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A New Trifluoromethylating Agent: Synthesis of Polychlorinated (Trifluoromethyl)benzenes and 1,3-Bis(trifluoromethyl)benzenes and Conversion into Their Trichloromethyl Counterparts and Molecular Structure of Highly Strained Polychloro-*m*-xylenes

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Mixtures of CCl_3F and $AlCl_3$ replace CF_3 for H in polychlorobenzenes. Thus, by treatment of a solution of the suitable polychlorobenzene in CCl_3F with $AlCl_3$, the following compounds can be prepared: pentachloro- (**2**), 2,3,4,5-tetrachloro- (**5**), 2,3,4,6-tetrachloro- (**8**), 2,3,5,6-tetrachloro- (**11**), 2,3,4-trichloro- (**14**), 2,4,5-trichloro- (**17**), and 2,4,6-trichloro-1-(trifluoromethyl)benzene (**20**), as well as 4,5,6-trichloro- (**31**) and 2,4,6-trichloro-1,3-bis(trifluoromethyl)benzene (**32**). The reaction of the above-mentioned trifluoromethylated compounds with $AlCl_3$ in CS_2 yields their trichloromethyl counterparts: **3**, **6**, **9**, **12**, **15**, **18**, **21**, **34**, and **36**. The chlorination of **32** or **36** by means of Silberrad's reagent (SO_2Cl_2, $AlCl_3$, and S_2Cl_2) affords perchloro-*m*-xylene (**38**), a new highly strained chlorocarbon whose synthesis was attempted repeatedly in the past. **9**, **15**, **17**, and **21**, when treated with oleum and then with water, are converted into 2,3,4,6-tetrachloro- (**22**), 2,3,4-trichloro- (**23**), 2,4,5-trichloro- (**24**), and 2,4,6-trichlorobenzoic acid (**25**), respectively; under similar treatment, **34**, **36**, and **38** give 4,5,6-trichloro- (**33**), 2,4,5-trichloro- (**35**), and tetrachloroisophthalic acid (**39**), respectively. The formation of the (trifluoromethyl)benzenes is discussed, and in this connection it has been found that CCl_3F solutions of **3** and **18** in the presence of $AlCl_3$ give back **2** and **17**, respectively. Molecular structures of highly strained *m*-xylenes **36** and **38**, as well as that of the much less strained **34**, ascertained by X-ray analysis, are reported and commented. IR, UV, and NMR spectral data of the compounds synthesized are presented. The interesting UV spectrum of **21** is discussed.

Introduction

Although pentachloro(trifluoromethyl)benzene (**2**) can be prepared by $FeCl_3$-catalyzed chlorination of (trifluoromethyl)benzene with Cl_2,[1,2] any attempt to obtain perchlorotoluene (**3**) by ring or side-chain chlorination with Cl_2 of chlorinated toluenes has been unsuccessful since the reaction stops before the replacement of the last hydrogen atom (ortho or α) or chlorinolysis of the $C(sp^2)$–$C(sp^3)$ bond takes place.[3a] These failures are mainly attributed to the large steric strain of the molecule on account of the strong repulsions between the trichloromethyl group and the surrounding chlorines.[3a,4] However, **3** can be prepared by aromatic chlorination of 2,3,4,5-tetrachloro-1-(trichloromethyl)benzene (**6**), (trichloromethyl)benzene or (trifluoromethyl)benzene by means of the cumbersome reagents BMC,[5,6] BMC-S,[7] and BMC-P[7] (mixtures of SO_2Cl_2, S_2Cl_2, and $AlCl_3$ in variable proportions), which cause significant chlorinolysis of the side chain. To overcome this difficulty, the synthesis of **3** by Friedel–Crafts condensation between pentachlorobenzene (**1**) and CCl_4 has been achieved (with low yields) under drastic conditions.[8] Perchloro-*p*-xylene[5] and some other strained perchloroaromatic (trichloromethyl)benzenes have also been obtained using reagent BMC.[9,10] Up to now, all attempts to synthesize perchloro-*o*- and *m*-xylenes have failed.[3b,9]

In this paper we describe principally an unexpected reaction leading to pentachloro(trifluoromethyl)benzene (**2**) and other polychloro(trifluoromethyl)benzenes; a new, easy route to prepare chlorocarbon **3** and other polychloro(trichloromethyl)benzenes; and the synthesis and structure of highly strained 2,4,6-trichloro-1,3-bis(trichloromethyl)benzene (**36**) and perchloro-*m*-xylene (**38**).

Results and Discussion

Polychloro(trifluoromethyl)benzenes and Polychloro(trichloromethyl)benzenes.[11] **(a) Pentachloro(trifluoromethyl)benzene (2) and Perchlorotoluene (3).** The treatment of pentachlorobenzene (**1**) with CCl_3F in the presence of $AlCl_3$,[13] in a (glass) pressure vessel[14] and at room temperature, afforded unexpectedly **2** in high yield. **2** reacts with the same inorganic chloride in CS_2 giving almost quantitatively **3**. This reaction can also be carried out in CCl_4, but with a much longer reaction time and lower yields.

$$\underset{\mathbf{1}}{C_6HCl_5} \xrightarrow{CCl_3F,\ AlCl_3} \underset{\mathbf{2}}{C_6Cl_5CF_3} \underset{AlCl_3,\ CCl_3F}{\overset{AlCl_3\ (CS_2)}{\rightleftharpoons}} \underset{\mathbf{3}}{C_6Cl_5CCl_3}$$

Since CCl_3F in the presence of $AlCl_3$ undergoes disproportionation under the alkylation conditions giving CCl_4, CCl_2F_2, and $CClF_3$ (identified by IR spectrum),[15] and **1** does not react with CCl_4 in the presence of $AlCl_3$, even under stronger reaction conditions (reflux temperature),

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(11) A short notice has been advanced on this subject.[12]

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(13) The excess of $AlCl_3$ is necessary since it has been observed that it reacts with CCl_3F losing the catalytic activity.

(14) A Buchi stirred laboratory autoclave Model BEP-280, with a 250 cm^3 borosilicate glass vessel was used.

0022-3263/91/1956-0103$02.50/0

Scheme I

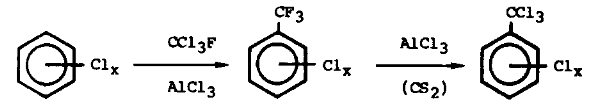
$$C_6Cl_5CX_2F + AlCl_3 \rightleftharpoons$$
(X, F or Cl)
$$C_6Cl_5CX_2^+\ AlCl_3F^- \rightleftharpoons C_6Cl_5CX_2Cl + AlCl_2F$$

the formation of **2** can be explained by assuming the alkylation of **1** by CCl_3F, CCl_2F_2, and/or $CClF_3$, followed by replacement of chlorine by fluorine in the resulting perhalotoluene. Accordingly, it has been found that the treatment of **3** with CCl_3F in the presence of $AlCl_3$ gives an almost quantitative yield of **2**. However, the possibility that the highly reactive CF_3^+ ion anchored on (or inside) the solid surface of $AlCl_3$ may be the alkylating species is not discarded.

The high-yield conversion of **2** into **3** can be accounted for by assuming that the equilibria of Scheme I are shifted toward the formation of **3** due to the presence of an excess of $AlCl_3$. The reversion of **3** to **2**, also in high yield, can be explained by assuming that in this case such equilibria are shifted toward the formation of **2**, due to the disappearance of the $AlCl_3$ through its reaction with CCl_3F giving $AlCl_2F$.

Related equilibria have been proposed to explain the conversion of $CCl_2{=}CClCClF_2$ into $CCl_2{=}CClCCl_3$ and $CCl_2{=}CClCF_3$ in the presence of $AlCl_3$.[16]

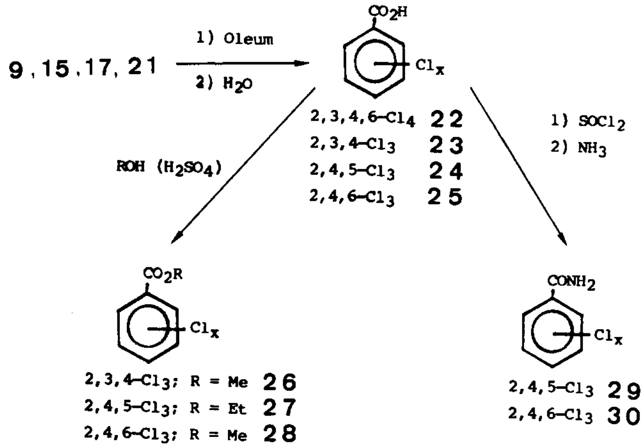
(b) Other Polychloro(trifluoromethyl)benzenes and Polychloro(trichloromethyl)benzenes. The treatment of polychlorobenzenes **4**, **7**, **10**, **13**, **16** and **19** with CCl_3F in the presence of $AlCl_3$, in a similar manner to **1**, afforded the following products: 2,3,4,5-tetrachloro- (**5**), 2,3,4,6-tetrachloro- (**8**), 2,3,5,6-tetrachloro- (**11**), 2,3,4-trichloro- (**14**), 2,4,5-trichloro- (**17**), and 2,4,6-trichloro-1-(trifluoromethyl)benzene (**20**), respectively. Similarly to **2**, these compounds react with $AlCl_3$ in CS_2 to give their trichloromethyl analogues, i.e. 2,3,4,5-tetrachloro- (**6**), 2,3,4,6-tetrachloro- (**9**), 2,3,5,6-tetrachloro- (**12**), 2,3,4-trichloro- (**15**), 2,4,5-trichloro- (**18**), and 2,4,6-trichloro-1-(trichloromethyl)benzene (**21**), respectively. In most cases, the yield of the alkylation and halogen-exchange reactions is above 90%. Such reactions not only allow the easy preparation of **5**,[17,18] **11**,[17] **12**,[5] **14**,[19] and **20**,[20] which had only been obtained in low yields as byproducts, but also the synthesis, for the first time, of **8** and **9**.



1,2,3,4-Cl4	**4**	2,3,4,5-Cl4	**5**	2,3,4,5-Cl4	**6**
1,2,3,5-Cl4	**7**	2,3,4,6-Cl4	**8**	2,3,4,6-Cl4	**9**
1,2,4,5-Cl4	**10**	2,3,5,6-Cl4	**11**	2,3,5,6-Cl4	**12**
1,2,3-Cl3	**13**	2,3,4-Cl3	**14**	2,3,4-Cl3	**15**
1,2,4-Cl3	**16**	2,4,5-Cl3	**17**	2,4,5-Cl3	**18**
1,3,5-Cl3	**19**	2,4,6-Cl3	**20**	2,4,6-Cl3	**21**

As expected, the treatment of a CCl_3F solution of **18** with $AlCl_3$ yields back **17**. This result shows that the usefulness of the CCl_3F–$AlCl_3$ reagent for converting CCl_3 (and obviously CCl_2F and $CClF_2$ groups) into CF_3 groups is not restricted to the case of **3**.

The treatment of **9** with oleum and then with water affords 2,3,4,6-tetrachlorobenzoic acid (**22**), thus confirming the structures of **9** and **8**. Also for identification purposes, the following reactions have been performed: (1) hydrolysis of **15**, **17**, and **21** to trichlorobenzoic acids **23**, **24**, and **25**, respectively; (2) esterification of these acids to alkyl esters **26**, **27**, and **28**, respectively; and (3) conversion of acids **24** and **25** into the corresponding amides **29** and **30**.

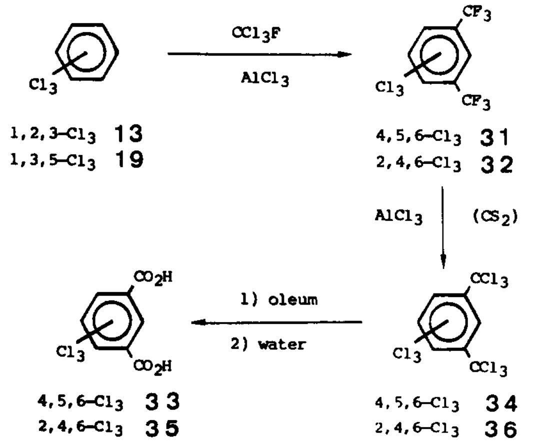


2,3,4,6-Cl4 **22**
2,3,4-Cl3 **23**
2,4,5-Cl3 **24**
2,4,6-Cl3 **25**

2,3,4-Cl3; R = Me **26**
2,4,5-Cl3; R = Et **27**
2,4,6-Cl3; R = Me **28**

2,4,5-Cl3 **29**
2,4,6-Cl3 **30**

Polychloro-*m*-xylenes. Extended treatment of 1,2,3- (**13**) and 1,3,5-trichlorobenzene (**19**) with CCl_3F in the presence of $AlCl_3$ affords 4,5,6- (**31**) and 2,4,6-trichloro-1,3-bis(trifluoromethyl)benzene (**32**), respectively. These new highly halogenated xylenes react with $AlCl_3$ in CS_2 to give their bis(trichloromethyl) analogues: 4,5,6- (**34**) and 2,4,6-trichloro-1,3-bis(trichloromethyl)benzene (**36**). The former, when treated with oleum and then with water, yields 4,5,6-trichloroisophthalic acid (**33**), which, in turn, was converted into its dimethyl ester (**37**). As expected, unknown xylene (**36**), when treated in a similar way as **34**, gives 2,4,6-trichloroisophthalic acid (**35**), not described before.

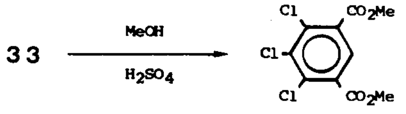


1,2,3-Cl3 **13**
1,3,5-Cl3 **19**

4,5,6-Cl3 **31**
2,4,6-Cl3 **32**

4,5,6-Cl3 **33**
2,4,6-Cl3 **35**

4,5,6-Cl3 **34**
2,4,6-Cl3 **36**



37

As expected, the chlorination of **32** with the mild Silberrad's chlorinating agent (a solution of $AlCl_3$ and S_2Cl_2 in SO_2Cl_2)[21] yields perchloro-*m*-xylene (**38**), which was

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(15) *Catalog of Selected Infrared Spectral Data*, Serial no. 952, 953, and 954, Thermodynamics Research Center Data Project, Thermodynamics Research Center, Texas A & M University, College Station, TX.

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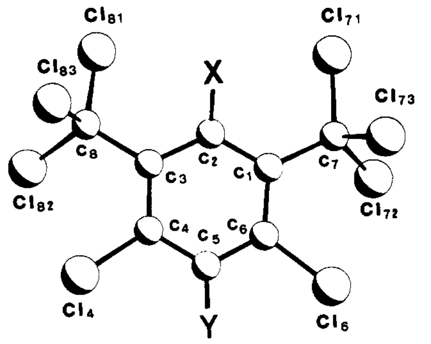
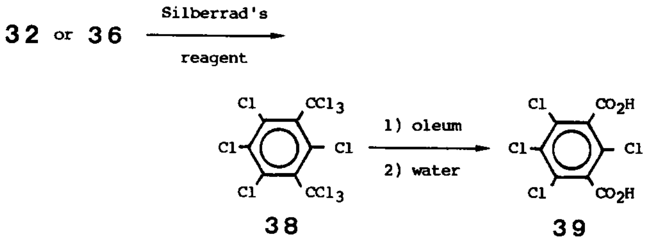


Figure 1. Representation of the molecules of xylenes **34** (X = H, Y = Cl), **36** (X = Cl, Y = H), and **38** (X = Y = Cl) with atom numbering.

inaccessible until now. This chlorocarbon can also be obtained by chlorination of **36** with the same chlorinating agent. The treatment of **38** with oleum and then with water affords tetrachloroisophthalic acid (**39**), thus confirming the structure of **38**.



Infrared Spectra. All the (trifluoromethyl)benzenes here described show a rather broad, intense peak around 1150 cm^{-1}, which is not present in the spectrum of their trichloromethyl analogues, indicating that this absorption is due to the C–F stretching vibrations of the CF_3 group. Interestingly, the two (trihalomethyl)benzenes with a hydrogen atom in position 3 (**8** and **9**) show two intense-to-medium peaks in the region 1600–1500 cm^{-1} that are not present in their isomers with the hydrogen in position 4 (**11** and **12**). This observation can be useful for identification by IR of other benzene derivatives of formula C_6HCl_4Y (Y, other substituent than chlorine). In fact, these peaks are also observed in the spectrum of acid **22** and not in that of 2,3,5,6-tetrachlorobenzoic acid.

Ultraviolet Spectra. It has been reported that the UV spectra of highly chlorinated alkylbenzenes can be either "normal" (the secondary band shows two peaks around 300 nm), or "abnormal" (the secondary band is deprived of fine structure and its maximum is located at an abnormally high wavelength);[22] typical of these two types of spectra are those of **6** (λ_{max} 292, 302 nm) and **3**, (λ_{max} 318 nm) respectively.[22] The great bathochromic shift of the secondary band and the disappearance of its vibrational structure in the UV spectrum of **3** (and **12** as well) have been accounted for in terms of out-of-plane distortion of the ring due to steric repulsions between the CCl_3 group and the two ortho chlorines.[22] Unexpectedly, it has now been found that **21**, in spite of having its CCl_3 group flanked by two ortho chlorines, shows a "normal" spectrum (λ_{max} 289, 297 nm). This fact suggests that the distortion of **21** takes place mostly in-plane. This is a very reasonable assumption, not only because the study of the benzocycloalkanes indicates that in-plane distortion does not cause any significant loss of vibrational structure and bathochromic shift of the secondary band,[23] but also because the absence of chlorines in positions 3 and 5 allows the in-plane bending of the C(2)–Cl and C(6)–Cl bonds.

Table I. Comparative Bond Lengths (Å) with Their esd's

bonds	**34**	**36**	**38**
C(1)–C(2)	1.391 (5)	1.412 (5)	1.409 (4)
C(2)–C(3)	1.386 (5)	1.401 (4)	1.406 (4)
C(3)–C(4)	1.392 (5)	1.414 (5)	1.401 (4)
C(4)–C(5)	1.404 (5)	1.368 (5)	1.402 (4)
C(5)–C(6)	1.376 (5)	1.390 (5)	1.387 (5)
C(6)–C(1)	1.387 (5)	1.389 (5)	1.406 (5)
C(1)–C(7)	1.516 (5)	1.535 (4)	1.533 (4)
C(3)–C(8)	1.528 (5)	1.534 (5)	1.536 (4)
C(2)–Cl(2)		1.737 (3)	1.730 (3)
C(2)–H(2)	0.84 (4)		
C(4)–Cl(4)	1.714 (3)	1.730 (3)	1.721 (3)
C(5)–Cl(5)	1.720 (3)		1.714 (3)
C(5)–H(5)		0.99 (4)	
C(6)–Cl(6)	1.729 (3)	1.737 (3)	1.720 (3)
C(7)–Cl(71)	1.767 (4)	1.777 (4)	1.781 (4)
C(7)–Cl(72)	1.784 (4)	1.767 (3)	1.773 (3)
C(7)–Cl(73)	1.775 (4)	1.788 (4)	1.782 (3)
C(8)–Cl(81)	1.761 (4)	1.771 (4)	1.779 (3)
C(8)–Cl(82)	1.778 (4)	1.771 (4)	1.768 (3)
C(8)–Cl(83)	1.778 (4)	1.786 (4)	1.787 (3)

Table II. Comparative Bond Angles (deg) with Their esd's

angles	**34**	**36**	**38**
C(6)–C(1)–C(2)	117.8 (3)	115.7 (3)	116.1 (3)
C(1)–C(2)–C(3)	123.2 (3)	123.3 (3)	122.4 (3)
C(2)–C(3)–C(4)	118.0 (3)	115.3 (3)	116.3 (3)
C(3)–C(4)–C(5)	119.6 (3)	121.4 (3)	120.7 (3)
C(4)–C(5)–C(6)	120.9 (3)	120.4 (3)	120.2 (3)
C(5)–C(6)–C(1)	120.6 (3)	121.3 (3)	121.0 (3)
C(7)–C(1)–C(2)	119.1 (3)	121.9 (3)	122.4 (3)
C(7)–C(1)–C(6)	123.1 (3)	122.5 (3)	121.5 (3)
Cl(2)–C(2)–C(1)		117.1 (2)	118.0 (2)
Cl(2)–C(2)–C(3)		118.6 (2)	118.4 (2)
H(2)–C(2)–C(1)	117 (2)		
H(2)–C(2)–C(3)	120 (2)		
C(8)–C(3)–C(2)	119.5 (3)	124.8 (3)	122.2 (3)
C(8)–C(3)–C(4)	122.5 (3)	119.8 (3)	121.5 (3)
Cl(4)–C(4)–C(3)	122.3 (3)	123.6 (3)	122.2 (2)
Cl(4)–C(4)–C(5)	118.2 (3)	114.6 (3)	116.7 (2)
Cl(5)–C(5)–C(4)	118.5 (3)		119.7 (3)
Cl(5)–C(5)–C(6)	120.7 (3)		120.1 (2)
H(5)–C(5)–C(4)		116 (2)	
H(5)–C(5)–C(6)		123 (2)	
Cl(6)–C(6)–C(5)	117.2 (3)	114.2 (3)	116.8 (2)
Cl(6)–C(6)–C(1)	122.2 (3)	124.1 (3)	121.9 (2)
C(1)–C(7)–Cl(71)	114.0 (2)	113.9 (2)	114.3 (2)
C(1)–C(7)–Cl(72)	110.6 (3)	110.6 (2)	110.4 (2)
C(1)–C(7)–Cl(73)	109.8 (2)	111.9 (2)	111.1 (2)
C(3)–C(8)–Cl(81)	113.3 (3)	116.2 (2)	114.2 (2)
C(3)–C(8)–Cl(82)	110.3 (2)	110.1 (2)	110.9 (2)
C(3)–C(8)–Cl(83)	110.6 (3)	109.8 (3)	111.0 (2)
Cl(71)–C(7)–Cl(72)	105.8 (2)	109.3 (2)	109.2 (2)
Cl(71)–C(7)–Cl(73)	106.9 (2)	102.4 (2)	101.7 (2)
Cl(72)–C(7)–Cl(73)	109.6 (2)	108.2 (2)	109.8 (2)
Cl(81)–C(8)–Cl(82)	107.0 (2)	108.3 (2)	108.7 (2)
Cl(81)–C(8)–Cl(83)	106.1 (2)	102.3 (2)	101.7 (2)
Cl(82)–C(8)–Cl(83)	109.4 (2)	109.8 (2)	109.9 (2)

In contrast to the "normal" spectrum of xylene **34**, in which both CCl_3 groups are buttressed by one hydrogen atom, xylenes **36** and **38** show "abnormal" spectra. These facts indicate that while the ring in **34** is essentially planar, in the other two xylenes it is out-of-plane distorted, as it has been confirmed by X-ray analysis (see later).

Molecular Structures of Polychlorinated *m*-Xylenes 34, 36, and 38. Molecular structures of **34**, **36**, and **38** have been ascertained by X-ray analysis. A representation of these molecules, identifying the atoms with a number is shown in Figure 1. Bond lengths and bond

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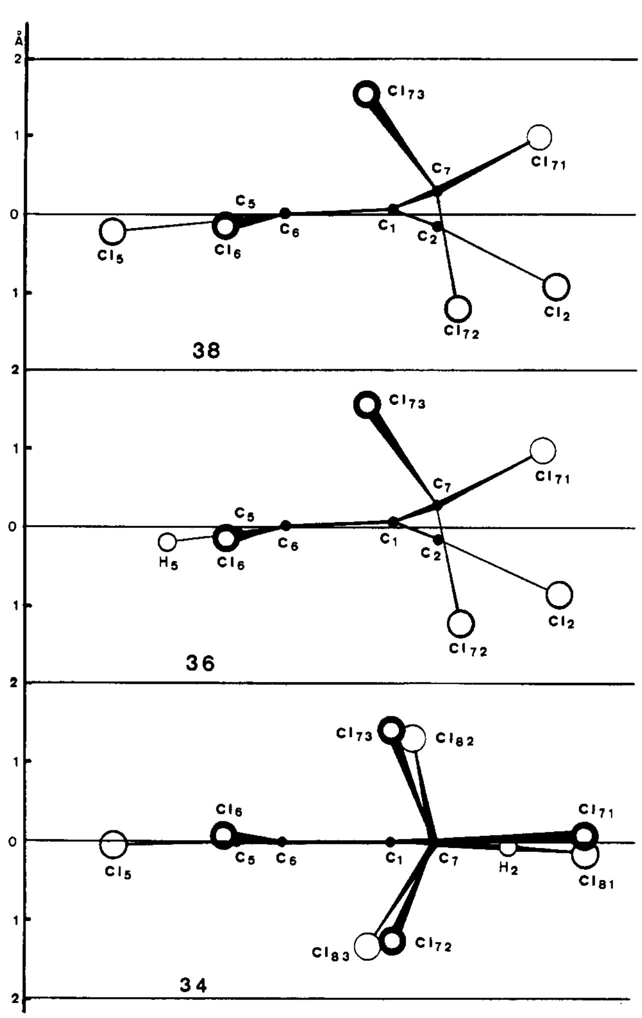

Figure 2. Side view of the molecules of xylenes **34**, **36**, and **38** showing the deviations of the atoms from the mean plane of the benzene ring.

angles are listed in Tables I and II, respectively.

The conformation of the CCl_3 groups of **34** appears to be different from those in **36** and **38** (see Figure 2). In **34**, steric repulsions between the atoms of the pairs Cl(6)-Cl(72), Cl(6)-Cl(73), Cl(4)-Cl(82), and Cl(4)-Cl(83) cause abnormal bond angles, but all the carbon atoms of the *m*-xylene skeleton lie essentially in a plane (Figure 2); accordingly, the sum of the bond angles centered at C(2) presents its normal value (360°).

Due to steric repulsions between the pairs Cl(6)-Cl(73), Cl(4)-Cl(83), Cl(2)-Cl(71), and Cl(2)-Cl(81), **36** and **38** are exceptionally distorted molecules. In contrast to **34**, the planarity of the *m*-xylene skeleton of **36** and **38** is lost, the ring adopting a boat-sofa conformation in which the prow corresponds to C(2) and the stern to C(5) (Figure 2); in both xylenes, the carbon and chlorine atoms flanked by the two trichloromethyl groups are moved about 0.1 and 1 Å, respectively, away from the mean plane of the benzene ring, and, accordingy, the sum of the bond angles centered at C(2) present significant deviations of −1.2° and −1.1° from 360°, respectively. In connection with their geometry it is mentioned that the ring of perchloro-*p*-xylene also adopts a boat conformation;[24] however, in this case, the prow and the stern of the boat correspond to C(1) and C(4) atoms, i.e., to the carbons that are directly bonded to the CCl_3 groups. Due to the fact that the hydrogen is much smaller than the chlorine, Cl(6)-C(6)-C(1) and Cl(4)-C(4)-C(3) angles are wider in **36** than in **38**.

The compact crystal packing of **38**, indicated by a relatively high density, is confirmed by numerous short Cl⋯Cl intermolecular distances, the shortest being Cl(83)⋯Cl(83)^{i} (3.280 Å, $i = -1 - x, -1 - y, -z$), Cl(83)⋯Cl(6)^{ii} (3.339 Å, $ii = 1 + x, y, z$), and Cl(81)⋯Cl(4)^{iii} (3.411 Å, $iii = -0.5 - x, -0.5 + y, 0.5 - z$), all of them lower than the sum of the van der Waals radii of two chlorine atoms (3.5 Å).[25]

Conclusions

Some advantages of the above-mentioned methods for the synthesis of polychlorinated (trifluoromethyl)benzenes and (trichloromethyl)benzenes over other conventional syntheses are (1) the possibility of synthesizing polychlorinated (trifluoromethyl)benzenes and (trichloromethyl)benzenes with or without aromatic hydrogens; (2) the use of milder reaction conditions; (3) an easier purification of the reaction mixture; (4) much higher yields; and (5) the use of less corrosive reagents, and the absence of chlorinolysis and subchlorinated products, in contrast to the exhaustive chlorination methods. By means of these methods, polychloro-1,3-bis(trifluoromethyl)benzenes and strained, or not, polychloro-1,3-bis(trichloromethyl)benzenes can also be obtained. CCl_3F in the presence of $AlCl_3$ is not only a very suitable reagent for the trifluoromethylation of polychlorobenzenes, but also for converting CCl_3 group into CF_3 group, at least in the cases of perchlorotoluene and 2,4,5-trichloro-1-(trichloromethyl)benzene.

Experimental Section

Instrumentation. IR spectra were recorded on a Perkin-Elmer 682 spectrometer. UV spectra were recorded on either a Beckman Acta M VI or a Perkin-Elmer Lambda Array 3840 spectrometer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker WP80SY spectrometer with TMS (internal) or TFA (10% in $CDCl_3$; external) calibration standards. X-ray data were collected on a Enraf-Nonius CAD 4 diffractometer using graphite monochromated Mo Kα radiation.

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

Synthesis of Polychloro(trifluoromethyl)benzenes and Polychloro-1,3-bis(trifluoromethyl)benzenes. General Method. Powdered anhydrous $AlCl_3$ was added to a solution of the suitable polychlorobenzene in CCl_3F, and the resulting mixture was stirred for several hours (4–8 h; 20 °C) in a pressure vessel (the internal pressure rises to about 2 atm). Then the mixture was cooled to −10 °C (to eliminate overpressure), $AlCl_3$ was added,[26] and the stirring was continued at the same temperature (4–16 h more). The reaction mixture was filtered, the solid being washed with CCl_4. The organic solution was evaporated to dryness giving either (a) the pure trifluoromethylbenzene, (b) an impure oil containing (IR spectrum) some starting polychlorobenzene, or (c) an impure oil containing (IR spectrum) some intermediate (trifluoromethyl)benzene (synthesis of *m*-xylenes). If not stated otherwise, the impure oils were treated again with CCl_3F and $AlCl_3$ as before, and the resulting mixture[27] was worked up to obtain the final product as a colorless oil or crystals.

The following products were obtained this way:

(1) Pentachloro(trifluoromethyl)benzene (2). Starting materials: pentachlorobenzene (1) (5.010 g), CCl_3F (100 mL), $AlCl_3$ (10.0 g; 10.0 g, 8 h); reaction time 24 h. The resulting oil was treated again with CCl_3F and $AlCl_3$ as before. The final product

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[24] Gali, S.; Miravitlles, C.; Font-Altaba, M. *Acta Crystallogr.* **1976**, *B32*, 3112.

[25] Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 56th ed.; CRC Press: Cleveland, 1975–1976; p D-178. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[26] The times quoted following the weight or volume data are the times elapsed when the additions were performed.

[27] This mixture does not contain any more starting polychlorobenzene or intermediate polychloro(trifluoromethyl)benzene (IR spectrum).

was crystallized (ethanol) to give 2 (4.018 g, 77%), mp 77.5–80.0 °C, identified by mp (lit.[2] mp 78–82 °C) and elemental analysis: IR (KBr) 1535 (w), 1512 (m), 1350 (s), 1330 (s), 1250 (s), 1168 (s), 1139 (s), 1080 (m), 715 (s), 628 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} 240 (sh) nm, 288 (sh), 295, 305 (ϵ 9580, 685, 1415, 1560); ^{19}F NMR ($CDCl_3$) δ 20.14; MS, 316 ($C_7{}^{35}Cl_5F_3$; M^+), 281 ($M^+ - Cl$), 246 ($M^+ - 2Cl$), 211 ($M^+ - 3Cl$).

(2) 2,3,4,5-Tetrachloro-1-(trifluoromethyl)benzene (5). Starting materials: 1,2,3,4-tetrachlorobenzene (4) (5.050 g), CCl_3F (100 mL), $AlCl_3$ (10.0 g; 5.0 g, 4 h); reaction time 8 h. The resulting oil was characterized as **5** (6.109 g, 92%): $n^{20}{}_D$ 1.5298; IR (film) 3095 (w), 1586 (m), 1418 (m), 1360 (s), 1290 (s), 1192 (m), 1150 (s), 1077 (m), 885 (m), 822 (m), 737 (m), 641 (m), 557 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 230 (sh) nm, 278 (sh), 285, 294 (ϵ 10750, 490, 825, 840); ^1H NMR ($CDCl_3$) δ 7.74 (s); ^{19}F NMR ($CDCl_3$) δ 12.73. Anal. Calcd for $C_7HCl_4F_3$: C, 29.6; H, 0.3; Cl, 50.0. Found: C, 29.7; H, 0.2; Cl, 49.8.

(3) 2,3,4,6-Tetrachloro-1-(trifluoromethyl)benzene (8). Starting materials: 1,2,3,5-tetrachlorobenzene (7) (5.071 g), CCl_3F (100 mL), $AlCl_3$ (10.1 g; 5.0 g, 8 h); reaction time 24 h. The resulting oil was characterized as 8 (6.432 g, 95%): $n^{20}{}_D$ 1.5280; IR (film) 3080 (w), 1568 (m), 1533 (m), 1420 (w), 1350 (s), 1270 (s), 1238 (m), 1192 (m), 1173 (m), 1145 (s), 1060 (s), 870 (m), 815 (s), 668 (s), 580 (m), 550 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 209, 233 (sh), 280 (sh), 288, 297 nm (ϵ 42 500, 9350, 675, 1140, 1330); ^1H NMR ($CDCl_3$) δ 7.60 (s); ^{19}F NMR ($CDCl_3$) δ 19.88. Anal. Calcd for $C_7HCl_4F_3$: C, 29.6; H, 0.3; Cl, 50.0. Found: C, 29.6; H, 0.2; Cl, 50.1.

(4) 2,3,5,6-Tetrachloro-1-**(trifluoromethyl)benzene (11).** Starting materials: 1,2,4,5-tetrachlorobenzene (**10**) (5.110 g), CCl_3F (100 mL), $AlCl_3$ (10.0 g; 10.0 g, 8 h); reaction time 24 h. The resulting oil was treated again with CCl_3F and $AlCl_3$ as before. The product obtained was crystallized (pentane) to give **11** (5.140 g, 77%): mp 64–5 °C;[28] IR (KBr) 3070 (w), 1555 (w), 1412 (m), 1400 (s), 1252 (s), 1190 (s), 1145 (s), 1070 (m), 940 (m), 880 (m), 822 (m), 609 (s), 590 (m), 540 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 230 (sh) nm, 295, 302 (ϵ 10 000; 2310, 2450); ^1H NMR ($CDCl_3$) δ 7.80; ^{19}F NMR ($CDCl_3$) δ 19.84. Anal. Calcd for $C_7HCl_4F_3$: C, 29.6; H, 0.3; Cl, 50.0. Found: C, 29.5; H, 0.2; Cl, 50.1.

(5) 2,3,4-Trichloro-1-(trifluoromethyl)benzene (14). Starting materials: 1,2,3-trichlorobenzene (**13**) (5.123 g), CCl_3F (100 mL), $AlCl_3$ (20.1 g); reaction time 4 h. The resulting oil containing some **13** (^1H NMR) (6.453 g) was submitted to column chromatography (silica gel, hexane) giving impure 4,5,6-trichloro-1,3-bis(trifluoromethyl)benzene (**31**) (0.505 g, 5.5%), identified by IR and ^1H NMR spectra (see later), and an oil characterized as **14** (4.327 g, 61%): $n^{20}{}_D$ 1.5120; IR (film) 3095 (w), 1593 (m), 1578 (m), 1450 (m), 1378 (s), 1307 (s), 1280 (m), 1180 (s), 1147 (s), 1117 (m), 1063 (m), 848 (m), 820 (m), 770 (m), 720 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 214 nm, 225 (sh), 271 (sh), 278, 287 (ϵ 11 310, 8860, 385, 610, 580); ^1H NMR ($CDCl_3$) δ 7.54 (d, 1 H, J = 8.5 Hz, H-C(6)), 7.46 (d, 1 H, J = 8.5 Hz, H-C(5)); ^{19}F NMR ($CDCl_3$) δ 12.42. Anal. Calcd for $C_7H_2Cl_3F_3$: C, 33.7; H, 0.8; Cl, 42.6. Found: C, 33.5; H, 0.8; Cl, 42.5.

(6) 2,4,5-Trichloro-1-(trifluoromethyl)benzene (17). Starting materials: 1,2,4-trichlorobenzene (**16**) (5.023 g), CCl_3F (100 mL), $AlCl_3$ (10.0 g; 10.0 g, 8 h); reaction time 24 h. The resulting oil was characterized as **17** (6.698 g, 97%): $n^{19}{}_D$ 1.5042; IR (film) 3105 (w), 1602 (m), 1555 (w), 1472 (m), 1363 (s), 1294 (s), 1260 (m), 1150 (s), 1111 (s), 1058 (s), 896 (m), 636 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 210 nm, 231, 236 (sh), 272 (sh), 280, 289 (ϵ 22 720, 11 360, 9110, 512, 761, 735); ^1H NMR ($CDCl_3$) δ 7.74 (1 H, s, H-C(6)), 7.59 (1 H, s, H-C(3)); ^{19}F NMR ($CDCl_3$) δ 12.60. Anal. Calcd for $C_7H_2Cl_3F_3$: C, 33.7; H, 0.8; Cl, 42.6. Found: C, 33.9; H, 0.8; Cl, 42.4.

(7) 2,4,6-Trichloro-1-(trifluoromethyl)benzene (20). Starting materials: 1,3,5-trichlorobenzene (**19**) (5.103 g), CCl_3F (100 mL), $AlCl_3$ (5.10 g; 5.10 g, 4 h); reaction time 8 h. The resulting oil was characterized as **20**[29] (6.902 g, 98%): $n^{20}{}_D$ 1.5120; IR (KBr) 3085 (w), 1582 (s), 1550 (s), 1375 (s), 1283 (s), 1270 (m), 1208 (s), 1140 (s), 1111 (s), 1028 (s), 860 (m), 840 (m), 815 (m), 800 (m), 528 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 222 (sh) nm, 274 (sh), 280, 289 (ϵ 9730, 650, 1000, 1010); ^1H NMR ($CDCl_3$) δ 7.47 (s); ^{19}F NMR ($CDCl_3$) δ 20.27. Anal. Calcd for $C_7H_2Cl_3F_3$: C, 33.7; H, 0.8; Cl, 42.7. Found: C, 33.9; H, 0.8; Cl, 42.6.

(8) 4,5,6-Trichloro-1,3-bis(trifluoromethyl)benzene (31). Starting materials: 1,2,3-trichlorobenzene (**13**) (5.026 g), CCl_3F (100 mL), $AlCl_3$ (10.0 g; 10.1 g, 8 h); reaction time 24 h. The resulting oil was treated again with CCl_3F and $AlCl_3$ as before. The final oil was characterized as **31** (7.023 g, 80%): $n^{20}{}_D$ 1.4803; IR (film) 3115 (w), 1613 (w), 1593 (m), 1424 (m), 1302 (s), 1280 (s), 1255 (m), 1190 (s), 1150 (s), 1072 (m), 908 (m), 830 (m), 720 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 212 nm, 228 (sh), 273 (sh), 281, 291 (ϵ 29 820, 9740, 650, 1150, 1250); ^1H NMR ($CDCl_3$) δ 7.97; ^{19}F NMR ($CDCl_3$) δ 12.14. Anal. Calcd for $C_8HCl_3F_6$: C, 30.2; H, 0.3; Cl, 33.5. Found: C, 30.0; H, 0.3; Cl, 33.4. This compound crystallized on standing to give colorless crystals, mp 35–8 °C (4.989 g, 55.3%), showing the same IR and UV spectra.

(9) 2,4,6-Trichloro-1,3-bis(trifluoromethyl)benzene (32). Starting materials: 1,3,5-trichlorobenzene (19) (5.020 g), CCl_3F (100 mL), $AlCl_3$ (10.0 g; 10.0 g, 8 h); reaction time 24 h. The resulting oil was treated again with CCl_3F and $AlCl_3$ as before. The final oil was characterized as **32** (7.518 g, 85.5%): $n^{20}{}_D$ 1.4830; IR (film) 3090 (w), 1568 (m), 1532 (m), 1368 (m), 1286 (s), 1247 (s), 1190 (m), 1140 (s), 1045 (s), 936 (m), 870 (m), 817 (s), 658 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 213 nm, 229 (sh), 276 (sh), 284, 293 (ϵ 35 180, 10 750, 460, 747, 745); ^1H NMR ($CDCl_3$) δ 7.65; ^{19}F NMR ($CDCl_3$) δ 20.20. Anal. Calcd for $C_8HCl_3F_6$: C, 30.2; H, 0.3; Cl, 33.5. Found: C, 30.1; H, 0.2; Cl, 33.8.

Synthesis of Polychloro(trichloromethyl)benzenes and Polychloro-1,3-bis(trichloromethyl)benzenes. General Method. Powdered anhydrous $AlCl_3$ was added to a solution of the suitable polychloro(trifluoromethyl)benzene (in CS_2 or CCl_4), and the resulting mixture was stirred (6.5–30 h) at room temperature. If not otherwise stated, the reaction mixture was treated with water under cooling (ice) and extracted with CCl_4. The organic layer was dried and evaporated. The following products were obtained this way:

(1) Perchlorotoluene (3). (a) In CCl_4. Starting materials: **2** (0.500 g), $AlCl_3$ (1.21 g; 1.53 g, 5 h[26]), CCl_4 (20 mL); reaction time 25 h. The residue was purified through silica gel (hexane) and crystallized (ethanol), giving **3** (0.514 g, 89%), mp 69–70 °C, identified by its melting point (lit.[5] mp 71.5–2.5 °C) and IR spectrum:[30] ^{13}C NMR ($CDCl_3$, ppm) 137.5, 135.5, 134.2, 132.5, 95.5.

(b) In CS_2. Starting materials: **2** (1.085 g), $AlCl_3$ (2.0 g), CS_2 (25 mL); reaction time 5 h. The residue was passed through silica gel (hexane) to give **3** (1.204 g, 96%), identified by IR spectrum.

(2) 2,3,4,5-Tetrachloro-1-(trichloromethyl)benzene (6). Starting materials: **5** (1.021 g), $AlCl_3$ (2.10 g), CS_2 (25 mL); reaction time 6 h. The residue was **6** (1.197 g, 99%), mp 121–2 °C, identified by its melting point (lit. mp 122–3 °C;[31] mp 123–4 °C[32]) and IR spectrum (benzenoid peaks):[33] IR (KBr) 3135 (w), 3090 (w), 1765 (w), 1567 (w), 1405 (s), 1333 (s), 1210 (s), 1200 (s), 1090 (m), 957 (s), 790 (s), 752 (s), 700 (m), 615 (m), 603 (m), 565 (m), 543 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.30.

(3) 2,3,4,6-Tetrachloro-1-(trichloromethyl)benzene (9). (a) In CCl_4. Starting materials: 8 (0.551 g), $AlCl_3$ (2.56 g), CCl_4 (20 mL); reaction time 6.5 h. The residue was an oil characterized as **9** (0.353 g, 55%): $n^{20}{}_D$ 1.6338; IR (film) 3120 (w), 3070 (w), 1555 (s), 1520 (s), 1400 (s), 1320 (s), 1190 (m), 1172 (m), 1105 (s), 930 (s), 864 (m), 800 (s), 768 (s), 698 (s), 625 (s), 605 (m), 502 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 212 nm, 300 (sh), 306 (ϵ 32 500, 1090, 1260); ^1H NMR ($CDCl_3$) δ 7.60. Anal. Calcd for C_7HCl_7: C, 25.3; H, 0.3; Cl, 74.7. Found: C, 25.5; H, 0.1; Cl, 74.3.

(b) In CS_2. Starting materials: 8 (6.333 g), $AlCl_3$ (12.1 g), CS_2 (125 mL); reaction time 4 h. The residue was identified as **9** (6.824 g, 91%) by IR spectrum.

(4) 2,3,5,6-Tetrachloro-1-(trichloromethyl)benzene (12). (a) In CCl_4. Starting materials: 11 (0.406 g), $AlCl_3$ (1.22 g), CCl_4 (10 mL); reaction time, 8 h. The residue was crystallized (pentane)

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(28) The literature[17] does not indicate the melting point.

(29) The literature[20] indicates a mixture of isomers as an oil, bp 200 °C.

(30) Ballester, M.; Castañer, J. *Anal. R. Soc. Españ. Fis. Quim.* **1966**, *62B*, 397.

(31) Ballester, M. *Anal. R. Soc. Españ. Fis. Quim.* **1954**, *50B*, 765.

(32) Harvey, P. G.; Smith, F.; Stacey, M.; Tatlow, J. C. *J. Appl. Chem.* **1954**, *4*, 325.

(33) Ballester, M.; Castañer, J.; Riera, J. *Afinidad* **1978**, *35*, 97.

to give **12** (0.369 g, 77%), mp 58–65 °C, identified by its melting point (lit.[5] mp 68–9 °C) and IR (benzenoid peaks):[33] IR (KBr) 3090 (w), 3040 (w), 1750 (w), 1542 (w), 1360 (s), 1160 (s), 1095 (m), 873 (s), 800 (m), 765 (s), 690 (m), 655 (s), 540 (m), 520 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81.

(b) In CS_2. Starting materials: **11** (1.100 g), $AlCl_3$ (2.00 g), CS_2 (25 mL); reaction time 5 h. The residue was passed through silica gel (hexane) to give **12** (1.185 g, 91%), mp 62–65 °C, identified by its melting point (lit.[5] mp 68–9 °C) and IR[33] spectrum.

(5) 2,3,4-Trichloro-1-(trichloromethyl)benzene (15). Starting materials: **14** (2.010 g), $AlCl_3$ (4.10 g), CS_2 (50 mL); reaction time 6 h. The residue was passed through silica gel (hexane) to give an oil characterized as **15** (2.246 g, 93%): n^{20}_D 1.6126 (lit.[34] n^{20}_D 1.6129); IR (film) 3105 (w), 1572 (m), 1435 (s), 1361 (s), 1220 (m), 1178 (s), 1168 (m), 923 (s), 798 (s), 754 (s), 728 (s), 708 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} 216 nm, 236 (sh), 276 (sh), 283, 292 (ε 22 630, 8930, 440, 655, 610); ^{1}H NMR ($CDCl_3$) δ 8.09 (d, 1 H, J = 8 Hz, H-C(6)), 7.46 (d, 1 H, J = 8 Hz, H-C(5)). Anal. Calcd for $C_7H_2Cl_6$: C, 28.1; H, 0.7; Cl, 71.2. Found: C, 28.1; H, 0.7; Cl, 71.5.

(6) 2,4,5-Trichloro-1-(trichloromethyl)benzene (18). Starting materials: **17** (1.068 g), $AlCl_3$ (2.0 g), CS_2 (25 mL); reaction time 6 h. The residue was passed through silica gel (pentane) to give **18** (1.206 g, 94%) mp 79–81 °C, identified by its melting point (lit.[35] mp 82 °C); IR (KBr) 3100 (w), 1578 (w), 1538 (w), 1450 (s), 1332 (m), 1320 (m), 1180 (m), 1070 (m), 942 (m), 890 (m), 865 (m), 803 (m), 750 (s), 680 (m), 610 (m), 600 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 214, 238, 276 (sh), 284, 294 nm (ε 30 400, 11 100, 515, 786, 735); ^{1}H NMR ($CDCl_3$) δ 8.25 (s, 1 H, H-C(6)), 7.63 (s, 1 H, H-C(3)). Anal. Calcd for $C_7H_2Cl_6$: C, 28.1; H, 0.7; Cl, 71.2. Found: C, 28.1; H, 0.7; Cl, 71.4.

(7) 2,4,6-Trichloro-1-(trichloromethyl)benzene (21). Starting materials: **20** (1.021 g), $AlCl_3$ (2.1 g), CS_2 (25 mL); reaction time 6 h. The residue was submitted to column chromatography (silica gel, pentane) to give an oil identified as **21** (0.937 g, 76.5%) (lit.[36] oil): n^{20}_D 1.6173; IR (film) 3085 (w), 1584 (s), 1540 (s), 1364 (s), 1182 (m), 1144 (m), 1073 (m), 872 (s), 857 (s), 808 (m), 784 (m), 765 (s), 684 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} 218 nm, 240 (sh), 280 (sh), 289, 297 (ε 27 200, 8325, 530, 825, 930); ^{1}H NMR ($CDCl_3$) δ 7.46. Anal. Calcd for $C_7H_2Cl_6$: C, 28.1; H, 0.7; Cl, 71.2. Found: C, 28.1; H, 0.6; Cl, 71.2.

(8) 4,5,6-Trichloro-1,3-bis(trichloromethyl)benzene (34). Starting materials: **31** (3.501 g), $AlCl_3$ (7.0 g), CS_2 (125 mL); reaction time 8 h. The residue was passed through silica gel (pentane) to give **34** (3.451 g, 75%), mp 129–31 °C, identified by its melting point (lit.[37] mp 131–2 °C): IR (KBr) 3160 (w), 3110 (w), 1795 (w), 1577 (m), 1410 (s), 1348 (m), 1245 (m), 1218 (m), 1010 (s), 819 (s), 788 (s), 753 (s), 723 (s), 709 (s), 550 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} 223 nm, 242, 282 (sh), 291, 302 (ε 31 860, 9280, 800, 1555, 1710); ^{1}H NMR ($CDCl_3$) δ 9.12. Anal. Calcd for C_8HCl_9: C, 23.1; H, 0.2; Cl, 76.7. Found: C, 23.2; H, 0.2; Cl, 76.8.

(9) 2,4,6-Trichloro-1,3-bis(trichloromethyl)benzene (36). **(a) In CCl_4.** Starting materials: **32** (1.120 g), $AlCl_3$ (1.1 g), CCl_4 (20 mL); *reaction time* 18 h. The *residue was crystallized* (hexane) to give **36** (0.636 g, 48%): mp 130–2 °C; IR (KBr) 3110 (w), 3065 (w), 1555 (s), 1502 (s), 1312 (s), 1176 (m), 1110 (m), 970 (s), 865 (m), 830 (s), 777 (s), 750 (m), 695 (s), 565 (m), 550 (m), 520 (m), 490 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 207 nm, 244, 315 (ε 15 400, 30 500, 520); ^{1}H NMR ($CDCl_3$) δ 7.51 (s); ^{13}C NMR ($CDCl_3$, ppm) 138.7, 138.4, 135.7, 133.2, 92.6. Anal. Calcd for C_8HCl_9: C, 23.1; H, 0.2; Cl, 76.7. Found: C, 23.2; H, 0.2; Cl, 76.6.

(b) In CS_2. Starting materials: **32** (1.02 g), $AlCl_3$ (2.0 g), CS_2 (20 mL); reaction time 6 h. The residue was identified as **36** (1.312 g, 98%) by its melting point and IR spectrum.

Reversion of 3 to 2. Powdered anhydrous $AlCl_3$ (0.60 g) was added to a solution of **3** (0.356 g) in CCl_3F (20 mL) and the resulting mixture was stirred under cooling (ice bath) for 7 h. The reaction mixture was filtered and the filtrate evaporated to give **2** (0.299 g, 97%), identified by its IR spectrum.

Reversion of 18 to 17. The reaction was performed as in the synthesis of **17** from **16**. Starting materials: **18** (0.500 g), CCl_3F (10 mL), $AlCl_3$ (1.0 g; 1.0 g, 8 h); reaction time 24 h. **17** (0.322 g, 77%) was obtained, which was identified by its IR spectrum.

Perchloro-*m*-xylene (38). (1) From 36. A solution of **36** (0.150 g) and S_2Cl_2 (0.150 g) in SO_2Cl_2 (6 mL) was added slowly to a refluxing solution of $AlCl_3$ (0.100 g) in SO_2Cl_2 (9 mL). The resulting dark solution was refluxed (2 h), keeping the volume constant by eventual additions of SO_2Cl_2, and then for 1 h more. The reaction mixture was poured over ice–water, and solid $NaHCO_2$ was added until no more gas evolution took place. The mixture was heated on a steam bath (30 min), acidified with concentrated aqueous HCl, cooled, and extracted with ether. The organic extract was dried and evaporated, yielding a solid, which was passed through silica gel (hexane) and crystallized (same solvent) to give **38** (0.100 g, 62%): mp 142–4 °C; IR (KBr) 1615 (m), 1588 (w), 1322 (s), 1300 (m), 1202 (m), 1112 (m), 980 (s), 910 (m), 797 (m), 774 (s), 705 (s), 685 (m), 638 (s), 546 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 221 nm, 254, 281 (sh), 330 (ε 14 010, 27 220, 3690, 916). Anal. Calcd for C_8Cl_{10}: C, 21.3; Cl, 78.7. Found: C, 21.5; Cl, 78.9.

(2) From 32. A solution of **32** (6.540 g) and Cl_2S_2 (15 g) in SO_2Cl_2 (750 mL) was added slowly to a refluxing solution of $AlCl_3$ (10.0 g) in SO_2Cl_2 (750 mL). The resulting solution was refluxed (4 h) and concentrated to about 100 mL. The reaction mixture was treated as in the preceding chlorination to give a residue (8.975 g), which by crystallization in hexane and column chromatography (silica gel, pentane) gave **38** (6.265 g, 67.5%), identified by its melting point and IR spectrum.

Hydrolysis of Trihalomethyl Derivatives. General Method. A mixture of the trihalomethyl compound and 30% oleum was stirred for 24 h. The reaction mixture was poured slowly over cracked ice and extracted with ether. The ethereal solution was extracted with aqueous $NaHCO_3$, and the aqueous solution obtained was acidified with concentrated HCl and extracted with ether. The resulting ethereal solution was dried and evaporated to give a solid which was generally crystallized. The following acids were obtained this way:

(1) 2,3,4,6-Tetrachlorobenzoic Acid (22). Starting materials: **9** (0.274 g), oleum (11 mL); room temperature. The crystals (from ether–hexane) were characterized as **22** (0.176 g, 82%): mp 143–4 °C; IR (KBr) 3400–2300 (m), 1720 (s), 1680 (s), 1570 (s), 1537 (m), 1430 (m), 1400 (m), 1355 (m), 1330 (s), 1260 (s), 1165 (m), 1102 (m), 900 (m), 870 (s), 820 (s), 770 (m), 730 (m), 615 (s), 550 (m), 532 (m), 495 (m), 473 (m) cm^{-1}. Anal. Calcd for $C_7H_2Cl_4O_2$: C, 32.3; H, 0.8; Cl, 54.6. Found: C, 32.3; H, 0.6; Cl, 54.6.

(2) 2,3,4-Trichlorobenzoic Acid (23). Starting materials: **15** (0.505 g), oleum (25 mL); room temperature. The solid obtained was **23** (0.367 g, 94%), mp 192–4 °C, identified by its melting point (lit.[38] mp 195–7 °C) and elemental analysis: IR (KBr) 3300–2300 (broad), 1710 (s), 1571 (s), 1412 (s), 1360 (s), 1285 (s), 1250 (s), 1182 (s), 1080 (m), 873 (m), 832 (m), 765 (m), 725 (m), 570 (m) cm^{-1}.

Methyl Ester 26. Esterification of **23** (0.108 g) with methanol and H_2SO_4 gave **26** (0.093 g, 81%), mp 63–6 °C, identified by its melting point (lit.[38] mp 67–8 °C): IR (KBr) 3100 (w), 2955 (w), 2930 (w), 1742 (s), 1578 (m), 1444 (m), 1428 (s), 1360 (s), 1283 (s), 1248 (m), 1190 (m), 1173 (m), 1137 (m), 1080 (m), 980 (m), 858 (s), 827 (s), 770 (s), 745 (m), 700 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64 (d, 1 H, J = 8 MHz, H-C(6)), 7.46 (d, 1 H, J = 8 MHz, H-C(5)), 3.96 (s, 3 H, CH_3).

(3) 2,4,6-Trichlorobenzoic Acid (24). Starting materials: **17** (1.051 g), oleum (25 mL); temperature 100 °C. The crystals (from CCl_4) were characterized as **24** (0.556 g, 53%): mp (DSC) 153 °C (endothermic peak), 156 °C (exothermic), 163 °C (endothermic) (lit. mp 163 °C,[39,40] mp 168 °C[41]); IR (KBr) polymorph (low melting point) 3500–2400 (m), 1720 (s), 1682 (s), 1580 (s), 1433 (s), 1360 (1300 (s), 1280 (s), 1258 (s), 1160 (m), 1131 (m), 1074 (s), 900 (s), 868 (s), 777 (m), 762 (m), 638 (m), 510 (m) cm^{-1}: polymorph (high melting point; crystals from melt) 3500–2400 (m), 1718 (s), 1580 (m), 1402 (s), 1330 (m), 1288 (m), 1250 (s), 1240 (m), 1160 (m),

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Table III. Fractional Atomic Coordinates ($\times 10^4$) with Their esd's and Equivalent Temperature Factors

	34				36				38			
atom	*X/A*	*Y/B*	*Z/C*	B_{eq}	*X/A*	*Y/B*	*Z/C*	B_{eq}	*X/A*	*Y/B*	*Z/C*	B_{eq}
Cl(2)					5913 (1)	3242 (1)	13462 (1)	4.57	−473 (1)	7003 (1)	4918 (1)	4.36
Cl(4)	6011 (1)	2855 (1)	5740 (1)	4.55	7133 (1)	−243 (1)	13436 (1)	4.88	−2441 (1)	4148 (1)	1922 (1)	4.61
Cl(5)	3033 (1)	3968 (1)	4815 (1)	4.26					340 (1)	4022 (1)	1410 (1)	4.36
Cl(6)	1683 (1)	5711 (1)	5997 (1)	4.95	6296 (1)	1641 (1)	8943 (1)	4.41	2486 (1)	5485 (1)	2161 (1	4.36
Cl(71)	4850 (1)	6652 (1)	9401 (1)	5.51	7778 (2)	4230 (1)	12071 (1)	6.16	708 (1)	8230 (1)	3296 (2)	5.86
Cl(72)	3251 (2)	7752 (1)	7572 (1)	6.46	5061 (1)	3777 (1)	9862 (1)	5.37	3126 (1)	7119 (1)	4703 (1)	5.51
Cl(73)	1983 (1)	5802 (1)	8421 (1	6.13	7937 (1)	3383 (1)	9696 (1)	5.56	2023 (1)	7414 (1)	1656 (1)	4.99
Cl(81)	8592 (1)	4378 (1)	9103 (1)	5.35	7941 (2)	2517 (1)	16155 (1)	6.50	−3581 (1)	7042 (1)	3169 (1)	4.09
Cl(82)	7664 (1)	2206 (1)	8114 (1)	5.29	5919 (1)	1043 (1)	15539 (1)	5.19	−3280 (1)	5352 (1)	4471 (1)	4.86
Cl(83)	8943 (1)	4017 (1)	7122 (1)	5.26	9052 (1)	846 (1)	15925 (1)	5.92	−4539 (1)	5616 (1)	1419 (1)	4.07
C(1)	4208 (4)	5512 (3)	7546 (3)	3.05	6801 (4)	2488 (2)	11476 (4)	3.01	611 (3)	6429 (2)	2990 (3)	2.83
C(2)	5601 (4)	5033 (3)	7939 (3)	3.09	6756 (4)	2395 (2)	12843 (3)	2.88	−570 (3)	6408 (2)	3431 (3)	2.81
C(3)	6214 (4)	4222 (3)	7415 (3)	2.95	7096 (4)	1599 (2)	13600 (2)	2.87	−1678 (3)	5802 (2)	2897 (3)	2.54
C(4)	5389 (4)	3877 (3)	6448 (3)	3.19	7076 (4)	828 (2)	12798 (4)	3.23	−1364 (3)	5052 (2)	2276 (3)	2.94
C(5)	3998 (4)	4375 (3)	6029 (3)	3.07	6856 (4)	879 (3)	11298 (4)	3.59	−62 (3)	4971 (2)	2071 (3)	3.03
C(6)	3420 (3)	5174 (3)	6573 (3)	3.09	6741 (4)	1701 (2)	10745 (3)	3.03	888 (3)	5660 (2)	2382 (3)	2.92
C(7)	3620 (4)	6366 (3)	8194 (3)	3.80	6862 (4)	3404 (2)	10832 (4)	3.41	1560 (3)	7233 (2)	3181 (4)	3.42
C(8)	7750 (4)	3739 (3)	7909 (3)	3.70	7444 (4)	1519 (2)	15183 (4)	3.55	−3144 (3)	5936 (2)	3016 (3)	2.88
H(2)	6089 (38)	5274 (30)	8512 (30)	1.97								
H(5)					6703 (38)	309 (23)	10886 (39)	3.16				

1125 (m), 1074 (s), 900 (m), 868 (m), 777 (m), 752 (m), 640 (m), 510 (m) cm^{-1}. Anal. Calcd for $C_7H_3Cl_3O_2$: C, 37.3; H, 1.3; Cl, 47.2. Found: C, 37.2; H, 1.2; Cl, 47.4.

Ethyl Ester 27. Esterification of **24** (0.150 g) with ethanol and H_2SO_4 gave **27** (0.143 g, 84%), mp 62–4 °C, identified by melting point (lit.[39,41] mp 65 °C): IR (KBr) 3105 (w), 2985 (w), 2940 (w), 1731 (s), 1580 (m), 1538 (m), 1470 (m), 1445 (m), 1395 (m), 1367 (m), 1330 (m), 1280 (s), 1242 (s), 1157 (m), 1110 (s), 1070 (s), 1018 (m), 900 (m), 867 (m), 770 (m), 678 (m), 638 (m), 495 (m) cm^{-1}.

Amide 29. **24** (0.151 g), treated with refluxing $SOCl_2$ and then with dry ammonia in benzene, gave **29** (0.135 g, 90%), mp 169–71 °C, identified by its melting point (lit.[39] mp 167.5 °C): IR (KBr) 3380 (m), 3195 (m), 1658 (s), 1625 (m), 1581 (w), 1548 (w), 1455 (m), 1400 (m), 1328 (m), 1128 (m), 1070 (m), 890 (m), 638 (m) cm^{-1}.

(4) **2,4,6-Trichlorobenzoic Acid (25).** Starting materials: **21** (1.021 g), oleum (25 mL); room temperature. The solid obtained was purified by sublimation to give **25** (0.623 g, 86%), mp 161–3 °C, identified by its melting point (lit. mp 162 °C,[42] mp 164 °C[43]) and elemental analyses: IR (KBr) 3300–2300 (broad), 1718 (s), 1580 (s), 1550 (s), 1385 (s), 1370 (m), 1278 (s), 1188 (m), 1162 (m), 1122 (s), 910 (m), 840 (s), 820 (s), 595 (m), 545 (s) cm^{-1}.

Methyl Ester 28. The esterification of **25** (0.065 g) with diazomethane in ether gave **28** (0.065 g, 94%), mp 40–3 °C, identified by its melting point (lit.[44] mp 43–4 °C): IR (KBr) 3085 (w), 2955 (w), 1750 (s), 1580 (s), 1548 (m), 1424 (m), 1370 (m), 1270 (s), 1185 (m), 1154 (m), 1114 (s), 1058 (m), 844 (s), 818 (m), 540 (m) cm^{-1}.

Amide 30. **25** (0.101 g), treated with refluxing $SOCl_2$ and then with dry ammonia in benzene, gave **30** (0.094 g, 87%): mp 179–80 °C (Kofler), DSC, 145 °C (endothermic), 177 °C (endothermic, mp), identified by its melting point (lit.[44] mp 181 °C); IR (KBr) polymorph α (from benzene) 3460 (m), 3430–3100 (broad), 3080 (w), 1670 (s), 1610 (s), 1580 (s), 1550 (s), 1380 (s), 1370 (s), 1192 (m), 1130 (m), 1060 (m), 890 (m), 850 (s), 838 (s), 820 (s), 795 (m), 690 (m), 680 (m), 590 (m), 545 (s), 525 (s), 430 (m) cm^{-1}; polymorph β (crystals from melt) 3470 (m), 3315 (s), 3185 (s), 3075 (w), 1670 (s), 1608 (s), 1580 (s), 1550 (s), 1460 (m), 1450 (m), 1373 (m), 1192 (m), 1130 (m), 1092 (m), 1060 (m), 890 (m), 860 (s), 834 (s), 814 (s), 795 (m), 685 (m), 592 (s), 550 (s), 518 (s), 430 (m) cm^{-1}.

(5) **4,5,6-Trichloroisophthalic Acid (33).** Starting materials: **34** (0.531 g), oleum (35 mL); room temperature. The crystals (from ether) were identified as **33** (0.273 g, 79%), mp 318–20 °C, identified by its melting point (lit. mp 318–20 °C,[45] mp 300 °C[37]) and elemental analysis: IR (KBr) 3400–2400 (m), 1710 (s), 1573 (m), 1528 (w), 1409 (m), 1385 (m), 1340 (m), 1272 (s), 1096 (m), 940 (m), 722 (m) cm^{-1}.

Methyl Ester 37. Esterification of **33** (0.063 g) with methanol and H_2SO_4 gave **37** (0.063 g, 89%), mp 142–4 °C, identified by its melting point (lit.[37] mp 143–4 °C): IR (KBr) 3095 (w), 3035 (w), 2975 (w), 1740 (s), 1570 (m), 1466 (m), 1454 (m), 1433 (m), 1415 (m), 1295 (s), 1268 (s), 1235 (s), 1192 (s), 1162 (s), 1088 (s), 958 (m), 910 (m), 892 (m), 772 (s), 622 (m) cm^{-1}.

(6) **2,4,6-Trichloroisophthalic Acid (35).** Starting materials: **36** (0.070 g), oleum (3 mL); room temperature. The crystals (from ether–hexane) were characterized as **35** (0.030 g, 66%): mp 304–7 °C; IR (KBr) 3400–2500 (m), 1720 (s), 1585 (s), 1550 (m), 1380 (m), 1350 (m), 1260 (s), 1172 (s), 1110 (m), 920 (m), 870 (m), 823 (m), 800 (m), 588 (m) cm^{-1}. Anal. Calcd for $C_8H_3Cl_3O_4$: C, 35.6; H, 1.1; Cl, 39.5. Found: C, 35.7; H, 1.2; Cl, 39.6.

(7) **Perchloroisophthalic Acid (39).** Starting materials: **38** (0.200 g), oleum (9 mL); room temperature. The crystals (from ether–hexane) were characterized as **39** (0.120 g, 89%): mp 288–90 °C (Lit.[46], mp 267–9 °C[48]); IR (KBr) 3400–2300 (m), 1720 (s), 1660 (s), 1632 (m), 1428 (s), 1352 (s), 1285 (s), 1250 (s), 932 (s), 782 (m), 753 (m), 732 (m), 680 (m), 610 (s), 470 (m) cm^{-1}. Anal. Calcd for $C_8H_2Cl_4O_4$: C, 31.6; H, 0.7; Cl, 46.7. Found: C, 31.6; H, 0.4; Cl, 46.7.

X-ray Analysis. Xylene 34. Prismatic colorless crystal, monoclinic, space group $P2_1/a$, $a = 9.440$ (8) Å, $b = 11.419$ (9) Å, $c = 13.590$ (8) Å, $\beta = 105.58$ (4)°, $V = 1411$ Å^3, $z = 4$, $D_{calcd} = 1.96$ g/cm^3, μ(Mo Kα) = 17.7 cm^{-1}, $R = 4.6\%$ (over 1734 reflections with $F > 4\sigma(F)$).

Xylene 36. Prismatic colorless crystal, monoclinic, space group $P2_1/a$, $a = 9.586$ (8) Å, $b = 15.041$ (4) Å, $c = 10.165$ (2) Å, $\beta = 109.68$ (3)°, $V = 1380$ Å^3, $z = 4$, $D_{calcd} = 2.00$ g/cm^3, μ(Mo Kα) = 18.1 cm^{-1}, $R = 4.2\%$ (over 1935 reflections with $F > 5\sigma(F)$).

Xylene 38. Prismatic colorless crystal, monoclinic, space group $P2_1/n$, $a = 10.056$ (1) Å, $b = 15.392$ (1) Å, $c = 10.090$ (2) Å, $\beta = 110.92$ (1)°, $V = 1458.9$ Å^3, $Z = 4$, $D_{calcd} = 2.05$ g/cm^3, μ(Mo Kα) = 19.0 cm^{-1}, $R = 4.0\%$ (over 2231 reflections with $F > 5\sigma(F)$).

The structures were solved using MULTAN 11/84;[49] the refinements were carried out with anisotropic full-matrix least-squares methods;[50] scattering factors were taken from ref 51.

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Fractional atomic coordinates are given in Table III.

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Registry No. **1**, 608-93-5; **2**, 384-83-8; **3**, 2605-69-8; **4**, 634-66-2; **5**, 97985-54-1; **6**, 2136-87-0; **7**, 634-90-2; **8**, 126278-82-8; **9**, 126300-29-6; **10**, 95-94-3; **11**, 7656-99-7; **12**, 2142-30-5; **13**, 87-61-6; **14**, 61841-45-0; **15**, 20020-72-8; **16**, 120-82-1; **17**, 56148-83-5; **18**, 27020-90-2; **19**, 108-70-3; **20**, 567-59-9; **21**, 14379-95-4; **22**, 50-40-8; **23**, 50-75-9; **24**, 50-82-8; **25**, 50-43-1; **26**, 89978-33-6; **27**, 86569-86-0; **28**, 86569-78-0; **29**, 70439-09-7; **30**, 23400-04-6; **31**, 327-72-0; **32**, 130199-73-4; **33**, 5002-24-4; **34**, 60047-51-0; **35**, 130199-74-5; **36**, 130199-75-6; **37**, 20019-06-1; **38**, 130199-76-7; **39**, 7401-89-0; CCl_3F, 75-69-4; $AlCl_3$, 7446-70-0.

Supplementary Material Available: Deviations of the atoms from the mean plane of the benzene ring (Table IV), anisotropic thermal parameters (Table V), and a stereoview of the unit cell of **38** (Figure 3) (3 pages); structure factors of **34**, **36**, and **38** (calculated and observed; Table VI) (34 pages). Ordering information is given on any current masthead page.

Reaction of Pyrrolo[1,2-*c*]imidazole Mesomeric Betaines with Diphenylcyclopropenone Derivatives

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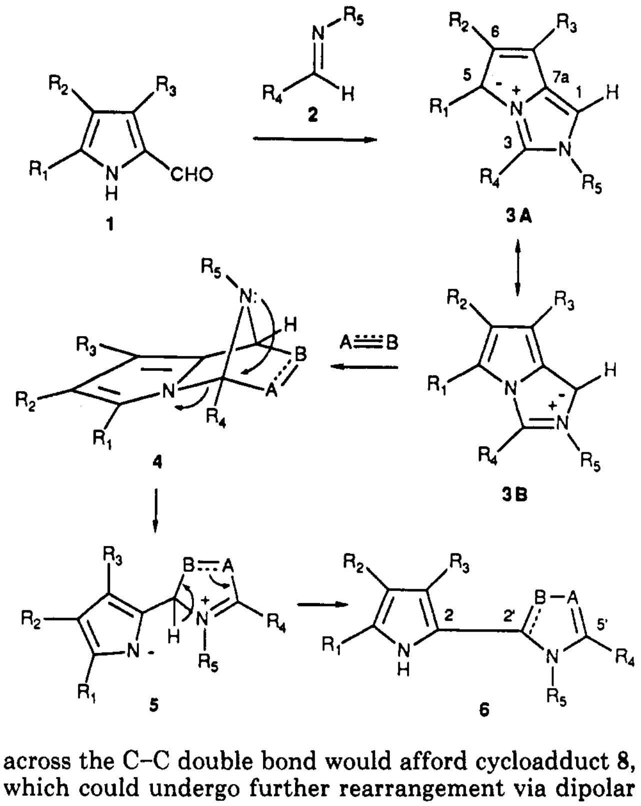
The cyloaddition reactions of title mesomeric betaines to diphenylcyclopropenone and diphenylcyclopropenethione have been studied. Cycloadditions lead to either 2(1*H*)-pyridone, 2(1*H*)-pyridinethione, or bicyclo[3.1.0]hex-3-en-2-one derivatives. Formation of the bicyclo[3.1.0]hex-3-en-2-ones is highly stereoselective with exclusive formation of C-6 *exo*-alkoxycarbonyl or the *exo*-acetyl diastereoisomer. Diphenylcyclopropenone and its thione enriched with ^{13}C at both the 2- and 3-positions were prepared and used to determine the structures of the cycloaddition products. Possible mechanistic pathways for these reactions are considered and compared with previous postulated mechanisms for the cycloadditions of cyclopropenones to N-heterocycles and enamines.

In our previous work[1] we described a condensation of 2-formylpyrroles **1** with aromatic imines **2** as a general method for the synthesis of a novel class of heteropentalene mesomeric betaines, pyrrolo[1,2-*c*]imidazole mesomeric betaines **3A** ↔ **3B** (Scheme I). We also investigated their participation in 1,3-dipolar cycloaddition reactions with representative acetylenic and olefinic dipolarophiles.[1] Addition to both classes of dipolarophiles was highly periselective, with the dipolarophile adding exclusively across the 1,3-azomethine ylide dipole **3B**. The products of cycloaddition, 2,2′-bipyrroles and 2′,3′-dihydro-2,2′-bipyrroles **6**, were assumed to be formed through the rearrangement of the expected cycloadduct **4** via zwitterionic intermediate **5**.

Due to their exceptional structural characteristics, cyclopropenone derivatives and their thiono analogues have been used as indispensable intermediates in reactions wih diverse classes of organic molecules,[2] including several classes of heterocyclic mesomeric betaines, such as mesoionic compounds[3] and conjugated heterocyclic *N*-ylides.[4] However, the chemistry of cycloadditions of cyclopropenones to heteropentalene mesomeric betaines have been investigated only under high pressure.[5] As part of our continuing interest in the properties of the title mesomeric betaines, we have studied their reactivity toward diphenylcyclopropenone (**7a**) and diphenylcyclopropenethione (**7b**). On the basis of the established reactivity pattern of **3** with acetylenic and olefinic dipolarophiles, the following types of diphenylcyclopropenone cycloaddition pathways were regarded as plausible (Scheme II): addition across the C–C double bond would afford cycloadduct **8**, which could undergo further rearrangement via dipolar

Scheme I



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