mL of EtOH was added 0.211 g (1.2 mmol) of iodic acid in a minimum of water dropwise with stirring. A precipitate formed immediately and the reaction was stirred 1 h additional at room temperature. Then it was warmed to 50 °C for 15 min. Filtration and washing with ethanol and water yielded 0.44 g (92%) of orange solid. ^{1}H NMR (DMSO): δ = 3.95 (3 H, s), 7.10 (1 H, dd, J = 8.72, 2.38 Hz), 7.10 (1 H, d, J = 2.38 Hz), 7.86 (1 H, d, J = 6.74 Hz), 8.35 (1 H, s), 8.46 1 H, s). IR (KBr): 3021, 1720, 1574, 1531, 1462, 1277, 1223, 1014, 910, 837 cm^{-1}. MS m/e: 478, 450, 351, 323, 196, 181, 125.

3-Hydroxyxanthane (13). To a suspension of 3-hydroxyxanthone[12] (2.41 g, 11.4 mmol) in 100 mL of THF was added 30 mL of borane/THF complex (1.0 M in THF) at room temperature under nitrogen. After stirring overnight, the reaction was quenched by adding water dropwise at 0 °C. The solvents were removed and 30 mL of 0.5 N HCl was added. The precipitate was collected and dissolved in NaOH. The solution obtained was filtered and acidified with 2 N HCl. 3-Hydroxyxanthane (2.2 g) was collected in 97% yield. ^{1}H NMR (d-DMSO; 200 MHz): δ 9.46 (2, 1 H), 7.18 (m, 2 H), 7.81 (m, 3 H), 6.47 (m, 2 H), 3.89 (s, 2 H). IR (KBr): 3276, 3067, 1609, 1462, 1234, 1149, 972, 843, 756 cm^{-1}. MS m/e: 198, 197.

2,4-Diiodo-3-fluorone (DIF) (14). Iodic acid (0.704 g, 4.0 mmol) was dissolved in a minimum of water and added dropwise to a solution of 3-hydroxyxanthane (0.40 g, 2 mmol) and iodine (1.02 g, 8.0 mmol) in 10 mL of EtOH. The mixture was stirred for 2 h at room temperature and the temperature then slowly raised to 60–70 °C for another 2 h. After cooling, the precipitate was filtered and washed with water and ethanol. 2,4-Diiodo-3-fluorone (0.81 g) was obtained in 90.8% yield. ^{1}H NMR (DMSO): δ 8.54 (s, 1 H), 8.38 (s, 1 H), 7.92 (d, 1 H, J = 7.6 Hz), 7.81 (m, 1 H), 7.67 (d, 1 H, J = 8.5 Hz), 7.48 (m, 1 H). IR (KBr): 3033, 1589, 1543, 1211, 914, 756 cm^{-1}. MS m/e: 448, 420, 321, 293, 254, 166, 148.

Conclusion

A new series of dyes based on the unsubstituted xanthene skeleton has been synthesized and their spectral properties have been reported.

Acknowledgment. This work has been supported by the Ohio Department of Development, Thomas Edison Seed Development Grant Program. We are grateful for this support. Krista Motschiedler, an REU Summer Undergraduate Scholar (1991), was involved in part of synthesis of DIMF. We are grateful to a number of our colleagues for helpful discussions.

Supplementary Material Available: ^{1}H NMR spectra for compounds **5**, **6**, **7**, **8**, **10**, **11**, **13**, and **14** (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis of the Sterically Hindered Bis(pentachlorophenyl)acetic Acid and Derived Stable Free Radicals

Pat O'Neill and Anthony F. Hegarty*

Chemistry Department, University College Dublin, Dublin 4, Ireland

Received January 2, 1992

Bis(pentachlorophenyl)acetic acid esters were synthesized from the α-hydroxydiaryl acetate esters **13** via the free radicals **15** formed on homolytic cleavage of the α-chloro compounds **14**. The acid **8** underwent rapid decarboxylation in basic solution (e.g., Et_3N in THF) but could be dehydrated to the corresponding ketene **17**. Nucleophilic addition to the ketene provided a route to the corresponding amides (**21** and **19**) and nitrile **20**, the enolates of which underwent ready oxidation to the corresponding stable free radicals **15**, **22**, and **23**. Evidence for the structure and unusual stability of these free radicals is presented. Attempts to observe enols of acids or esters on the addition of water or alcohols to the sterically hindered ketene **17** were unsuccessful.

The stabilization of otherwise transient species by the introduction of bulky substituents is well-known.[1] Diverse examples include carbocations,[2] free radicals,[1,3] enols,[4] antiaromatic compounds[5] and compounds with carbon to second-row element pπ–pπ bonds.[6]

We have for some time been interested in the use of steric hindrance to stabilize ene-1,1-diols **2** which are the enol tautomers of carboxylic acids **1**. The ene-1,1-diol

1 **2**

isomers of substituted acetic acids can be stabilized by substitution with bulky aryl groups, such as 2,4,6-trimethyl- and pentamethylphenyl.[7,8] Nevertheless, their reactivity is still high, since they decay to the keto forms (the acids) in a matter of minutes, and they also react readily with molecular oxygen. Therefore, we have attempted to stabilize the ene-1,1-diol form by introducing two geminal C_6Cl_5 groups since (a) they would confer a moderate thermodynamic stabilization by π–π interaction

(1) (a) Ballester, M.; Riera, J. *J. Am. Chem. Soc.* **1964**, *86*, 4505. Ballester, M.; Riera, J. Castaner, J.; Badia, C.; Monso, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215. (b) Tidwell T. T. *Tetrahedron* **1978**, *34*, 1855.
(2) Ballester, M.; Riera, J.; Rodriquez-Siurana, A. *Tetrahedron Lett.* **1970**, 3615.
(3) Sabacky, M. J.; Johnson, C. S.; Smith, R. G.; Gutowsky, H. S.; Martin, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2054.
(4) Rappoport, Z.; Nadler, E. *J. Am. Chem. Soc.* **1987**, *109*, 2112.
(5) Masamune, S.; Nakamura, N.; Suda, M.; Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481.
(6) Duus, F. *Comprehensive Organic Chemistry*, Pergamon Press: New York, 1979; Vol. 3, Chapter 11.22.
(7) Hegarty, A. F.; O'Neil, P. *J. Chem. Soc., Chem. Commun.* **1987**, *744*.
(8) Hegarty, A. F.; Allen, B.; O'Neill, P. *J. Chem. Soc., Perkin Trans. 2*, **1992**, 927.

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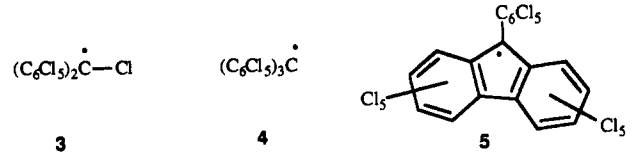
between that group and the enol C=C bond, as in perchloro trityl radicals;[1a] (b) they would destabilize the keto form on account of greater steric repulsions between the two C_6Cl_5 groups; (c) the four ortho chlorines would shield the C=C bond from attack; and (d) they would diminish nucleophilicity of the C=C on account of the total negative inductive effect of the 10 aryl chlorines (vs addition reactions, molecular oxygen attack, etc.). In fact, Sheppard[9] has found a σ_p value of 0.24 for C_6Cl_5—which is identical to that for C_6F_5 and intermediate between the phenyl and CF_3 groups in electron-withdrawing power. There are many chemical examples of the electron-withdrawing power of the C_6Cl_5 group, such as the failure of pentachlorostyrene to undergo ionic addition of HBr and the facile nucleophilic addition of sodium methoxide to the same olefin to give 1-(pentachlorophenyl)ethyl methyl ether.[10]

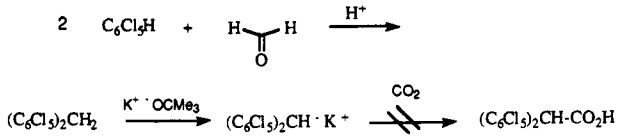
The steric protection afforded by C_6Cl_5 is very elegantly shown in the pioneering work of Ballester and co-workers.[1,2,11] Examples include perchlorodiphenylmethyl (3), trityl (4), and 9-phenylfluorenyl radicals (5).



3 4 5

Some of the radicals are so stable that they have been termed "inert free radicals"[1a] being inert to O_2, halogens, NO, and refluxing toluene. Their stability exceeds that of most tetracovalent organic compounds. That steric hindrance was the primary factor in the stabilization of these compounds was shown by the similar stability of the corresponding perchlorocarbocations[2] and carbanions.[12] It appears that the tricovalent carbon atom is buried in a crowd of substituents possessing high shielding capacity. The chloride shield is almost impregnable. In addition, the strength of the Cl–sp^2 carbon bond is high.

The initial route attempted to synthesize bis(pentachlorophenyl)acetic acid (8) involved the metalation and carboxylation of bis(pentachlorophenyl)methane (6). This compound was produced in 65% yield by the acid (25% oleum)-catalyzed condensation of pentachlorobenzene with formaldehyde.

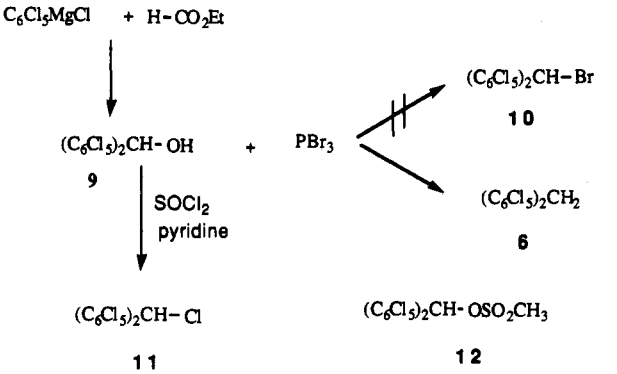


6 7 8

Diarylmethane 6 was extremely insoluble in most solvents but afforded a red potassium salt on treatment with potassium *tert*-butoxide in THF. However, the potassium salt was inert to carboxylation by CO_2. Reaction of solutions of 7 with ethyl chloroformate or phenyl isocyanate were also unsuccessful. The inertness of salt 7 to the latter two reagents is surprising but has parallels in organofluorine chemistry. Thus, Filler et al.[13] found highly fluorinated diarylmethyl carbanions to be unreactive toward CO_2 and that the corresponding acid, octafluorofluorene-9-carboxylic acid decarboxylates very readily.

An alternative strategy involved displacement by cyanide of a leaving group in α-substituted bis(pentachlorophenyl)methane derivatives. The necessary precursors were synthesized from bis(pentachlorophenyl)methanol (9). This compound was synthesized by reaction of pentachlorophenylmagnesium chloride with ethyl formate in yields of 60%.

Attempted bromination of alcohol 9, in refluxing chlorobenzene, with PBr_3 failed to give any α-bromobis(pentachlorophenyl)methane (10) but instead afforded bis(pentachlorophenyl)methane (6) in high yield. This unusual reduction most likely proceeds either via a homolytic pathway involving the α-H-bis(pentachlorophenyl)methyl radical, $(C_6Cl_5)_2CH^{\bullet}$, or via the formation of a Wittig compound. Both reactions have been precedented.[14]



11 12

Alcohol 9 was found to react with thionyl chloride in pyridine solution. Quenching of the resulting blue solution into dilute acid led to quantitative yields of α-chlorobis(pentachlorophenyl)methane (11).

The methanesulfonate 12 was prepared in good yield by treatment of 9 with methanesulfonyl chloride in pyridine. For use in nucleophilic displacement reactions, the mesylate 12 was preferred because of its much greater solubility.

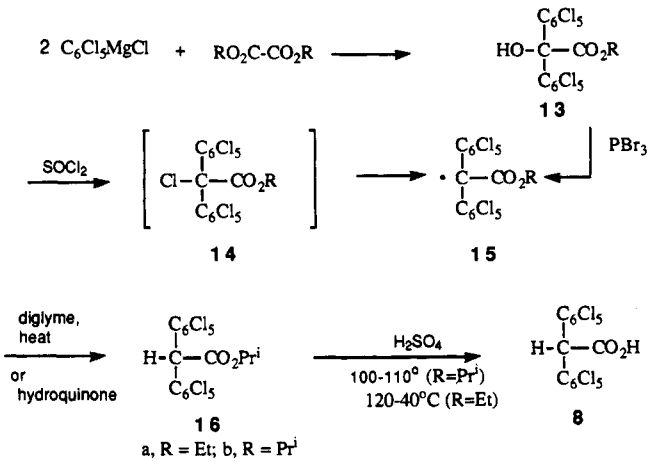
On refluxing solutions of mesylate 12 in DMF with either copper(I) or zinc cyanides, intractable mixtures were obtained of which diarylmethane 6 was a major component. Mesylate 12 or chloride 11 when heated with CuCN without solvent gave a mixture of nonpolar products (ν_{CN} absent). When 12 was refluxed with excess CuCN in DMSO, the only reaction to occur was with the solvent, forming perchlorobenzophenone in 52% yield.

In view of these negative results it was decided to investigate the reaction between oxalate esters and pentachlorophenyl magnesium chloride as a route to the molecular framework required.

On addition of alkyl oxalates (ethyl or isopropyl) to a solution of pentachlorophenylmagnesium chloride in THF at ambient temperature[15] a vigorously exothermic reaction occurred. Workup gave the decachlorobenzilate **13a** in 52% yield. The isopropyl ester was used in subsequent work because of its greater ease of removal.

It was hoped that reduction of benzilic ester **13b** to the corresponding diarylacetate ester, isopropyl bis(pentachlorophenyl)acetate (**16b**) would occur on treatment with HI, generated from I_2, red phsophorus, and acetic acid in analogy to the reduction of decafluorobenzilic acid to bis(pentafluorophenyl)acetic acid.[13] However, on application of this procedure to benzilate **13b**, no reaction occurred presumably due to the hindered nature of the hydroxyl group. Ballester et al.[1a] noted that when α-chlo-

(9) Sheppard, W. *J. Am. Chem. Soc.* **1970**, *92*, 5419.
(10) Ross, S.; Makarian, M.; Young, H.; Nazzewski, M. *J. Am. Chem. Soc.* **1950**, *172*, 1133.
(11) Ballester, M.; Castaner, J.; Pujadas, J. *Tetrahedron Lett.* **1971**, 1699.
(12) Ballester, M.; de la Fuente, G. *Tetrahedron Lett.* **1970**, 4509.
(13) Filler, R.; Fiebig, A.; Pelister, M. *J. Org. Chem.* **1980**, *45*, 1290.
(14) Ballester, M. *Adv. Phys. Org. Chem.* **1989**, *25*, 306, 360.
(15) Chambers, R., Clark, M.; Spring, D. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2464.



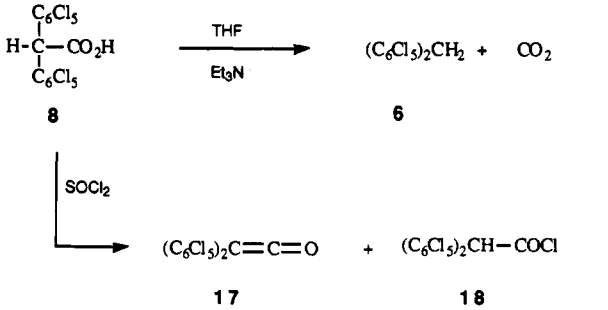
robis(polychloroaryl)methanes were refluxed in diglyme, reduction to the diarylmethanes occurred. As discussed earlier, this is probably a homolytic cleavage process. To this end, it was attempted to convert the benzilic ester **13b** to isopropyl perchlorodiphenylacetate (**14b**) prior to α-dechlorination to isopropyl bis(pentachlorophenyl)acetate (**16b**). When a solution of benzilic ester **13b** in thionyl chloride was refluxed, the solution became bright red in color within a few minutes. TLC analysis of the solution indicated only two components, the benzilic ester **13b** and a red spot (less polar). Refluxing for three days did not apparently change the TLC chromatogram. For reasons which will be elaborated on later, the identity of the red compound was established as isopropoxycarbonyl bis(pentachlorophenyl)methyl (**15b**), a stable α-ester free radical. This surprising result indicates that isopropyl perchlorodiphenylacetate (**14b**) is unstable with respect to cleavage of the α-carbon–chlorine bond. This homolysis is presumably due to relief of B and F strain[16] which occurs on breakage of this bond in **14b**.

However, when the benzilic ester **13b** was refluxed with excess PBr_3 in diglyme, the solution became dark red in color. Radical **15b** was detected by TLC. On continued refluxing the red color disappeared, and on cooling the yellow solution, isopropyl bis(pentachlorophenyl)acetate (**16b**) was obtained in 83% yield.

The diarylacetate ester **16b** could also be obtained by treatment of benzilate ester **13b** with $SOCl_2$ in pyridine at ambient temperature. A suspension of radical **15b** was formed. Reduction of this to **16b** was easily achieved by addition to a solution of hydroquinone in methanol. The overall yield of **16b** by this procedure was 58%. Apparently, even under these mild conditions, the intermediate isopropyl perchlorodiphenylacetate (**14b**) undergoes decomposition.

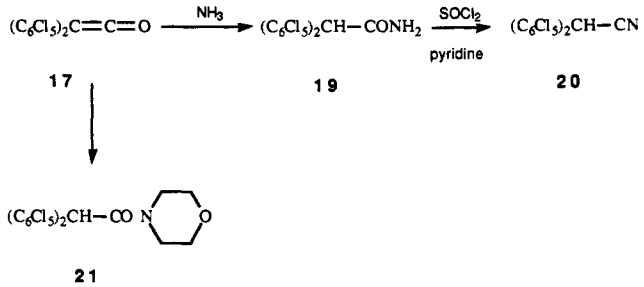
Dealkylation of the ester **16b** to the acid was achieved by heating a suspension in H_2SO_4 at 100–110 °C for several hours. On pouring the solution into ice and recrystallization from xylene, bis(pentachlorophenyl)acetic acid (**8**) was obtained in 85% yield. Use of the ethyl ester **16a** requires higher temperatures (120 °C). Diarylacetic acid **8** was unstable in polar solvents such as alcohols and THF, depositing the diphenylmethane. This process was inhibited by the addition of a small amount of a strong acid. On addition of a catalytic amount of triethylamine, **6** was immediately formed. This behavior also explains the earlier failure to carboxylate the potassium salt of **6**.

The ease with which diarylacetic acid **8** undergoes decarboxylation can be contrasted with the relative resistance



of bis(pentafluorophenyl)acetic acid[13] to undergo decarboxylation. Since the electronic effects of C_6F_6 and C_6Cl_5 groups are very similar,[9] the difference must be due to steric effects. Relief of F strain (between the CO_2^- group and the two aryl groups) and B strain (between the two aryl groups) could provide the necessary driving force.

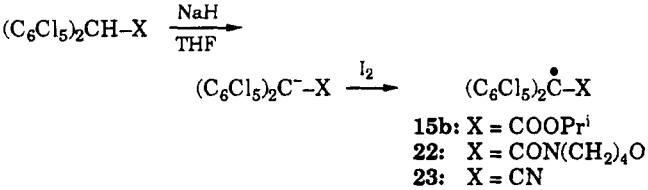
When the acid **8** was refluxed with thionyl chloride, the product was impure bis(pentachlorophenyl)ketene (**17**), which contained some acid chloride **18**. Purification of ketene **17** was hard to achieve due to its extreme reactivity to atmospheric moisture (formation of diarylacetic acid **8**). The IR spectrum showed an intense heterocumulene absorption at 2130 cm^{-1}.



The spontaneous elimination of HCl from acid chloride **18** to give **17** shows again the tendency of carbon atoms with two bulky aryl groups to adopt sp^2 hybridization.

The ketene **17** reacted normally with nucleophiles giving bis(pentachlorophenyl)acetamide (**19**) on treatment with ammonia and bis(pentachlorophenyl)acetylmorpholine (**21**) on treatment with morpholine. Dehydration of the acetamide **19** with thionyl chloride in pyridine gave bis(pentachlorophenyl)acetonitrile (**20**) in good yield.

The isopropyl ester **16b**, morpholide **21**, and nitrile **20** reacted readily with sodium hydride in THF to give yellow solutions of the sodium salts. These salts are very stable and resist oxidation by atmospheric oxygen or protonation by water. However, in solution on addition of excess iodine, and subsequent pouring into aqueous KI solution (to remove iodine), **15b**, **22**, and **23** were obtained in virtually quantitative yields.



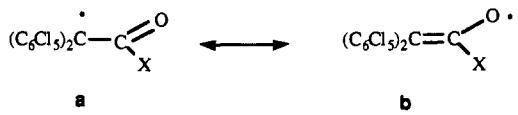
These radicals (except **23**) are indefinitely stable in the solid state and represent the first stabilized α-functionalized radicals.[17] Comparison of the IR spectra of **15b** and **22** with their CH precursors **16b** and **20**, respectively, is informative.

Ester **16b** shows carbonyl absorption at 1742 cm^{-1} and morpholide **21** at 1671 cm^{-1}. In the radicals **15b** and **22**

(16) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, New York, 1972.

(17) Neumann, W.; Stapel, R. *Chem. Ber.* **1986**, *119*, 3422.

the respective values are 1697 and 1609 cm^{-1}. These much lower ν_{CO} values for the radicals indicate increased single-bond character in the carbonyl group. This is good evidence for significant resonance stabilization involving the carbonyl oxygen (i.e., the radical equivalent of enolate resonance):



a b

15b X = OPr^i
22 X = $N(CH_2)_4O$

The α-cyano radical **23** showed no ν(C≡N) in the IR spectrum but the precursor, bis(pentachlorophenyl)-acetonitrile (**20**), showed only extremely weak cyano absorption. Presumably, this is due to the electron-withdrawing effect of the aryl groups which reduces the dipole change on C≡N stretching.

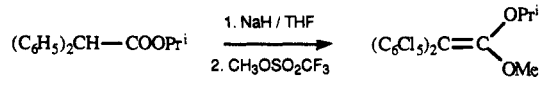
The ESR spectra of all three radicals support the significant resonance interaction between the trivalent carbon and the functional group. The radicals **15** and **22** showed simple one-line spectra (in chloroform as solvent) with g values of 2.0045 and 2.0043, respectively. The broadness of the signals can be ascribed[2] to unresolved hyperfine interactions with the aromatic chlorines. The α-cyano radical showed a well-resolved three-line ESR spectrum with g = 2.0047 and α_N = 5.997G. This is evidence for some delocalization of spin density onto the cyano nitrogen atom, giving some "keteniminyl" character (**24b**).

$$(C_6Cl_5)\dot{C}—CN \leftrightarrow (C_6Cl_5)_2C=C=\dot{N}$$
24a **24b**

The stability of these radicals far exceeds that of their nonchlorinated analogues such as (alkoxycarbonyl)diphenylmethyls and cyanodiphenylmethyl, which[17] are stable only in very dilute solution in the absence of oxygen and light.

All three radicals are rapidly reduced to their CH precursors on treatment with hydroquinone. The α-ester radical is the most stable, mp 182–3 °C, while the α-amide radical and α-cyano radical both decomposed on heating.

Attempts were made to observe the enol tautomer of the isopropyl ester **16b**. As a model for the enol **27**, the ketene acetal **25** which was expected to have similar spectroscopic characteristics was synthesized via alkylation of the sodium enolate **26** with methyl trifluoromethanesulfonate in a 70% yield. The intermediate sodium enolate was resistant to methyl iodide and sulphate.

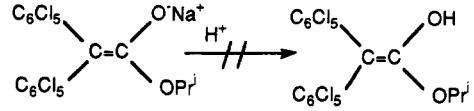


16b **25**

None of the C-alkylated product was detected in this reaction. The ketene acetal **25** showed ν(C=C) at 1610 cm^{-1} (very strong) and λ_{max} = 308 nm (log ε = 3.92). The resistance of **25** to acid-catalyzed hydrolysis was extreme, it being stable to 50:50 methanol–trifluoroacetic acid and 6 M HCl indefinitely.

An attempt at flash protonation of the sodium enolate **26** in THF by injection into aqueous solutions buffered at pH 2–7 failed to produce evidence for the existence of a relatively long-lived enol. This method has been used to generate unstable enols in solution, such as isobutyraldehyde enol,[18] and relies on kinetic protonation (on oxygen) followed by relaxation to the more stable keto form.

The sodium enolate **26** had λ_{max} = 390 nm (log ε = 2.46) while the ester is transparent in this region. The UV



26 **27**

spectrum taken immediately after injection into aqueous buffer solutions (pH 2–7) corresponds to that of ester **16b**. No absorption near 308 nm (the λ_{max} of ketene acetal **25**) was detected. Apparently, the enol **27**, if formed, reverts very quickly to the ester. The reason for this rapid ketonization cannot lie in a facile acid-catalyzed mechanism as the closely related ketene acetal **25** is highly resistant to acid. Presumably, ketonization is via the anion, even in acidic media. Thus, kinetic protonation (easily reversible) of enolate **26** would give enol **27** but thermodynamic protonation (irreversible under the conditions) would afford ester **16b**.

In conclusion, we have synthesized the first stable α-alkoxycarbonyl, α-carbamoyl, and α-cyano carbon free radicals kinetically stabilized by shielding due to bulky aryl substitutents. Interaction between the trivalent carbon atom and the α-functional group is clearly visible in the IR and ESR spectra of the radicals. Attempts to observe the enol tautomers of alkyl bis(pentachlorophenyl)acetates were unsuccessful.

Experimental Section

Bis(pentachlorophenyl)methane (6). Oleum (38 mL, 65%) was added cautiously to sulfuric acid (52 mL) in a 500-mL flask to produce 25% oleum. This solution was cooled with stirring and paraformaldehyde (10 g, 0.3 mol) added, followed by pentachlorobenzene (25 g, 0.08 mol). The flask was protected from moisture with a calcium chloride tube and the mixture stirred at 100–110 °C overnight. At first, the pentachlorobenzene melted to a liquid on top of the oleum but solidification later occurred. The mixture was allowed to cool to room temperature and was thrown onto a large quantity of ice, and the resulting gray solid was filtered and air dried. Due to the very low solubility of this compound, it was recrystallized in the following way. The crude solid was extracted with xylene (bp 140 °C in a Soxhlet apparatus for 6 h. On cooling of the xylene solution crystals appeared. These were filtered and extracted again with carbon tetrachloride overnight. On cooling and concentration of the solution, bis(pentachlorophenyl)methane (**6**) was obtained (16.5 g, 65%), mp 290–292 °C (sublimes). Due to the low solubility in all solvents, a ^1H NMR spectrum was not obtained. IR: ν(CH) 2970, 1370, 1354 cm^{-1} (C_6Cl_5). $C_{13}H_2Cl_{10}$ requires: C, 30.41; H, 0.39; Cl, 69.2. Found: C, 30.32; H, 0.43; Cl, 69.36.

Bis(pentachlorophenyl)methanol (9). Pentachlorophenylmagnesium chloride was prepared from hexachlorobenzene (66 g, 0.23 mol) and magnesium (8.44 g, 1.5 equiv) in 150 mL of THF–150 mL of benzene. After the spontaneous refluxing had ceased, the solution was allowed to cool to ambient temperature and stirred for 1 h. The solution was then heated to reflux and ethyl formate (40 mL, excess) added by syringe through a septum. A vigorous reaction occurred, with spontaneous refluxing. The solution was allowed to cool to ambient temperature, with stirring. After 1 h, methanol (20 mL) was added and the solution evaporated. The resulting dark brown solid was washed with aqueous HCl, methanol, and ethyl acetate to remove some of the colored impurities. It was recrystallized from toluene–pyridine (4:1) to yield pure bis(pentachlorophenyl)methanol (**9**) (35 g), mp 301–303 °C. The compound was too insoluble to record a ^1H NMR spectrum. IR: ν(OH) 3576, 1368, 1342 cm^{-1} (C_6Cl_5). Found: C, 29.81; H, 0.41; Cl, 67.51. $C_{13}H_2Cl_{10}O$ requires: C, 29.41; H, 0.37; Cl, 67.11.

The alcohol is not affected by sulfuric acid but dissolved in 10% oleum to produce a blue solution of the bis(pentachlorophenyl)methyl carbocation.

(18) Chiang, Y.; Kresge, A.; Walsh, P. *J. Am. Chem. Soc.* **1986**, *108*, 6314.

Bis(pentachlorophenyl)methyl Methanesulfonate (12). A solution of bis(pentachlorophenyl)methanol (9) (15.0 g, 0.029 mol) in 50:50 benzene–pyridine (300 mL) was prepared by the application of external heat. When all the alcohol had dissolved, the solution was treated with methanesulfonyl chloride (20 mL) via a syringe. The solution was stirred overnight at ambient temperature and the solvent evaporated. The resulting solid was washed with methanol (200 mL) and recrystallized from acetonitrile to yield bis(pentachlorophenyl)methyl methanesulfonate (12) (13.5 g, 78%). IR: ν(CH) 3040, 2960, 1340, 1320 (C_6Cl_5) cm^{-1}. ^{1}H NMR: δ 3.18 (s, 3 H), 7.64 (s, 1, H). Anal. Calcd for $C_{14}H_4Cl_{10}O_3S$: C, 27.67; H, 0.66; Cl, 58.48; S, 5.27. Found: C, 27.62; H, 0.59; Cl, 58.17; S, 5.36.

Attempted Reaction of Bis(pentachlorophenyl)methyl Methanesulfonate (12) with Copper(I) or Zinc(II) Cyanides in DMF. A solution of the mesylate 12 (2.0 g, 3.29 mmol) and 5 equiv of CuCN or $Zn(CN)_2$ in DMF (25 mL) was refluxed for 2 h or until TLC (10% ether–petrol) indicated the disappearance of the mesylate. The mixture was thrown into dilute HCl (caution! HCN) and the dark brown solid filtered. TLC and IR spectroscopy showed this to be bis(pentachlorophenyl)methane (6).

Attempted Reaction of Bis(Pentachlorophenyl)methyl Methanesulfonate (12) with Copper(I) Cyanide in DMSO. A solution of the mesylate (0.5 g, 0.82 mmol) and CuCN in DMSO (10 mL) was refluxed for 1 h. The solution turned an orange red color. On cooling, the solution deposited needles (0.26 g) of perchlorobenzophenone mp > 320 °C. IR: ν(CO) 1706, 1342, 1309 cm^{-1} (C_6Cl_5). Found: C, 29.58; H, 0.0; Cl, 67.44. $C_{13}Cl_{10}O$ requires: C, 29.60; H, 0.0; Cl, 67.36.

Attempted Reaction of Bis(pentachlorophenyl)methyl Mesylate (12) with Copper(I) Cyanide without Solvent. An intimately ground mixture of the mesylate 12 (3.0 g, 4.94 mmol) and CuCN (3.0 g, 6.78 mmol) was heated with a free flame for about 5 min. The resulting black solid was extracted with boiling xylene. TLC of the solution (10% ether–petrol) indicated only one spot, $R_f \sim 0.95$, due to bis(pentachlorophenyl)methane (6).

Chlorobis(pentachlorophenyl)methane (11). A solution of bis(pentachlorophenyl)methanol (9) (3.0 g, 5.67 mmol) in pyridine (30 mL) was cooled to 0 °C. Thionyl chloride (2 mL) was added, via syringe, to produce a dark blue solution which was stirred overnight. On pouring into dilute HCl, the blue color discharged. The solid was filtered, washed with water and methanol, and dried. The solid (0.5 g) was recrystallized from toluene (200 mL) to afford chlorobis(pentachlorophenyl)methane (11) (0.35 g). This compound is insoluble or very sparingly soluble in all solvents tried but yields a blue anion on reaction with potassium *tert*-butoxide in THF. IR: 2944 (ν(CH)), 1360, 1329 cm^{-1} (C_6Cl_5). Found: C, 28.34; H, 0.08; Cl, 71.4. $C_{13}HCl_{11}$ requires: C, 28.5; H, 0.19; Cl, 71.3.

Ethyl Decachlorobenzilate (13a). Magnesium turnings (7.9 g, 0.33 mol) were activated in THF (20 mL) with ethylene dibromide (1 mL). When ethylene evolution commenced, THF (390 mL) was added, followed by hexachlorobenzene (62.54 g, 0.22 mol). Within 5 min, spontaneous refluxing commenced, necessitating external cooling. The dark brown solution of pentachlorophenylmagnesium chloride was allowed to cool to ambient temperature, with stirring. It was immersed in an ice bath, and diethyl oxalate (30 mL) was added over 10 min via a syringe. Stirring was continued at ambient temperature for 1 h. The solution was thrown into dilute HCl (2 L) with stirring to dissolve excess magnesium. The resulting black oil solidified on cooling to a dark brown solid. This was filtered, washed with methanol to remove some of the colored impurities, and dried. It was then recrystallized from ligroin with charcoal treatment and finally from 1-butanol to afford ethyl decachlorobenzilate (13a) (34.61 g, 52%), mp 173–175 °C. IR: 3460, 1725 cm^{-1}. ^{1}H NMR: δ 5.2(s, 1 H, exchangeable), 4.37 (q, 2 H), 1.28 (d, 3 H). Anal. Calcd for $C_{16}H_6Cl_{10}O_3$: C, 31.95; H, 1.00; Cl, 59.07. Found: C, 32.09; H, 1.12; Cl, 58.89.

Ethyl Bis(pentachlorophenyl)acetate (16a). Method A. Phosphorus tribromide (15 mL) was added dropwise to a suspension of ethyl decachlorobenzilate (25.0 g, 0.042 mol) in diglyme (200 mL). On heating to reflux, the color of the solution changed to purple and TLC (10% ether–petrol) indicated the presence of the ethoxycarbonyl bis(pentachlorophenyl)methyl radical. This color faded after about 20 min to a pale yellow. The solution was allowed to cool to ambient temperature, and water (200 mL) was added. The resulting solid was filtered, washed with water and methanol, and dried. It was recrystallized from chloroform–methanol (1:5) to afford 20.27 g (83%) of ethyl bis(pentachlorophenyl)acetate (16a), mp 228–230 °C. IR: (ν(CH)) 2932; (ν(CO)) 1745, 1351, 1317 cm^{-1} (C_6Cl_5). ^{1}H NMR: δ 6.21(s, 1 H), 4.41 (q, 2 H), 1.32 (d, 3 H). Anal. Calcd for $C_{16}H_6Cl_{10}O_2$: C, 32.82; H, 1.03; Cl, 60.68. Found: C, 33.09; H, 1.08; Cl, 61.12.

Isopropyl decachlorobenzilate (13b) and ispropyl bis(pentachlorophenyl)acetate (16b) were made in an analogous manner from diisopropyl oxalate; isopropyl decachlorobenzilate, mp 174–5 °C; isopropyl bis(pentachlorophenyl acetate, mp 224–7 °C.

Ethyl Bis(pentachlorophenyl)acetate (16a). Method B. Thionyl chloride (2 mL) was added, via a syringe, to a cold (0 °C) solution of ethyl decachlorobenzilate (1.0 g, 1.6 mmol) in pyridine (10 mL). After stirring at this temperature for 10 min, the color of the solution became bright red. (TLC showed that (ethoxycarbonyl)bis(pentachlorophenyl)methyl was present). The solution was stirred at ambient temperature for 3 h and poured into a solution of quinol (2 g) in methanol (100 mL) to reduce the radical. On cooling, a solid was deposited which was washed with water and methanol and air-dried. IR and TLC comparison with authentic material showed the compound to be ethyl bis(pentachlorophenyl)acetate (16a) (0.52 g, 55%).

Bis(pentachlorophenyl)acetic Acid (8). A suspension of isopropyl bis(pentachlorophenyl)acetate (5.0 g, 8.35 mmol) in sulfuric acid (100 mL) was stirred at 100 °C for 4 h. (For the ethyl ester, temperatures of 120 °C must be used). The suspension was allowed to cool to ambient temperature and poured onto ice (400 g) and the solid filtered. It was dried and recrystallized from xylene **without** charcoal treatment to give bis(pentachlorophenyl)acetic acid (3.87 g, 84%), mp > 300 °C. Due to the insolubility of this compound in nonpolar solvents and its sensitivity to decarboxylation in more polar solvents, a ^{1}H NMR spectrum was not obtained. IR: (ν(OH)) 3400–2200, (ν(CO)) 1724 cm^{-1}. Anal. Calcd for $C_{14}H_2Cl_{10}O_2$: C, 30.16; H, 0.36; Cl, 63.73. Found: C, 30.77; H, 0.37; Cl, 64.65.

Decarboxylation of Bis(pentachlorophenyl)acetic Acid (8). Triethylamine (0.5 mL) was added to a stirring solution of bis(pentachlorophenyl)acetic acid (0.5 g, 0.9 mmol) in THF. An immediate white precipitate occurred. This was filtered off and identified by IR spectroscopy and mixed melting point as bis(pentachlorophenyl)methane (6).

Bis(pentachlorophenyl)ketene (17). A solution of bis(pentachlorophenyl)acetic acid (1.0 g, 1.8 mmol) in thionyl chloride (15 mL) was refluxed for 24 h. The thionyl chloride was rotary evaporated to leave a pale yellow solid (quantitative yield). Due to the extreme sensitivity of this ketene to moisture, attempts to recrystallize it led to bis(pentachlorophenyl)acetic acid (8). IR: (ν(C=C=O)) 2130 cm^{-1}.

Bis(pentachlorophenyl)acetomorpholine (21). Bis(pentachlorophenyl)ketene (17) was synthesized from bis(pentachlorophenylacetic acid (8) (5.79 g, 0.01 mol) and thionyl chloride (60 mL). After evaporation of the $SOCl_2$, the crude ketene was dissolved in anhydrous toluene (60 mL) and the flask fitted with a septum. The solution was cooled to 0 °C and morpholine (6.0 mL) added via syringe. The resulting suspension was stirred at ambient temperature for 1 h, and the solvents were evaporated. The residual solid was recrystallized from propanol and then from 1:6 chloroform–methanol to afford bis(pentachlorophenyl)-acetomorpholine (21) (5.86 g, 92%), mp 246–248 °C. IR: (ν(CH)) 2857, (ν(CO)) 1671 cm^{-1}. ^{1}H NMR: δ 6.31 (s, 1 H); 3.18–3.75 (m, 8 H). Anal. Calcd for $C_{18}H_9Cl_{10}NO$: C, 35.41; H, 1.48; Cl, 58.20. Found: C, 35.36; H, 1.39; Cl, 57.99

Bis(pentachlorophenyl)acetamide (19). Bis(pentachlorophenyl)ketene (17) was synthesized from bis(pentachlorophenyl)acetic acid (5.2 g, 9.93 mmol) as before. The crude ketene was dissolved in anhydrous toluene (70 mL) and dry ammonia gas bubbled in for 1 h. he precipitated solid was filtered and recrystallized from dioxane–petrol (1:4) to afford bis(pentachlorophenyl)acetamide (19) (3.34 g, 62%), mp > 300 °C. IR: ν(CO) 1694 ν(NH) 3146, 3172 cm^{-1}. Anal. Calcd for $C_{14}H_3Cl_{10}NO$: C, 30.21; H, 0.54; Cl, 63.85. Found: C, 29.96; H, 0.48; Cl, 63.95.

Bis(pentachlorophenyl)acetonitrile (20). Thionyl chloride (1.0 mL, 5 equiv) was added, via syringe, to a stirred suspension of bis(pentachlorophenyl)acetamide (19) (1.46 g, 2.63 mmol) in

pyridine (15 mL). The amide, initially only partially soluble, dissolved to an orange-yellow solution. The solution was stirred at ambient temperature for 1 h and poured into excess dilute HCl. The solid was filtered and recrystallized from xylene–petrol (1:4) to afford bis(pentachlorophenyl)acetonitrile (**20**) (0.94 g, 66%). IR: ν(CH) 2895, ν(CN) 2258 (vw), $\nu(C_6Cl_5)$ 2353 cm^{-1} (s). Anal. Calcd for $C_{14}HCl_{10}N$: C, 31.23; H, 0.18; Cl, 65.99. Found: C, 31.21; H, 0.15; Cl, 66.03.

(Isopropoxycarbonyl)bis(pentachlorophenyl)methyl Radical (15b). Isopropyl bis(pentachlorophenyl)acetate (**16b**) (3.0 g, 5.0 mmol) was added to a stirring suspension of sodium hydride (0.32 g, 15 mmol) in anhydrous THF (30 mL). The orange solution of sodium 1-isopropoxy-2,2-bis(pentachlorophenyl)-ethenolate was stirred at 30–40 °C for 1 h and then cooled to 0 °C. Iodine (5.0 g, 19.08 mmol) was added to produce a dark brown solution which was stirred at 0 °C for 10 min. The solution was added to 10% aqueous potassium iodide solution and the solid filtered. It was washed with 10% KI solution until the washings were colorless. It was then washed with methanol and air dried to afford (isopropoxycarbonyl)bis(pentachlorophenyl)methyl radical (**15**) (2.91 g, 90%) as a red powder, mp 182–3 °C. IR: ν(CO) 1697 cm^{-1}. ESR ($CHCl_3$): g = 2.0045. Anal. Calcd for $C_{17}H_7Cl_{10}O_2$: C, 34.11; H, 1.17; Cl, 59.36. Found: C, 33.96; H, 1.08; Cl, 59.24.

Cyanobis(pentachlorophenyl)methyl Radical (23). This was synthesized from bis(pentachlorophenyl)acetonitrile (**20**) (0.93 g, 1.73 mmol) and sodium hydride (0.124 g, 5.17 mmol) in THF (10 mL). The workup is analogous and afforded cyanobis(pentachlorophenyl)methyl radical (**23**) (0.85 g, 91%) as a purple solid. It decomposed on melting. ESR ($CHCl_3$): g = 2.0047; a_N = 5.997 G. Anal. Calcd for $C_{14}Cl_{10}N$: C, 31.28; H, 0.0; Cl, 66.11. Found: C, 31.09; H, 0.3; Cl, 65.81.

(*N*-Morpholinocarbonyl)bis(pentachlorophenyl)methyl Radical (22). Sodium hydride (0.14 g of 80% oil dispersion, 4.67 mmol) was washed with dry petrol (5 mL) three times before being transferred to a flask containing anhydrous THF (10 mL). Bis(pentachlorophenyl)acetic acid morpholide (**21**) (1.0 g, 1.6 mmol) was then added and the solution stirred at 30–40 °C for 1 h with a calcium chloride tube to exclude moisture. The orange solution of sodium 1-morpholino-2,2-bis(pentachlorophenyl)-ethenolate was cooled to 0 °C in an ice bath, and iodine (2.0 g, 7.63 mmol) was added to produce a dark solution. After stirring for 10 min at 0 °C, the solution was added to cold 10% aqueous potassium iodide solution (50 mL). The solid was filtered and washed with 10% aqueous KI solution (100 mL) or until the washings were colourless. It was then washed with methanol and air dried to afford (*N*-morpholinocarbonyl)bis(pentachlorophenyl)methyl radical (**22**) (0.95 g, 95%) as a red-purple powder, mp 170–2 °C dec. IR: ν(CO) 1609 cm^{-1}. ESR ($CHCl_3$): g = 2.0043. Anal. Calcd. for $C_{18}H_8Cl_{10}NO$: C, 35.47; H, 1.31; Cl, 58.12. Found: C, 35.21; H, 1.24; Cl, 58.12.

Reduction of (Isopropoxycarbonyl)- (15b), (*N*-Morpholinocarbonyl)- (22), and Cyanobis(pentachlorophenyl)methyl (23) Radicals by Hydroquinone. A solution of the radical (0.2 mmol) in THF (0.5 mL) was cooled, with stirring, to 0 °C. Hydroquinone (0.11 g, 1 mmol) was added, and decolorization of the solution to yellow (quinone) occurred immediately. Addition of methanol (2 mL), followed by cooling to ca. −10 °C led to crystallization of the CH precursor. These were identified by TLC and IR comparison with authentic samples.

Reduction of (Isopropoxycarbonyl)-, (*N*-Morpholinocarbonyl)-, and Cyanobis(pentachlorophenyl)methyl Radicals by n-Butyllithium. A solution of the radical (0.2 mmol) in THF (0.5 mL) was cooled to −5 °C, with stirring. *n*-Butyllithium (0.135 mL, 1.5 M, 0.2 mmol) in hexane was added via a syringe. The red-purple colors of the radicals exchanged to the orange of the enolates. After 5 min, acetic acid (0.5 mL) and methanol (2 mL) were added to effect crystallization of the CH precursor.

Bis(pentachlorophenyl)ketene Methyl Isopropyl Acetal (25). Isopropyl bis(pentachlorophenyl)acetate (**16b**) (1.00 g, 1.66 mmol) was added to a stirring suspension of sodium hydride (0.16 g, 6.64 mmol) in THF (10 mL). The solution was stirred at 30 °C for 1 h and then cooled to −5 °C. Methyl trifluoromethanesulfonate (1 mL, excess) was added via a syringe to the orange solution. The orange color faded within 30 s to colorless. This solution was allowed to stir at ambient temperature for 1 h and then added to water (20 mL). The oily residue was extracted into diethyl ether (50 mL) and the ether layer processed in the usual way. On rotary evaporation an oily residue (containing derivatives of methylated THF) was obtained. This was chromatographed on silica gel using 10% THF–petrol as the eluting solvent. The band with R_f = 0.5 gave a solid which was recrystallized from chloroform–petrol (1:5) to afford bis(pentachlorophenyl)ketene methyl isopropyl acetal (**25**) (0.7 g, 70%), mp 174–6 °C. IR: ν(C=C) 1610 cm^{-1}. ^1H NMR: δ 1.25 (m, 6 H), 3.74 (s, 3 H), 4.29 (m, 1 H). Anal. Calcd for $C_{18}H_{10}Cl_{10}O_2$: C, 35.24; H, 1.63; Cl, 57.91. Found: C, 34.88; H, 1.51; Cl, 57.40.

Attempted Isolation of 1-Isopropoxy-2,2-bis(pentachlorophenyl)ethenol (25). Sodium hydride (0.55 g of 80% oil dispersion, 1.1 equiv) was added to a solution of isopropyl bis(pentachlorophenyl)acetate (**16b**) (10.0 g, 16.69 mmol) in THF (50 mL). The yellow suspension was stirred at 40–50 °C for 1 h to give a clear yellow-orange solution of sodium 1-isopropoxy-2,2-bis(pentachlorophenyl)ethenolate (**26**). This solution was cooled to −5 °C and acetic acid (1.1 g, 18.33 mmol) added rapidly. Analysis of the resulting colorless solution by IR spectroscopy showed only carbonyl absorption at 1745 cm^{-1} confirming the product to be diarylacetate ester **16b**.

Likewise, injections of 1 μL of the above enolate solution in to a UV cell containing either water or 1:1 NaH_2PO_4 buffer (10^{-3} M) showed no significant absorbance at 310 nm (the λ_{max} of ketene acetal **25**). The spectra produced were identical to that of ester **16b**.

Registry No. **6**, 33240-72-1; **8**, 107846-89-9; **9**, 33240-66-3; **11**, 33119-38-9; **12**, 141709-02-6; **13a**, 141709-01-5; **13b**, 112312-91-1; **15**, 112312-95-5; **16a**, 141725-93-1; **16b**, 107846-82-2; **17**, 107846-85-5; **18**, 141709-03-7; **19**, 112312-93-3; **20**, 112312-94-4; **21**, 112312-92-2; **22**, 112312-96-6; **23**, 112312-97-7; **25**, 107846-84-4; C_6Cl_5H, 107846-84-4; C_6Cl_5MgCl, 31279-13-7; EtO_2CCO_2Et, 95-92-1; *i*-PrO_2CCO_2Pr-*i*, 615-81-6.