Therefore, in order to assess the relative role of these factors, an investigation of the general stability and reactivity of PPF and related radicals, compared to those of the PTM series, was undertaken.

Results and Discussion

Syntheses of Perchloro-9-phenylfluorenyl (PPF) Radical^{5,6} (Scheme I). As in the synthesis of radical PTM,¹ the preparation of radical PPF was attempted starting with the corresponding hydrocarbon, i.e., 9phenylfluorene (1). However, aromatic perchlorination of 1 with the BMC⁷ reagent does not give 9H-tridecachloro-

(5) A short notice on the synthesis of radical PPF has been advanced.⁶ (6) Ballester, M.; Castañer, J.; Pujadas, J. Tetrahedron Lett. 1971, 1699



9-phenylfluorene (6), the expected immediate precursor of radical PPF but instead results in chlorinolysis yielding αH -pentadecachloro-2-biphenylylphenylmethane (2). Surprisingly, heating the α H compound 2 above its melting point gave a green substance, which was identified as the

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desired radical PPF. Actually, this almost quantitative cyclization at 280-300 °C constituted the first synthesis of PPF. In this process PPF could arise by an initial HCl elimination either giving chlorocarbon 7, which subsequently homolyzes to PPF (see later), or perchloro-(2-biphenylyl)phenylcarbene, which cyclizes to PPF with the loss of a chlorine.

It was previously observed that radical PTM melts with decomposition at about 305 °C, also giving a green compound suggesting the formation of radical PPF. In fact, the thermolysis of PTM above 305 °C affords another high-vield synthesis of PPF.

The "normal" PPF precursor, the 9H-tridecachloro-9phenylfluorene (6), was obtained from the perchloro-2phenyldiphenylmethyl anion (3) by cyclization, under the conditions leading to its own formation (i.e., αH compound 2 and NaOH-ether-Me₂SO), to perchloro-9-phenylfluorenyl anion (4), followed by treatment with acid. This cyclization takes place presumably through the sequence $3 \rightarrow 7 \rightarrow 4 \rightarrow 6$. The second step is a positive chlorine reaction with the powerful reducing mixture NaOH-Me₂SO.^{8a} Perchlorodiphenylmethane is reduced to perchlorodiphenylmethyl anion under these same conditions.¹

As in the PTM series, treatment of 9H compound 6 with base, followed by oxidation with I_2 of the carbanion 4 formed, affords PPF, although in poor yield. PPF is also formed by illumination of the radical PTM with an incandescent light.

The radical PPF is isolated as deep-green crystals melting without change at about 300 °C in air. It decomposes at around 350 °C. Obviously, its thermal stability is greater than that of radical PTM. PPF is completely disassociated at room temperature, even in solid form according to magnetic susceptibility measurements. In cyclohexane solution, it does not react with O_2 in the dark, but it oxidizes under illumination with an incandescent light.

Stabilities of Radical PPF. The stability of PPF at room temperature toward a variety of chemical agents has been tested. It is stable to concentrated H_2SO_4 (2 days), concentrated HNO₃ (1 day), chlorine in the dark (CCl_4 , 2 days), bromine in the dark (CCl₄, 1 day), hydroquinone (ether, 7 days), and p-quinone (ether, 7 days). However, it reacts readily with NO in CCl₄ and decomposes slowly in boiling toluene.

Chlorinations and Oxidations of Radical PPF. (1) PPF reacts with Cl_2 in CCl_4 , in the presence of I_2 , giving a good yield of a new chlorocarbon, the perchloro-9phenylfluorene (7), the structure of which has been ascertained by its spectra. This reaction is presumably due to attack by iodine chloride since PPF does not react with Cl₂ alone. Chlorocarbon 7 reverts to radical PPF either by thermolysis at 230-240 °C or by dechlorination with FeCl₂ in ether (Scheme I).

(2) By treatment of radical PPF with SbCl₅ in CCl₄ or CH₂Cl₂ and then with water a mixture of perchloro-9phenylfluoren-3-one (9) and perchloro-4-(9fluorenylidene)cyclohexa-2,5-dienone (10) is obtained, along with recovered PPF (Scheme II). The formation of these ketones presumably takes place through perchloro-9-phenylfluorenylium (5) hexachloroantimonate (ref 3), since the hydrolysis of that salt, obtained from chlorocarbon 7 and $SbCl_5$ (CCl₄), gives essentially the same mixture of ketones. The structure of the fluorenone 9 has been established by X-ray measurements.⁹ Since therScheme II



molysis of perchlorofuchsone (11)^{2,3,10} also gives a mixture of ketones 9 and 10, the structure given for 10 is settled as well.

The fact that the hydrolysis of salt 5.SbCl₆ does not give perchloro-9-phenylfluoren-9-ol (8), the normal product of hydrolysis, is accounted for by the shielding of the 9-carbon of cation 5. Analogous behavior is observed in the hydrolysis of perchlorotriphenylcarbenium hexachloroantimonate.³

These results are interpreted to mean that salt 5.SbCl_e, in CCl_4 or CH_2Cl_2 , exists as a mixture of two different "loose" ion pairs—the SbCl₆ being either near the para position of the phenyl ring or near the distal positions (3) or 6) of the fluorene system. Each species would then hydrolyze to its structurally related perchloro ketone (9 or 10). On the other hand in SO_2Cl_2 solution, where because of the higher polarity there should not be such ion pairing, the hydrolytic attack takes place exclusively in the fluorene system, where the positive charge is highly delocalized,¹¹ so yielding fluorenone 9 only.

In the oxidative hydrolysis of radical PPF (SbCl₅, CCl₄, or CH₂Cl₂), a substantial proportion of "recovered" radical is isolated, along with the perchloro ketones. Since chlorocarbon 7 also gives radical PPF (49%) and perchloro ketones (31%) by the same treatment, it is concluded that the PPF is not simply unreacted material but is formed somehow from the fluorenylium ion 5 in the subsequent hydrolysis. It is tentatively suggested that in the CCl_4/H_2O interface the fluorenylium ion 5 is reduced to PPF by chloride ion. In this connection, it was previously observed that perchlorotriphenvlcarbenium hexachloroantimonate is reduced readily to PTM by bromide ion.³

(3) Treatment of PPF with oleum at room temperature also yields a mixture of perchloro ketones 9 and 10 (Scheme II). This oxidation is interpreted as taking place through the perchloro-9-phenylfluorenylium ion (5), which

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 (10) Ballester, M.; Riera, J.; Rodriguez, A. Tetrahedron Lett. 1970.

^{3615.}

⁽⁸⁾ Ballester, M.; Olivella, S. "Polychloroaromatic Compounds"; Suschitzky, H., Ed.; Plenum Press: London, 1974; (a) p 127; (b) p 130; (c) p 104.

⁽¹¹⁾ On account of strong steric repulsions in the fluorenylium ion 5, the plane of the pentachlorophenyl group and the mean plane of the fluorene system form a high angle. Therefore, delocalization of the positive charge in the former group is not so extensive as in the latter system.



reacts with HS_2O_7 , presumably giving those ketones and chlorosulfonic acid. Chlorocarbon 7, under the same reaction conditions, also gives the same ketones. They are also formed in the photooxidation of PPF with O_2 and white light (CCl₄).

(4) Radical PPF, when treated with a solution of anhydrous AlCl₃ in SO₂Cl₂, is converted to the green fluorenvlium ion 5, which is presumably associated with counterion $AlCl_4^-$ (or $Al_2Cl_7^-$). Subsequent treatment with water does not yield ketones but instead chlorocarbon 7 (Scheme I), indicating that "tight" ion pairs are involved.¹² It has previously been found that under the same conditions the perchlorodiphenylmethyl (PDM) radical¹ gives first the perchlorodiphenylcarbenium ion, and then, after hydrolysis, perchlorodiphenylmethane.^{8b} However, if the treatments are carried out at low temperature, i.e., below -15 °C, the major product is perchlorobenzylidenecyclohexa-1,4-diene,^{8b} suggesting that the attack of chloride ion takes place on the peripheral, less-shielded 4-position followed by isomerization of the resulting product to the thermodynamically more stable perchlorodiphenylmethane.^{8c} Consequently, since the scale models show that the 9-carbon of radical PPF is highly shielded, it is reasonable to assume that initially the "tight" ion pairing takes place at a peripheral position and that subsequently the hydrolytic treatment gives a methylenecyclohexadienechlorocarbon, which isomerizes to the fully aromatic chlorocarbon 7.

Reductions of Radical PPF (Scheme I). PPF undergoes reduction to 9H compound 6 with HI in refluxing acetic acid or by treatment with NaOH-ether-Me₂SO followed by aqueous acid. In the latter reduction, carbanion 4 is presumably formed, which is then hydrolyzed to 6. This type of reduction has also been described for radicals of the PTM series.¹⁻³



3-Methoxydodecachloro-9-phenylfluorenyl Radical (17) (Scheme III). By reduction with aqueous HI/I_2 , fluorenone 9 gives a good yield of 9*H*-dodecachloro-9phenylfluoren-3-ol (14), which in air reverts slowly to 9. 14 is methylated with CH_2N_2 and acetylated with acetic anhydride to give 9*H*-3-methoxydodecachloro-9-phenylfluorene (16) and 9*H*-3-acetoxydodecachloro-9-phenylfluorene (12), respectively. Treatment of the methoxyfluorene 16 with NaOH in ether-Me₂SO, followed by oxidation of the carbanion 18 formed, gives a good yield of the green, completely disassociated methoxyfluorenyl radical 17, mp 295.5-300.0 °C, whose general stability is comparable to that of PPF. However, under the preceding treatment, the acetoxyfluorene 12 hydrolyzes to the fluorenone 9 instead of giving the corresponding radical.

It was previously observed that the reduction of perchlorofuchsone (11) with HI/I_2 gives the tetradecachloro-4-hydroxytriphenylmethyl radical instead of αH tetradecachloro-4-hydroxytriphenylmethane.³ Consequently, it is assumed that hydroxyfluorenyl radical 13 is formed, but because of its greater reactivity it is further reduced to 9H compound 14. Under those conditions, dienone 10 is stable toward aqueous HI/I_2 . This result is explained by the loss in dienone 10 of the π -electron delocalization between the quinomethane moiety and the fluorene system in that process. Consistent with this explanation, X-ray measurements show that in fluorenone 9, and presumably in methoxyfluorenyl radical 17, the 9-pentachlorophenyl ring is virtually perpendicular (89.5°) to the mean plane of the fluorenone system.⁹

When the methoxyfluorenyl radical 17 is treated with $SbCl_5$ in CH_2Cl_2 a blue color is formed. Subsequent treatment with water results in an excellent yield of the fluorenone 9. Therefore, it is assumed that the $SbCl_5$ causes the formation of the fluorenylium ion 15 (ref 3), which immediately undergoes S_N2 attack by chloride ion to give the fluorenone 9 and CH_3Cl . The fluorenone 9 also gives the same blue color with $SbCl_5$.

Perchloro-9-(4-biphenylyl)fluorenyl Radical (22) (Scheme IV). As in the thermolysis of radical PTM (which gives radical PPF), heating perchloro-4-biphenylyldiphenylmethyl radical¹ (21) to about 340 °C gives

⁽¹²⁾ Counterion AlCl4^ is much smaller than $SbCl6^-$ and, consequently, less susceptible to steric shielding. 6



radical 22. The latter is a dark-green radical with chemical inertness similar to that of PPF, and it possesses a very high thermal stability. It melts and decomposes at about 370–380 °C. Since cyclization could also have given the perchloro-3,9-diphenylfluorenyl radical (23), the structure of the product was ascertained independently by direct, thermal cyclization of αH -nonadecachloro-2-biphenylyl-4-biphenylylmethane (20), which in turn was obtained by exhaustive chlorination of 9-(4-biphenylyl)fluorene (19) with the BMC reagent.⁷

3-Methyldodecachloro-9-phenylfluorenyl Radical (28) (Scheme V). The synthesis of the fluorenyl radical 28 was accomplished by a sequence starting from 3methylfluorenone (24), through 3-methyl-9-(pentachlorophenyl)fluoren-9-ol (25), 3-methyl-9-(pentachlorophenyl)fluorene (26), and 9H-3-methyldodecachloro-9phenylfluorene (27). Radical 28 is a perfectly stable blue solid melting at 187–189 °C. However, it decomposes in ethyl ether, even at room temperature. It also decomposes when subjected to TLC (silica gel; hexane).

Perchloro-9-(2-biphenylyl)fluorenyl Radical (34) (Scheme VI). 9-(2-Biphenylyl)fluorene (31), obtained by reduction of 9-(2-biphenylyl)fluoren-9-ol (29) with LiAlH₄, affords a mixture of 9*H*-heptadecachloro-9-(2biphenylyl)fluorene (33) and perchloro-9,9'-spirobifluorene (32) when chlorinated with the BMC reagent.⁷ The latter was obtained independently in excellent yield by perchlorination with that reagent of the 9,9'-spirobifluorene (30), which in turn was synthesized by acidic cyclization of the fluorenol 29.

By treatment of the 9H compound 33 with NaOHether-Me₂SO, followed by oxidation with I_2 of the red anion 35 formed, the fluorenyl radical 34 was obtained. The latter *is not* an inert carbon free radical. It cyclizes readily to spiro compound 32, even in the solid phase, but rapidly in refluxing CCl₄. Such reactivity is attributed to the proximity of the two bonding carbons, i.e., the trivalent 9-carbon of the fluorenyl system and the 2'-carbon of the 2-biphenylyl substituent as seen in a space-filling model.

Ultraviolet-Visible Spectra (Figure 1). (1) 2-Biphenylylphenylmethanes. α H compounds 2 and 20 display the so-called "primary band" group (~220 nm) and a dentate "secondary band" (¹L_b, ~295 nm) characteristic of highly chlorinated benzenes.^{1,2,13} No biphenylyl band





Figure 1. UV-vis spectra of α H compound 2 (----), 9H compound 6 (...), radical PPF (--), fluorenone 9 (-----), dienone 10 (----).



appears because of complete steric inhibition of resonance¹⁴ due to steric repulsions among the four central substituents. In perchlorobiphenyl the rings are oriented at an angle of 87°.¹⁵

(2) 9-Phenylfluorenes. The spectrum of 9-phenylfluorene (1) in the near visible region consists mainly of two intense bands with maxima at 265 nm (ϵ 15900) and

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(15) (a) Galí, S.; Miravitlles, C.; Solans, X.; Font-Altaba, M. Butll. Inst. Cat. Hist. Nat. 1979, 43, 51. (b) Pedersen, F. B. Acta Crystallogr., Sect. B 1975, B31, 2931.

292 and 305 nm (ϵ 5000 and 7900).¹⁶ They can be regarded as related, respectively, to the "second" primary and the secondary bands of benzenoid compounds,¹⁷ which in biphenyl systems are found around 250 (K or conjugation band) and 270 nm, the latter usually being swamped by the former. Because of the in-plane bond strain due to methylene bridging, the band near 300 nm in the fluorenes is unusually intense (about 10-fold),¹⁸ and it therefore appears as a separate band.

In the 9H-quasiperchloro-9-phenylfluorenes 6, 12, 14, 16, 27, 33, and the spirane 32, the band at longer wavelengths appears as a shoulder of the "K" band, being shifted both bathochromically and hyperchromically with respect to those of 1, the parent hydrocarbon. This is a normal effect of the perchlorosubstitution in aromatic systems.^{14,17,19} (For comments on the UV-vis spectrum of chlorocarbon 7, see later.)

(3) 9-Phenylfluorenyl Radicals. Four bands are found in the near ultraviolet-visible spectra of the radicals PPF, 17, 22, 28, and 34, centered around 290, 380,20 480,20 and $600^{20}\,\text{nm}.\,$ The first band is regarded as the K band of the fluorene system, and the other three are presumably due to the radical character. In the PTM radical series they are located near 385, 510, and 560 nm.¹

(4) Perchloro Ketones. The spectra of ketones 9 and 10 beyond 250 nm consist of three bands of decreasing intensity, the last one appearing as a shoulder. The wavelengths of the maxima are essentially the same and occur near 300, 425, and 480 nm, although their intensities differ markedly. The bands near 425 and 480 nm are assigned to the methylenecyclohexadienone system. Since the 9-phenyl ring in the fluorenone 9 is perpendicular to the fluorene system (see above), only 14 out of the 20 π electrons are involved in the relevant spectral transitions. Therefore, it might be expected that at least a few bands of the absorption spectrum of fluorenone 9 would be displaced hypsochromically with respect to that of dienone 10. However, no such a shift is observed (see above), and this is accounted for by steric inhibition of resonance in dienone 10 due to twisting and/or bending of the quinomethane system in 10 with respect to the rest of the molecule.

Infrared Spectra. All fluorenes here described, and others still unpublished, have a characteristic mediumto-intense peak near 1400 cm⁻¹ not found in other perchloroaromatic compounds. However, as in the latter, they also show the first benzenoid peak near 1525 cm⁻¹, and the second group near 1333 cm⁻¹.²¹

Spectra and Structure of Chlorocarbon 7. The UV-vis spectrum of this chlorocarbon is very similar to those of the 9H-quasiperchloro-9-phenylfluorenes and is the basis for the structural assignment. However, a significant bathochromic shift is observed, which is attributed to an out-of-plane distortion of the fluorene system due to steric repulsions among the 9-position and neighboring chlorines.¹⁷ This rules out the possibility that it possesses a methylenecyclohexadiene structure, which would result by chlorine addition to the less-shielded peripheral positions, other than the 9-position, of radical PPF. Furthermore, the IR spectrum of chlorocarbon 7 displays the

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Table I. ESR Spectral Data of Radicals in CCl.

			line width.	splittings, MHz	
radical	g	lines	MHz	H	α- ¹³ C
PPF	2.0043	1	13.3		58.0
17	2.0038	1	11.5		51.8
22	2.0038	1	11.5		60.0
28	2.0032	4	10.9	12.0	
34	2.0046	1	15.0		60.0

characteristic peak around 1400 cm⁻¹ of the perchloroaromatic 9-phenylfluorenes, and it does not show any C==C stretching absorption, which in perchloroaryl ethylenes is usually found around 1600 cm⁻¹.²¹

Electron Spin Resonance Spectra. The relevant data are shown in Table I. The g values (~ 2.0040) are higher than those for perchlorotriphenylmethyls (~ 2.0027),¹⁻⁴ and this is attributed to some spin-orbit coupling. This is similar to the ESR spectra of the radicals of the perchlorodiphenylmethyl (PDM) series where coupling with the α -chlorine is relatively high (g ~2.0055).¹ Such spinorbit coupling is related to the higher spin density on the fluorenic chlorines due to an increased spin delocalization inherent in the high degree of planarity of the fluorene system. Also the line widths of the PPFs are greater (~ 12 MHz) than those of the PTMs (~ 3.5 MHz).¹⁻⁴ In both series the line widths are mainly due to unresolved chlorine couplings. As expected, the hyperfine structure of the methylfluorenyl radical 28 consists of four lines due to coupling (12 MHz) with the three protons, which is greater than that for the 4-methyltetradecachlorotriphenylmethyl radical (6.0 MHz).² This again is presumably due to increased spin delocalization. The coupling with the 9^{-13} C satellites (~55 MHz) are lower than those for the α -¹³C in PTMs (\sim 82 MHz),¹⁻⁴ also suggesting a higher spin delocalization.

Magnetic Susceptibilities. The variation of the magnetic susceptibility of radicals with temperature allows the calculation of the Bohr magnetons $(\mu_{\rm B})$ and the corresponding number of spins per mole. For this purpose the Curie-Weiss expression is employed (eq 1) where χ is

$$\mu_{\rm B}^2 = 8(\chi - \chi_{\rm dia})(T - \theta)M \tag{1}$$

the experimental specific susceptibility, χ_{dia} is the specific diamagnetic susceptibility, T is the temperature (K), Mis the molecular mass, and θ is the Weiss constant, which usually differs little from zero. However, all fluorenyl radicals here described have an unusually low value of θ (Table II), which is regarded as an indication of antiferromagnetism.²²⁻²⁴ In such cases, the appropriate expression is

$$\mu_{\rm B}^2 = \frac{kT}{Ng^2} (\chi - \chi_{\rm dia}) (3 + e^{-2J/T}) M = 2(\chi - \chi_{\rm dia}) (3 + e^{-2J/T}) M$$

in which k is the Boltzmann constant, N is Avogradro's number, g is the Lande's factor, and J is the spin-exchange constant.²⁴ This expression coincides at high temperatures with that of Curie–Weiss, when $\theta = J/2$. The data shown in Table II have been calculated with that expression. Those calculations suggest that all of the radicals except 34 are pure.

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⁽¹⁷⁾ Ballester, M.; Castañer, J. J. Am. Chem. Soc. 1960, 82, 4259.

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(b) Ballester, M. "Quimica Orgánica Fisica. Fundamentos y Espectrometrias", Pirámide: Madrid, Spain, 1978; pp 330-332. (19) Ballester, M.; Castañer, J.; Riera, J.; Parés, J. An. Quim. 1980,

⁷⁶C, 157. (20) Two intense maxima.

⁽²²⁾ Spin interaction that in extreme cases would be covalent bonding. 23

⁽²³⁾ Earnshaw, A. "Introduction to Magnetochemistry"; Academic (24) Veyret, C.; Blaise, A. "Molecular Physics" 1973, 25(4), 873.

			J, K		
compd	$\mu_{\mathbf{B}}$	10º _{X dia} ,ª emu	θ, Κ	(spin exchange)	purity, %
PPF	1.73	-0.514	-14.5	-29	100
22	1.72	-0.514	-10	-20	98.7
17	1.72	-0.506	-17.5	-35	99.4
28	1.73	-0.525	$^{-4.5}$	9	99.7
34	1.36^{b}	-0.514	-10^{c}	-20^{c}	61.6 ^b

^a Calculated independently from modified Pascal's data.^b Calculated from data at room temperature only. ^c Estimated.

through alumina (CCl_4) and recrystallized (hexane- CCl_4), giving PPF radical (1.264 g, 93.1%), dark-green crystals: mp 300-301

triphenylmethyl radical (PTM) to a perchloro-9-phenylfluorenyl radical (PPF) involves deep changes in steric and electronic characteristics. The propeller-like configuration is lost, and, consequently, the relevant shielding of the trivalent carbon afforded by the proximal chlorines decreases, although delocalization of the lone electron is substantially increased. Accordingly, the inertness of the PPFs is not as high as that of the PTMs, although they can also be regarded as "inert" radicals. However, their thermal stability is higher, and in solid form they are able to withstand temperatures well above 300 °C in air.

Conclusion. The process of going from a perchloro-

Experimental Section

General Methods. The IR, UV-vis, ESR, ¹H NMR, and mass spectra were recorded with Perkin Elmer 457, Beckman Acta M VI, Varian E4, Perkin Elmer R 12B, and AEI MS-902S spectrometers, respectively. The magnetic susceptibilities were measured in He with a Varian 4-in. magnet with constant force caps and a Cahn RG electrobalance.

Unless otherwise indicated the reactions were performed at room temperature. Radicals in solution were handled in the dark. The identities of the products of the reactions were established at least by IR spectroscopy.

Since the locations of the IR peaks of perchloroorganic compounds differ markedly from those of their nonchlorinated counterparts, they are included in this section.

The ESR and magnetic susceptibility data for the radicals described below are given in Tables I and II, respectively.

Chlorination of 9-Phenylfluorene (1) with Reagent BMC.⁷ A solution of 1²⁵ (3.115 g) in SO₂Cl₂ (100 mL) was added gradually to a solution of anhydrous $AlCl_3$ (0.75 g) and S_2Cl_2 (1.50 g) in refluxing SO_2Cl_2 (300 mL). The solution was concentrated (~30 mL) and then refluxed (15 h), keeping the volume constant with small additions of SO₂Cl₂. The resulting mass was treated with water (10 mL), the SO₂Cl₂ was eliminated in vacuo, and the residue was treated with water and $NaHCO_3$, heated on a steam bath, and acidified with aqueous HCl. The precipitate formed was filtered, washed with water, dried, digested with CCl₄, and recrystallized (CHCl₃), giving α H compound 2: 6.017 g, 61.5%; mp 242-243 °C dec; UV (C₆ H_{12}) 214 nm, 293, 303 (ϵ 106 100, 1390, 1550); IR (KBr) 2990 (vw), 1525 (w), 1370 (m), 1347 (s), 1327 (s), 1295 (m), 833 (s), 800 (s), 758 (m), 696 (s), 675 (s), 650 (m), 630 (m), 515 (s) cm⁻¹; ¹H NMR (CCl₄) τ 2.93 (s). Anal. Calcd for C₁₉HCl₁₅: C, 30.0; H, 0.1; Cl, 69.9. Found: C, 29.9; H, 0.3; Cl, 70.0.

9H-Tridecachloro-9-phenylfluorene (6). A mixture of α H compound 2 (0.100 g), powdered NaOH (0.80 g), ethyl ether (130 mL), and Me₂SO (30 mL) was shaken (43 h) under argon in the dark. The solution, which turned gradually from blue to garnet, was poured into degasified aqueous HCl. The organic layer was washed with water, dried, and evaporated. The residue by recrystallization (hexane) gave the 9H-fluorene 6: 0.083 g, 91.5%; mp 292.0–292.5 °C; UV (C₆H₁₂) 218 nm, 230 (sh), 297 (ϵ 65 300, 60 500, 24 900); IR (KBr) 2905 (vw), 1525 (w), 1355 (m), 1330 (s), 1235 (m), 1165 (m), 840 (m), 820 (s), 796 (m), 655 (m), 630 (m) cm⁻¹; ¹H NMR (CCl₄) τ 2.65 (s). Anal. Calcd for C₁₉HCl₁₃: C,

33.1; H, 0.1; Cl, 66.8. Found: C, 33.2; H, 0.2; Cl, 66.7. Perchloro-9-phenylfluorenyl Radical (PPF). (1) From αH Compound 2. Compound 2 (1.500 g) was heated (280-300 °C, 1 h) under argon in the dark. The resulting mass was purified

°C; UV-vis (C₆H₁₂) 217 nm, 230 (sh), 293, 320 (sh), 345 (sh), 373, 388, 408 (sh), 460, 498, 530, 573, 622 (e 73 500, 47 000, 45 500, 13 600, $5500,\,5180,\,6150,\,3790,\,1330,\,1170,\,645,\,2030,\,5080);\,\mathrm{I\!R}$ (KBr) 1486 (vw), 1380 (s), 1342 (s), 1305 (s), 1298 (s), 1260 (s), 1090 (m), 815 (s), 698 (m), 640 (m) cm⁻¹. Anal. Calcd for C₁₉Cl₁₃: C, 33.1; Cl, 66.9. Found: C, 33.1; Cl, 66.9.

(2) From Perchlorotriphenylmethyl Radical (PTM) with Heat. Radical PTM¹ (0,100 g) was heated (310-320 °C, 10 min) under argon in the dark. By treating the reaction mass as before radical PPF (0.071 g, 78%) was obtained.

(3) From Radical PTM with Light. A solution of radical PTM (0.079 g) in CCl₄ (25 mL) was illuminated (45 min) with a 500-W incandescent lamp (20-cm distance under argon; the solution turned from red to green). By evaporation of the solvent a residue was obtained, which by purification through alumina (CCl₄) yielded a material (0.049 g) containing radical PPF (14%) (UV-vis spectroscopy).

(4) From 9H Compound 6. A mixture of 6 (0.100 g), NaOH (0.7 g), ethyl ether (130 mL), and Me₂SO (25 mL) was shaken for 3 min under argon in the dark. The resulting red solution was filtered over I_2 (0.4 g) under argon in the dark. It was allowed to stand for 15 min, washed first with aqueous NaHSO₃ and then with water, dried, and evaporated. The residue was purified through silica gel (CCl_4) and crystallized $(CCl_4-hexane)$ to give impure radical PPF (0.052 g). UV-vis spectroscopy indicated that the yield of PPF was 32%

(5) From Perchloro-9-phenylfluorene (7) with Heat. Chlorocarbon 7²⁶ (0.101 g) was heated (230-240 °C, 30 min) under argon in the dark. By treating the resulting mass as before, radical PPF (0.051 g, 53%) was obtained.

(6) From Chlorocarbon 7 with FeCl₂. A mixture of 7²⁶ (0.100 g), FeCl₂·2H₂O (0.080 g), and ethyl ether (25 mL) was refluxed (20 min) under argon in the dark. The resulting solution was washed with water, dried, and evaporated to give a residue, which by purification through alumina (CCl₄) yielded radical PPF (0.089 g, 84%).

Perchloro-9-phenylfluorene (7) from Radical PPF. (1) With Cl_2 and I_2 . A stream of dry Cl_2 was passed (1.5 h) through a solution of radical PPF (0.100 g) and I_2 (0.100 g) in CCl₄ (5 mL) in the dark. By evaporation of the solvent a solid was obtained, which by recrystallization (hexane) yielded chlorocarbon 7: 0.084 g, 80%; mp 180–210 °C dec; UV ($\check{C}_{6}H_{12}$) 218 nm, 237, 272 (sh), 310 (ϵ 71 500, 54 000, 21 600, 15 400); IR (KBr) 1520 (w), 1400 (m), 1323 (s), 1300 (s), 1250 (m), 1220 (m), 1180 (m), 1170 (m), 848 (m), 830 (m), 810 (m), 780 (m), 690 (m), 652 (s), 630 (m), 522 (m), 510 (s) cm⁻¹. Anal. Calcd for C₁₉Cl₁₄: C, 31.5; Cl, 68.5. Found: C, 31.6; Cl, 68.4.

(2) With AlCl₃ and SO₂Cl₂. Radical PPF (0.100 g) was added to a cooled (-15 °C) solution of anhydrous AlCl₃ (0.13 g) in SO₂Cl₂ (15 mL), and the resulting mixture was stirred (1.5 h) at the same temperature. The resulting green solution was poured onto cracked ice and the SO_2Cl_2 removed by evaporation in vacuo. The residue was treated with aqueous NaHCO₃, acidified with aqueous HCl, and extracted with ether. The organic layer was washed with water, dried, and evaporated to give a solid, which by purification through silica gel (hexane) and crystallization (same solvent) yielded chlorocarbon 7 (0.068 g, 65%).

Reductions of Radical PPF. (1) With NaOH-Ether-Me₂SO. A mixture of PPF (0.100 g), powdered NaOH (0.40 g), ethyl ether (75 mL), and Me₂SO (15 mL) was shaken (2.5 h) under

⁽²⁶⁾ The synthesis of this compound is described later.

argon. The resulting solution was filtered and poured into water, and the organic layer was decanted, washed with water, dried, and evaporated to give a residue, which by purification (alumina; hexane) gave 9H compound 6 (0.066 g, 66%).

(2) With HI. A mixture of PPF (0.104 g), 51% aqueous HI (1 mL), and acetic acid (7 mL) was refluxed (48 h) under argon. The resulting solution was poured into aqueous NaHSO₃ and extracted with ether. The ethereal layer was washed with aqueous NaHCO₃ and with water, dried, and evaporated to give a residue, which was purified as before to give 9H compound 6 (0.052 g, 50%).

Perchloro-9-phenyl-3-fluorenone (9) and Perchloro-4-(9fluorenylidene)cyclohexa-2,5-dienone (10). (1) From Chlorocarbon 7 with Oleum. A mixture of chlorocarbon 7 (0.102 g) and 20% oleum (50 mL) was stirred (8 h). The resulting dark green solution was poured onto cracked ice and extracted with CHCl₃. The organic layer was washed with aqueous NaHCO₃ and with water, dried, and evaporated to give a residue, which was cromatographed in the dark (silica gel, CCl₄). Two products were obtained: (a) a solid, which by recrystallization (hexane) yielded dienone 10 [0.023 g, 24%; yellow crystals, mp 270-303 °C dec; UV-vis (C₆H₁₂) 217 nm, 290, 303, 325 (sh), 404, 427, 452, 480 (sh), (e 63 900, 41 200, 43 300, 12 000, 3100, 3700, 2800, 400); IR (KBr) 1725 (s), 1600 (s), 1555 (m), 1350 (s), 1295 (m), 1280 (m), 1250 (m), 975 (s), 870 (m), 825 (m), 725 (m), 698 (m), 683 (m), 504 (m) cm⁻¹. Anal. Calcd for C₁₉Cl₁₂O: C, 34.1; Cl, 63.5. Found: C, 34.1; Cl, 63.7.] and (b) a solid, which by recrystallization (hexane) afforded fluorenone 9 [0.035 g, 37%; brown-reddish crystals, mp 240 °C dec; UV-vis (C₆H₁₂) 217 nm, 305, 400 (sh), 428, 452, 485 (sh) (\$\epsilon 85 300, 26 300, 3500, 6200, 6700, 2400); IR (KBr) 1652 (s), 1578 (m), 1525 (m), 1370 (s), 1362 (s), 1345 (s), 1302 (m), 1180 (m), 1150 (m), 1115 (m), 1012 (s), 830 (m), 792 (m), 770 (m), 759 (m), 725 (m), 681 (m), 655 (m), 530 (m), 512 (m) cm⁻¹. Anal. Calcd for C₁₉Cl₁₂O: C, 34.1; Cl, 63.5. Found: C, 34.1; Cl, 63.3.]. These ketones show halochromy in oleum.

(2) From Chlorocarbon 7 with SbCl₅. SbCl₅ (1 mL) was added to a solution of chlorocarbon 7 (0.075 g) in CCl₄ (20 mL), and the solution was left undisturbed (24 h) under argon in the dark. The resulting dark green solution was poured into water and extracted with CCl₄. The organic layer was washed with water, dried, and evaporated to give a residue (0.070 g), which was fractionated by TLC (silica gel, CCl₄) to yield radical PPF (0.035 g, 49%), dienone 10 (0.012, 17%), and fluorenone 9 (0.010 g, 14%).

(3) From Radical PPF with $SbCl_5$ in CCl_4 . $SbCl_5$ (1 mL) was added to a solution of radical PPF (0.100 g) in CCl_4 (20 mL), and the mixture was left undisturbed (40 h) under argon in the dark. The resulting mass was treated as in (2), giving radical PPF (0.020 g, 20% recovery), dienone 10 (0.028 g, 29%), and fluorenone 9 (0.028 g, 29%).

(4) From Radical PPF with $SbCl_5$ in CH_2Cl_2 . The preceding reaction was repeated by using CH_2Cl_2 (50 mL) as the solvent. The products isolated were radical PPF (0.016 g, 16% recovery), dienone 10 (0.013 g, 13%), and fluorenone 9 (0.025 g, 26%).

(5) From Radical PPF with SbCl₅ in SO_2Cl_2 . The preceding reaction was repeated by using SO_2Cl_2 (70 mL; 48 h) as the solvent. The products isolated were radical PPF (0.020, 20% recovery) and fluorenone 9 (0.051 g, 52%).

(6) From Radical PPF with Cold Oleum. A mixture of radical PPF (0.101 g) and 20% oleum (50 mL) was stirred (24 h) in the dark. The resulting solution was poured onto cracked ice and worked up as in (1), giving dienone 10 (0.041 g, 42%) and fluorenone 9 (0.025 g, 26%).

(7) From Radical PPF with O_2 and Light. A solution of radical PPF (0.103 g) in CCl₄ (50 mL) was illuminated (30 min) with a 500-W incandescent lamp (20-cm distance). The resulting solution was evaporated, and the residue was worked up as before, giving dienone 10 (0.029 g, 29%) and fluorenone 9 (0.021 g, 21%). No PPF was detected.

(8) From α H Compound 2 with Oleum. A stirred mixture of α H compound 2 (0.500 g) and 20% oleum (100 mL) was heated (120 °C; 40 h). The solution gradually became dark blue and was then worked up as in (1), giving radical PPF (0.057 g, 13%) and a solid, which by recrystallization (hexane) yielded fluorenone 9 (0.370 g, 84%).

(9) From Dodecachloro-3-methoxy-9-phenylfluorenyl Radical (17). The reaction of fluorenyl radical 17^{26} (0.075 g) with

SbCl₅ in CH₂Cl₂ as in (4) gave fluorenone 9 (0.066 g, 90%).

(10) Thermolysis of Perchlorofuchsone (11). Perchlorofuchsone 23,10 (11, 0.034 g) was heated gradually (10 min) from room temperature up to 325 °C under argon and maintained at this temperature for 10 min. By TLC (silica gel; CCl₄), fluorenone 9 (0.008 g, 26%) and dienone 10 (0.011 g, 36%) were isolated.

9*H***-Dodecachloro-9-phenylfluoren3-ol** (14). Aqueous (57%) HI (1.7 mL, containing some I₂) was added to a solution of the fluorenone 9 (0.407 g) in benzene (60 mL), and the resulting mixture was stirred (24 h) under argon. The benzene layer was decanted, washed with aqueous (50%) H₂PO₃, with aqueous HCl and with water, and then dried and evaporated to give a solid (0.330 g), which by recrystallization (benzene) yielded fluorenol 14: 0.317 g, 77.7%; mp 241 °C dec; UV (C_6H_{12}) 219 nm, 228, 297, 305 (sh) (ϵ 68300, 67000, 25100, 22200); IR (KBr) 3480 (m), 2910 (vw), 1530 (w), 1414 (w), 1370 (s), 1350 (s), 1338 (m), 1255 (m), 1200 (m), 1168 (m), 878 (m), 832 (m), 785 (m), 670 (m) cm⁻¹; ¹H NMR (C_6D_6) τ 4.25 (s, CH); ms, m/e M⁺ calcd for $C_{19}H_2^{35}Cl_{12}O$ 666, found 666. Anal. Calcd for $C_{19}H_2Cl_{12}O$: C, 34.0; H, 0.3; Cl, 63.3. Found: C, 33.7; H, 0.3; Cl, 63.1.

9*H*-3-Acetoxydodecachloro-9-phenylfluorene (12). A mixture of the fluorenol 14 (0.200 g) and acetic anhydride (100 mL) was refluxed (3 h) under argon in the dark. Evaporation of the solvent in vacuo gave a residue, which was dissolved in CHCl₃ and passed through silica gel to yield, after evaporation of the solvent, the acetoxy derivative 12: 0.189 g, 89%; mp 293-296 °C; UV (C_6H_{12}) 219 nm, 226 (sh), 293, 304 (sh) (ϵ 71 500, 66 300, 25 100, 23 700); IR (KBr) 2920 (vw), 1789 (s), 1530 (w), 1424 (w), 1400 (w), 1350 (s), 1259 (w), 1245 (w), 1183 (s), 1163 (m), 1118 (m), 1021 (m), 901 (m), 840 (m), 688 (m) cm⁻¹; ¹H NMR (C_2Cl_4) $r_{3.73}$ (s, 1, CH), 7.64 (s, 3, CH₃); ms, m/e M⁺ calcd for C_{21} -H₄³⁵Cl₁₂O₂ 708, found, 708. Anal. Calcd for C_{21} H₄Cl₁₂O₂: C, 35.3; H, 0.6; Cl, 59.6.

9*H*-**Dodecachloro-3-methoxy-9-phenylfluorene** (16). An excess of CH_2N_2 in ether was added to a solution of fluorenol 14 (0.250 g) in $CHCl_3$ (15 mL). The residue obtained by evaporation was purified by TLC (silica gel; CCl_4) to give methoxyfluorene 16: 0.237 g, 93%; mp 273–276 °C; UV (C_6H_{12}) 218 nm, 228, 296, 306 (sh) (ϵ 67 600, 65 900, 25 100, 21 900); IR (KBr) 2920 (w), 2840 (vw), 1530 (w), 1450 (w), 1356 (s), 1259 (m), 1241 (m), 1165 (m), 1035 (m), 838 (m), 680 (m) cm⁻¹; ¹H NMR (CCl_4) τ 3.83 (s, 1, CH), 6.04 (s, 3, CH_3); ms, m/e M⁺ calcd for $C_{20}H_4^{35}Cl_{12}$ O 680, found 680. Anal. Calcd for $C_{20}H_4$ (Cl_2) C, 35.0; H, 0.6; Cl, 62.0. Found: C, 35.2; H, 0.5; Cl, 62.2.

Dodecachloro-3-methoxy-9-phenylfluorenyl Radical (17). Treatment of methoxyfluorene **16** (0.175 g) with NaOH in ether–Me₂SO and then with I₂ as in the synthesis of PPF from 9H compound **6** gave fluorenyl radical **17** (0.132 g, 75.5%) as dark green crystals: mp 296.5–300.0 °C; UV–vis (C_6H_{12}) 219 nm, 226 (sh), 259 (sh) 291, 320 (sh), 341, 369, 383, 401 (sh), 457, 494, 519, 563, 609 (ϵ 54 900, 52 000, 23 100, 43 200, 12 800, 3900, 5600, 6800, 4500, 1700, 1800, 1000, 2700, 6200); IR (KBr) 2920 (vw), 2840 (vw), 1520 (w), 1480 (w), 1390 (s), 1373 (m), 1340 (s), 1274 (s), 1131 (m), 1000 (m), 828 (m), 680 (m), 658 (m) cm⁻¹. Anal. Calcd for C₂₀H₃Cl₁₂O: C, 35.1; H, 0.4; Cl, 62.1. Found: C, 35.0; H, 0.5; Cl, 62.1.

Reaction of Methoxyfluorenyl Radical 17 with SbCl₅. Radical 17 (0.075 g) was treated with SbCl₅ (1 mL) in CH_2Cl_2 (25 mL) as described above for radical PPF. An intense blue color was immediately formed and fluorenone 9 (0.066 g, 90%) was obtained.

Reaction of Acetoxy Compound 12 with NaOH in Ether-Me₂SO. 12 (0.070 g) was treated with a mixture of NaOH (0.07 g), ether (2 mL), and Me₂SO (0.4 mL) and then with I_2 (0.3 g) as in the synthesis of methoxyfluorenyl radical 17. Fluorenone 9 (0.036 g, 55%) was obtained.

Reaction of Dienone 10 with HI. Dienone 10 (0.032 g) was treated with HI/I_2 (0.15 mL) in benzene (10 mL) as in the reduction of fluorenone 9. Only 10 (0.029 g, 91%) was recovered.

 α *H*-Nonadecachloro-2-biphenylyl-4-biphenylylmethane (20). The chlorination leading to α H compound 20 was performed as described above for 9-phenylfluorene (1) by utilizing 9-(4-biphenylyl)fluorene²⁷ (19, 0.993 g), AlCl₃ (0.250 g), S₂Cl₂ (0.500 g),

⁽²⁷⁾ Bowden, K.; Cockerill, A. F. J. Chem. Soc. B 1970, 173.

and SO₂Cl₂ (130 mL). The crude product was passed through silica gel (CCl₄-hexane) and recrystallized (same solvent), giving α H compound **20**: 1.688 g, 55.5%; mp 295–298 °C; UV (C₆H₁₂) 215 nm, 295 (sh), 301 (ϵ 161 400, 2500, 2930); IR (KBr) 1520 (w), 1335 (s), 1260 (m), 1145 (m), 1090 (m), 830 (m), 800 (m), 752 (s), 744 (m), 692 (s), 652 (m), 510 (s) cm⁻¹; ¹H NMR (CCl₄) τ 3.09 (s). Anal. Calcd for C₂₅HCl₁₉: C, 30.8; H, 0.1; Cl, 69.1. Found: C, 30.9; H, 0.3; Cl, 69.1.

Perchloro-9-(4-biphenylyl)fluorenyl Radical (22). (1) **Thermolysis of** α**H Compound 20.** α**H** compound **20** (0.140 g) was heated (300–340 °C, 30 min) under argon. The resulting solid was passed through silica gel (CCl₄) and recrystallized (CCl₄), giving fluorenyl radical **22** (0.098 g, 76%; dark green crystals, 370–80 °C dec; UV–vis (C₆H₁₂) 214 nm, 230 (sh), 292, 346, 371, 387, 407, 460, 496, 525, 569, 618 (ϵ 100 600, 70 000, 40 400, 5120, 6160, 7100, 4660, 1990, 1800, 1020, 2470, 5690); IR (KBr) 1485 (w), 1378 (s), 1360 (w), 1338 (s), 1300 (s), 1270 (m), 1235 (m), 1090 (m), 870 (m), 840 (m), 750 (m), 690 (m), 654 (m), 640 (m), 570 (m), 510 (m), 500 (m) cm⁻¹. Anal. Calcd for C₂₅Cl₁₇: C, 33.2; Cl, 66.8. Found: C, 33.4; Cl, 66.7.

(2) Thermolysis of Perchloro-4-biphenylyldiphenylmethyl Radical (21). Radical 21^1 (0.053 g) was heated (220-230 °C, 15 min; 335-345 °C, 5 min) under argon. The crude product was treated as before to give fluorenyl radical **20** (0.025 g, 51%).

3-Methyl-9-(pentachlorophenyl)-9-fluorenol (25). A solution of (pentachlorophenyl)magnesium chloride in THF (from hexachlorobenzene, 4.114 g; Mg, 0.78 g; THF, 180 mL) was added slowly to a solution of 3-methylfluoren-9-one²⁸ (24, 0.706 g) in the same solvent (21 mL). The mixture was allowed to stand for 24 h, and the ethereal layer was washed with water, dried, and evaporated to dryness. The residue was dissolved in hexane and the solution chromatographed through silica gel. The hexane effluent contained pentachlorobenzene (2.112 g). Further elution with CHCl₃ gave a solid, which by recrystallization (CHCl₃) afforded fluorenol 25: 0.974 g, 60.2%; mp 196–197 °C; UV (C₆H₁₂) 216 nm, 232 (sh), 240 (sh), 268, 277 (sh), 290 (sh), 300 (sh), 312 $(\epsilon\,80\,900,\,57\,400,\,42\,000,\,11\,700,\,11\,450,\,9360,\,7170,\,3890);\,{\rm IR}$ (KBr) 3520 (m), 3400 (m), 3040 (w), 2910 (w), 1610 (w), 1485 (w), 1445 (m), 1330 (s), 1310 (s), 1215 (m), 1105 (m), 1035 (m), 1000 (m), 970 (m), 930 (m), 902 (m), 830 (m), 810 (s), 762 (s), 740 (s), 695 (s), 605 (s) cm⁻¹; ¹H NMR (CDCl₃) τ 2.7 (m, 7, Ar H), 6.83 (s, 1, OH), 7.69 (s, 3, CH₃). Anal. Calcd for C₂₀H₁₁Cl₅O: C, 54.0; H, 2.5. Found: C, 54.2; H, 2.6.

3-Methyl-9-(pentachlorophenyl)fluorene (26). A mixture of fluorenol 25 (0.372 g), acetic acid (18 mL), and 57% aqueous HI (2.6 mL) was refluxed (17 h). The reaction mixture was poured into water and extracted with ether. The ethereal layer was washed with aqueous NaHSO₃, with aqueous NaHCO₃, and with water, and then dried and evaporated. The residue was recrystallized from ether-hexane to give fluorene 26: 0.338 g, 94.5%; mp 163.5-165.0 °C; UV (C_6H_{12}) 230 (sh) nm, 240 (sh), 266, 293, 304 (ϵ 104 700, 38 700, 24 100, 12 150, 6470, 7010); IR (KBr) 3030 (w), 3015 (w), 2910 (w), 1605 (w), 1445 (m), 1355 (s), 1270 (s), 1110 (m), 930 (m), 835 (s), 805 (s), 760 (s), 735 (s), 720 (s), 680 (s), 650 (s), 3CH₃). Anal. Calcd for $C_{20}H_{11}Cl_5$: C, 56.1; H, 2.6. Found: C, 56.2; H, 2.4.

9H-3-Methyldodecachloro-9-phenylfluorene (27). A solution of fluorene 26 (1.013 g) in SO_2Cl_2 (35 ml) was added quickly to a boiling solution of anhydrous $AlCl_3$ (0.202 g) and S_2Cl_2 (1.866 g) in 70 mL of SO_2Cl_2 . The resulting solution was refluxed (5 min), treated with ice-water and with aqueous NaHCO₃, heated on a steam bath, and acidified with aqueous HCl. The resulting mixture was extracted with CCl₄, and the organic layer was dried, concentrated, and then passed through silica gel. By evaporation a solid was obtained, which was recrystallized (CCl₄) to give chlorinated fluorene 27: 1.016 g, 64.0%; mp 288-289 °C; UV (C_6H_{12}) 216 nm, 228 (sh), 297, 308 (sh) (ϵ 82 800, 68 100, 25 200, 21800); IR (KBr) 2900 (vw), 1520 (w), 1430 (w), 1345 (s), 1330 (s), 1255 (m), 1235 (m), 1160 (s), 1020 (m), 860 (m), 830 (s), 780 (m), 705 (m), 680 (m), 655 (m) cm⁻¹; ¹H NMR (CCl₄) τ 3.79 (s, 1, CH), 7.31 (s, 3, CH₃). Anal. Calcd for C₂₀H₄Cl₁₂: C, 35.9; H, 0.6. Found: C, 36.0; H, 0.7.

3-Methyldodecachloro-9-phenylfluorenyl Radical (28). A mixture of 9H-fluorene 27 (0.154 g), NaOH (6 g), ethyl ether (150 mL), and Me₂SO (20 mL) was shaken in the dark. The NaOH was filtered off, the filtrate was poured onto I₂ (0.48 g), and after 10 min the resulting solution was treated with water, with aqueous NaHSO₃ to destroy the excess of I₂, again with water to eliminate the Me₂SO and dried. Upon partial evaporation by passing a stream of N₂ through the solution, methylfluorenyl radical 28 (0.084 g, 55%) precipitated as blue crystals: mp 187–190 °C; UV-vis (CCl₄) 287 nm, 317 (sh), 345, 367, 382, 400 (sh), 457, 494, 525, 566, 612 (ϵ 41 700, 13 800, 4300, 6250, 7300, 4590, 1550, 1620, 855, 2550, 6050); IR (KBr) 1490 (w), 1430 (vw), 1378 (s), 1340 (s), 1322 (m), 1298 (m), 1268 (s), 1193 (m), 1170 (s), 1112 (m), 1038 (m), 829 (s), 787 (m), 700 (m), 636 (m) cm⁻¹. Anal. Calcd for C₂₀H₃Cl₁₂: C, 35.9; H, 0.5. Found: C, 36.4; H, 0.5.

9-(2-Biphenylyl)fluorene (31). 9-(2-Biphenylyl)fluoren-9-ol²⁹ (**29**, 0.500 g) was added to a solution of anhydrous $AlCl_3$ (0.70 g) and $LiAlH_4$ (0.10 g) in ethyl ether (100 mL), and the resulting mixture was refluxed (16 h). After cooling, ice-water was added slowly, and the ethereal layer was decanted, dried, and evaporated. The residue after purification (alumina; CCl_4) and recrystallization (CCl_4) gave fluorene **31**: 0.370 g, 77.8%; mp 220-221 °C. Anal. Calcd for $C_{25}H_{18}$: C, 94.3; H, 5.7. Found: C, 94.5; H, 5.6.

Spiro-9,9'-bifluorene (30). A mixture of fluorenol **29** (2.00 g), sodium formate (29.0 g), and formic acid (91 g) was refluxed (3 h) under argon. After being cooled, the resulting mixture was poured into water, and the solid formed was filtered, washed with water, dried, purified (alumina; CCl_4), and recrystallized (CCl_4) to give spiro compound **30**: 1.74 g, 92.0%; mp 200–201 °C (lit.²⁹ mp 198–199 °C). Anal. Calcd for $C_{25}H_{16}$: C, 94.3; H, 5.6. Found: C, 94.3; H, 5.4.

Chlorination of Fluorene 31. This chlorination was carried out as described for fluorene 1 (fluorene 31, 1.00 g; AlCl₃, 0.30 g; S_2Cl_2 , 0.60 g; SO_2Cl_2 , 250 mL; reaction time, 90 min). The resulting residue (2.87 g) was submitted to column chromatography (alumina; hexane-CCl₄) to yield (a) 9H-heptadecachloro-9-(2-biphenylyl)fluorene (33) [1.66 g, 58.5%; mp 300-303 °C; UV (C₆H₁₂) 216 nm, 302, 310 (sh) (\$\epsilon 103 700, 20 700, 18 700); IR (KBr) 2920 (w), 1530 (w), 1401 (m), 1392 (m), 1357 (s), 1345 (s), 1337 (s), 1260 (m), 1232 (m), 1208 (m), 1199 (m), 851 (m), 840 (s), 831 (s), 800 (m), 760 (m), 718 (m), 710 (m), 698 (m), 661 (m), 637 (m), 572 (m), 520 (m) cm⁻¹; ¹H NMR (CCl₄) τ 3.80. Anal. Calcd for C₂₅HCl₁₇: C, 33.2; H, 0.1; Cl, 66.7. Found: 33.0; H, 0.1; Cl, 66.8.] and (b) perchlorospiro-9,9'-bifluorene (32) [0.590 g, 21.6%; mp 388-397 °C; UV (C₆H₁₂) 240 nm, 290 (sh), 303, 320 (sh) (\$\epsilon 74 200, 25 900, 37 300, 25 500); IR (KBr) 1530 (w), 1402 (m), 1330 (s), 1250 (m), 1232 (m), 1200 (m), 1178 (m), 1040 (m), 850 (m), 828 (s), 786 (m), 640 (s), 580 (m), 520 (m), 500 (m) cm⁻¹. Anal. Calcd for C25Cl16: C, 34.6; Cl, 65.4. Found: C, 34.2; Cl, 65.1.].

Chlorination of Spiro Compound 30. This chlorination was carried out as described for fluorene 1 (spiro compound 30, 1.114 g; AlCl₃, 0.18 g; S_2Cl_2 , 0.36 g; SO_2Cl_2 , 100 mL; reaction time, 15 h). The residue was purified (alumina; CCl₄) and recrystallized (chlorobenzene) to give spiro compound 32 (2.569 g, 84.0%).

Formation and Stability of Sodium Perchloro-9-(2-biphenylyl)fluorenide (35). The preparation was carried out as in the synthesis of 9H compound 6 (9H compound 33, 0.100 g; NaOH, 0.40 g; ether, 75 mL; Me₂SO, 15 mL; reaction time, 2.5 h). Treatment of the red solution with water gave back 33 (0.086 g, 86% recovery).

Perchloro-9-(2-biphenylyl)fluorenyl Radical (34). This reaction was carried out as in the synthesis of radical PPF, starting from 9H compound 6 (9H compound 33, 0.185 g; NaOH, 0.70 g; ether, 150 mL; Me₂SO, 30 mL; reaction time, 2.5 h. I₂, 0.8 g; reaction time, 2 h). The raw product was purified (alumina; CCl₄) and recrystallized (hexane) to give green crystals of fluorenyl radical 34: 0.115 g, 62.0%; UV-vis (C₆H₁₂) 215 nm, 299, 382 (sh), 391, 455 (sh), 495, 572, 620 (ϵ 138 000, 45 500, 4300, 5250, 1800, 1130, 1230, 2540); IR (KBr) 1380 (s), 1332 (s), 1300 (s), 1260 (m), 1180 (m), 1100 (m), 840 (m), 690 (m), 640 (m), 512 (m) cm⁻¹. Anal. Calcd for C₂₅Cl₁₇: C, 33.2; Cl, 66.7. Found: C, 33.4; Cl, 66.8.

Cyclization of Fluorenyl Radical 34. A solution of fluorenyl radical 34 (0.061 g) in CCl₄ (50 mL) was refluxed (1 h) under argon

in the dark. The resulting solution was evaporated and the residue purified (alumina, CCl₄) and recrystallized (CCl₄) to give spiro compound 32 (0.046 g, 82%).

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Asymmetric Induction in Carbonyl Analogues: Comments on Models

Diana Kruger, Alan E. Sopchik, and C. A. Kingsbury*

Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588

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Organometallic reagent additions to certain carbonyl analogues are reported. The compounds in question have $C = C(CN)_2$ or $C = C(CO_2R)_2$ in place of CO. The ground-state conformation of these analogues is quite specific. Some of the additions obey the Cram et al. rules for asymmetric induction but require that approach of the organometallic reagent occurs over the L group in the ground-state conformation. This is taken as an indication that the ground-state conformation is not relevant, in agreement with the Curtin-Hammett principle. In other cases, little asymmetric induction is observed. A third type of behavior concerns opposite modes of addition to the dicyanide vs. the diester substrates. The variability of the data are discussed in terms of the validity of rules for asymmetric induction. Secondary isotope effects are explored in an attempt to resolve the dichotomy between additions to cyclic vs. acyclic ketones. The suggestion is made that the dichotomy in stereochemistry of addition may be related to a kinetically significant conformational change in cyclohexanones vs. acyclic substrates or cyclopentanones.

In recent years, a variety of approaches to asymmetric induction has resulted in systems showing high enantiomeric purities in the reaction products.¹⁻³ These striking successes have shifted interest from consideration of the fundamental bases of the phenomenon. Studies on the steric course of additions to carbonyl date from the 1950's when Barton codified the major findings for cyclohexanones. In acyclic systems, Cram and ElHafez established the rule for asymmetric induction (cf. model 1), a



model that still is widely used for predictive purposes.⁴

Later, Leitereg and Cram extended this work to include 1.3-asymmetric induction.⁵ Cram emphasized the growing space demands of the carbonyl oxygen as charge develops in the course of addition, a factor often disregarded in more recent work.

In 1967, Karabatsos formulated an alternative approach (model 2) based on extensive studies of the conformations of carbonyl compounds.⁶ Approach to carbonyl was considered most likely to occur over the small group (usually hydrogen) in the conformation in which the medium-sized group is eclipsed with carbonyl. However, subsequent work on substrates with large R groups was interpreted in terms of a different model.^{6c} In 1968, Chérest, Felkin, and Prudent suggested a third approach (cf. 3). This model emphasizes the transition state, not the ground state, as seems reasonable on the basis of the Curtin-Hammett principle.⁷⁻⁹ These workers agree with Karabatsos and others that the transition state is "early"; i.e., it resembles the starting structure rather than the product with regard to the extent of bond formation. However, torsional interactions in the developing bond to

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