Acknowledgment. One of us (J. L. D.) wishes to thank the Alexander von Humboldt Stiftung for a postdoctoral fellowship. We are indebted to Professor M. Hanack for his contribution to this work and for stimulating discussions and we gratefully acknowledge the assistance of Dr. W. E. Heyd in the preparation of the manuscript.

Registry No.—I, 622-76-4; *cis*-III, 1560-09-4; *trans*-III, 1005-64-7; *cis*-IV, 15324-90-0; *trans*-IV, 935-00-2; V, 1515-78-2; VI, 33598-22-0; *cis*-VII, 51175-89-4; *trans*-VII, 51175-90-7; VIII, 51175-91-8; IX, 51175-92-9; XXI, 4468-42-2; XXII, 51175-93-0; phenylacetylene, 536-74-3.

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(8) We wish to thank Dozent Dr. H. Stegmann, Chemisches Institut der Universität Tübinge, for obtaining these measurements for us.

(9) Although a small amount of phenylbutane could have been formed by reduction of the starting material by the hydrogen formed with the metal during the hydrolysis process, this cannot be responsible for the large amount of II that we observed. Moreover, II was also present after hydrolysis of samples pipetted out carefully avoiding the presence of metal particles.

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(33) As far as we know the ir spectrum of 1-phenyl-2-butyne (VI) has not been reported in the literature. We would like, however, to thank Professor R. Gelin (Institut National des Sciences Appliquées de Lyon, France) for sending us the nmr data of that compound.

Gaseous Chlorine Action on Solid-State Phenols

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During study of the chlorination of 26 alkylmonophenols in the solid state by gaseous chlorine, 13 new substances were prepared, isolated, and characterized: four chlorophenols, eight chlorocyclohexadienones, and one chlorocyclohexenone. The main characteristic of these gas–solid reactions is that they are very rapid and nearly always lead to the total transformation of the initial product in the absence of solvent and catalyst. Consideration of the steric and electronic effects of the groups attached to the phenolic nucleus leads to a consistent interpretation.

During the study of organic solid-state reactivity,[1] we became interested in the chlorination of a number of solid-state phenols by gaseous chlorine. Under the conditions of our reactions and varying with the alkylphenol

Table I
Chlorination of Alkylphenols in the Solid State by Gaseous Chlorine[a,b]

Phenol	Registry no.	Product (yield, %)	Registry no.	Identification
Phenol	108-95-2	2,4,6-Trichlorophenol (97)	88-06-2	w, vpc, uv, ir, nmr
		2,4-Dichlorophenol (3)		
4-Methyl-	106-44-5	2-Chloro-4-methylphenol (20)	6640-27-3	w, vpc, uv
		2,6-Dichloro-4-methylphenol (80)	2432-12-4	
4-Ethyl-	123-07-9	2-Chloro-4-ethylphenol (30)	18980-00-2	w, vpc, uv
		2,6-Dichloro-4-ethylphenol (70)	7495-69-4	
4-Isopropyl-	99-89-8	2-Chloro-4-isopropylphenol (30)	51202-00-7	w, vpc, uv
		2,6-Dichloro-4-isopropylphenol (65)	2432-13-5	
		Chlorocyclohexadienone (5)		
4-*tert*-Butyl-	98-54-4	2,6-Dichloro-4-*tert*-butylphenol (68)	34593-75-4	w, vpc, uv, ir, nmr
		I 2,4,6-Trichloro-4-*tert*-butyl-2,5-cyclohexadienone (32)	51202-01-8	
2,6-Dimethyl-	576-26-1	Chlorophenols ($\sim$55)		w, uv[3]
		o-Chlorocyclohexadienones ($\sim$25)		
		Chlorocyclohexenones ($\sim$20)		
3,5-Dimethyl-	108-68-9	2,4,6-Trichloro-3,5-dimethylphenol (20)	6972-47-0	w, vpc, uv, ir, nmr
		2,4-Dichloro-3,5-dimethylphenol (78)	133-53-9	
		4-Chloro-3,5-dimethylphenol (2)		
3-Methyl-5-ethyl-	698-71-5	II 2,4,6-Trichloro-3-methyl-5-ethylphenol (98)	15460-04-5	w, vpc, uv, ir, nmr
		2,4-Dichloro-3-methyl-5-ethylphenol (2)		
3,5-Diethyl-	1197-34-8	III 2,4,6-Trichloro-3,5-diethylphenol (80)	51202-02-9	w, vpc, uv, ir, nmr
		2,4-Dichloro-3,5-diethylphenol (20)	38730-38-0	
3-Methyl-5-isopropyl-	3228-03-3	IVa 2,4,6-Trichloro-3-methyl-5-isopropylphenol (94)	51202-03-0	w, vpc, uv, ir, nmr[4]
		IVb 2,4,4,6-Tetrachloro-3-methyl-5-isopropyl-2,5-cyclohexadienone (6)	51202-04-1	
3-Methyl-2-isopropyl-	3228-01-1	6-Chloro-3-methyl-2-isopropylphenol (5)		w, uv, vpc[4]
		4,6-Dichloro-3-methyl-2-isopropylphenol (95)	51202-05-2	
2-Methyl-3-isopropyl-	4371-48-6	6-Chloro-2-methyl-3-isopropylphenol (8)		w, uv, vpc
		4,6-Dichloro-2-methyl-3-isopropylphenol (92)	51202-06-3	
3,5-Diisopropyl-	3374-41-2	Va 2,4,6-Trichloro-3,5-diisopropylphenol (73)	51202-07-4	w, vpc, uv, ir, nmr
		2,4-Dichloro-3,5-diisopropylphenol (4)		
		Vb 2,4,4,6-Tetrachloro-3,5-diisopropyl-2,5-cyclohexadienone (23)	51202-08-5	
2,6-Di-*tert*-butyl-	128-39-2	4-Chloro-2,6-di-*tert*-butylphenol (45)	4096-72-4	w, vpc, uv, ir, nmr[5]
		4-Chloro-2,6-di-*tert*-butyl-2,5-cyclohexadienone (20)	26330-92-7	
		4,6-Dichloro-2,6-di-*tert*-butyl-2,4-cyclohexadienone (35)	26330-93-8	
2,5-Di-*tert*-butyl-	5875-45-6	Chlorophenols (40)		w, vpc, uv, ir, nmr
		VIa 4,4,6-Trichloro-2,5-di-*tert*-butyl-2,5-cyclohexadienone	51202-09-6	
		VIb 4,6,6-Trichloro-2,5-di-*tert*-butyl-2,4-cyclohexadienone (60)	51202-10-9	
		VIc 2,4,6-Trichloro-2,5-di-*tert*-butyl-3,5-cyclohexadienone	51202-11-0	
2,4-Di-*tert*-butyl-	96-76-4	Chlorophenols (37)		w, vpc, uv, ir, nmr
		VII 4,6-Dichloro-2,4-di-*tert*-butyl-2,5-cyclohexadienone (63)	34896-06-5	
3,5-Di-*tert*-butyl-	1138-52-9	Chlorophenols (37)		w, vpc, uv, ir, nmr[6]
		VIIIa 2,4,4-Trichloro-3,5-di-*tert*-butyl-2,5-cyclohexadienone	51202-12-1	
		VIIIb 2,4,4,6-Tetrachloro-3,5-di-*tert*-butyl-2,5-cyclohexadienone (63)	51202-13-2	
2,4,6-Trimethyl-	527-60-6	Chlorocyclohexenones ($\sim$30)		w, uv, nmr
3,4,5-Trimethyl-	527-54-8	Chlorocyclohexenones ($\sim$40)		w, uv, nmr
4-Methyl-3,5-diisopropyl-	15269-17-7	Chlorophenols ($\sim$90)		w, uv
		Chlorocyclohexadienones ($\sim$10)		
4-Methyl-2,5-diisopropyl-	15269-16-6	Chlorophenols ($\sim$85)		w, uv
		Chlorocyclohexadienones ($\sim$15)		
2,6-Dimethyl-4-*tert*-butyl	879-97-0	IX 2,5,6-Trichloro-2,6-dimethyl-4-*tert*-butyl-3-cyclohexenone (95)	51202-14-3	w, uv, ir, nmr
4-Methyl-2,6-di-*tert*-butyl	128-37-0	4-Chloro-4-methyl-2,6-di-*tert*-butyl-2,5-cyclohexadienone (47)	19487-11-7	w, uv, ir, nmr
2,4,6-Triisopropyl-	2934-07-8	Chlorocyclohexenone ($\sim$40)		w, uv
		Chlorocyclohexadienone ($\sim$60)		
2,4,6-Tri-*tert*-butyl-	732-26-3	4-Chloro-2,4,6-tri-*tert*-butyl-2,5-cyclohexadienone (92)	5457-60-3	w, uv, ir, nmr[5]

[a] w: by weighing preparations before and after reaction the weight of fixed chlorine is determined. [b] The substances preceded by a Roman numeral are new ones; they are described and characterized in the Experimental Section.

considered, the appearance of three types of substances is worth noting. It appears that the alkyl substituents carried by the phenolic nucleus[2] determine the formation of the product. The consideration of steric and electronic effects leads us to conclusions which are compatible with the experimental results obtained.

Results

The results obtained for the 26 phenols studied are listed in Table I.

As shown in Table I, several methods have been used to characterize and titrate the substances obtained during the chlorination reaction. When the starting phenols produced new substances, larger scale preparations were undertaken so as to obtain appreciable quantities. Generally phenols and chlorophenols are detected in the uv toward 280 nm and *o*- and *p*-cyclohexadienones toward 340 and 250 nm, respectively, according to Denivelle and Fort.[7] Lastly, cyclohexenones were found in the neighborhood of 220 or 260 nm according to the isomer considered, as shown by Denivelle and Fort[8] and Morita and Dietrich.[9] Titrations were carried out at maximum absorption after determining the molecular extinction coefficients. In the few cases in which the reaction products could not be isolated, average coefficients made possible an estimation of the quantities of substance produced. The knowledge of the transformation rate, specific to the reaction studied, estimated by vpc and uv and the determination of weight of chlorine fixed on a given quantity of phenol, make it possible to appreciate in many cases the number of chlorine atoms fixed on the nucleus.

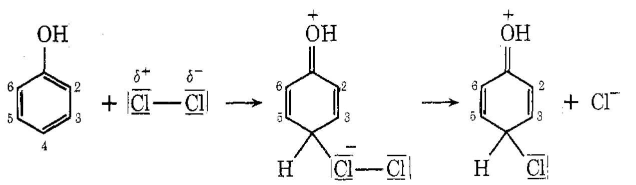
There are three criteria for the ,choice of phenols to be used for this study. In the first place, we selected phenols with a high melting point, so as to give the reaction the best chance of occurring in the solid state. Secondly, two series of phenols were considered in more detail: the 3,5-dialkylphenol series and the 2,4,6-trialkylphenol series. The first series corresponds to substances in which all the positions usually reactive during electrophilic substitution reactions are free; moreover, for this series, interactions between the OH and alkyl groups are reduced and the interpretation of the results is made easier.

On the other hand, the 2,4,6-trialkylphenol series corresponds to substances which have no reactive position and knowledge of their behavior is a useful element for the clear understanding of the reaction of the chlorination studied. Lastly, the results obtained with 4-alkylphenols and various other phenols generalize the conclusions which have been drawn.

In the 3,5-dialkylphenol series, it is to be noted that 3,5-dimethyl-, 3-methyl-5-ethyl-, and 3,5-diethylphenol produce exclusively chlorophenols. In the case of 3-methyl-5-isopropyl- and 3,5-diisopropylphenol, 6 and 23% of the chlorocyclohexadienones are formed, respectively, in addition to chlorophenols. Lastly, in the case of 3,5-di-*tert*-butylphenol, chlorocyclohexadienones are obtained. Thus, for phenols substituted on the same carbon, the products obtained are different according to the nature of the hydrocarbon groups carried by these carbons. The same phenomenon is observed with 4-alkylphenols, since 4-methyl- and 4-ethylphenol give exclusively chlorophenols, whereas 4-isopropylphenol gives traces of chlorocyclohexadienones (5%) and 4-*tert*-butylphenol produces considerable chlorocyclohexadienone (32%). With 2,4,6-trialkylphenols, no chlorophenols are obtained since the meta positions of the OH group are not very reactive. However, once again, according to the substituents present on carbon at 2, 4, and 6, the products obtained vary and are either chlorocyclohexadienones or chlorocyclohexenones, or mixtures. In particular, it is interesting to note that the two compounds, 2,6-dimethyl-4-*tert*-butyl- and 2,6-di-*tert*-butyl-4-methylphenol, give a chlorocyclohexenone and a chlorocyclohexadienone, respectively. Lastly, regarding phenols not belonging to a particular group, it is noticed that all di-*tert*-butylphenols give approximately the same mixture of chlorophenols and chlorocyclohexadienones and that a number of polymethylphenols are transformed into chlorocyclohexenones.

Discussion

In view of the conditions, the chlorination reaction can be represented in the following manner.[10]



Because of the absence of solvent and catalyst during this reaction, gaseous chlorine molecules can only be polarized by the corresponding nucleus of the initial phenol.[11,12]

During the reaction, rearrangements may occur. As shown by Waring,[13] in the presence of acid cyclohexadienones with alkyl groups in position 4 produce phenols by migration of an alkyl group. Likewise, de la Mare's work[14] on the bromination of 2,6-di-*tert*-butylphenol shows a dienone–phenol rearrangement in acetic acid with migration of hydrogen on carbon to oxygen. This same type of rearrangement was considered by Curtin[15] in Claisen rearrangement during which a cyclohexadiene intermediate (6-alkyl-2,6-dimethyl-2,4-cyclohexadienone) could be isolated.

On the other hand, in some cases an inverse rearrangement takes place; this is the dienone–phenol rearrangement, which occurs without real migration. Some authors[16,17] have observed such a rearrangement during halogenation reactions of phenols already halogenated.

In any case,[13] it appears that the reaction path followed by a particular dienone depends on steric and polar effects. The consideration of these effects is compatible with the results we have obtained. In the 3,5-dialkylphenol series, increase of the steric effect in 3,5-di-*tert*-butylphenol can be supplanted by the polar effect of *tert*-butyl groups and thus, by polychlorination, give cyclohexadienones. In the case of 3,5-dimethylphenol, polar effects are much weaker, and, although steric hindrance is reduced, the products obtained are only chlorophenols. Moreover, examination of the results from 4-methyl-2,6-di-*tert*-butylphenol (A) and 2,6-dimethyl-4-*tert*-butylphenol (B) show that, once again, the results obtained can be explained by steric and polar effects specific to the *tert*-butyl and methyl groups. In spite of steric hindrance, the polar effects in A are sufficient to allow the addition of a chlorine to the carbon atom carrying a methyl group, and, under these conditions, to produce cyclohexadienone.

In the case of product B, a medium polar effect combined with the absence of steric hindrance in positions 2 and 3 make possible the development of a chlorine addition reaction to produce a chlorocyclohexenone (IX).

In conclusion, we may say that an increase in the number of donor effect substituents increases the rate of for- of chlorophenols. If the products with a great number of donor effect substituents have some positions for which steric hindrance is reduced, chlorocyclohexenones are obtained preferentially.

Experimental Section

The phenols prepared in the laboratory (P) or available commercially (C) are grouped in Table II, where their melting points are indicated.

Equipment. The various chlorination experiments were carried out in a Pyrex glass thermoregulated reactor. A set of valves let in the gaseous chlorine dried on calcium chloride and let out the hydrochloric acid formed. The regulation systems controlled the temperature to ±0.1°.

The uv spectra were measured in hexane solution (Merck) with a Unicam SP 800B spectrophotometer. Chromatographic analyses were made with an Intersmat apparatus, IGC 12 M model, equipped with a catharometer. The column was filled with Chromosorb W 60/80 impregnated with diethylene glycol succinate. The peak area was determined with the help of a LTT M 924 numerical integrator coupled with the chromatograph.

The ir spectra were measured with a Perkin-Elmer 457 spectrophotometer. The nmr spectra were made in acetone-d_6 solution using tetramethylsilane as an internal standard, with a Varian A-60 spectrometer.

Preparation and Separation of Products. The phenols, handled in a drybox, were crushed manually into fine powder in a mortar, then sifted. The calibrated powders were arranged in thin layers in a small cup, then weighed (quantities of 0.005 mol of phenol were used). These powders were first placed in the thermoregulated reactor at 20°, then subjected to a flow of dry gaseous chlorine for 10 min. The reaction mixtures were treated with hexane; after one or more recrystallizations either chlorophenols or chlorocyclohexadienones were obtained.

A general method of separation could be applied to all the substances described. In some cases, however, manual sorting with tweezers was necessary to extract the chlorocyclohexadienones from the mixtures. In the case of 3,5-di-*tert*-butylphenol chlorination, after recrystallization in hexane, a mixture of *p*-chlorocyclohexadienones was found.

Sorting with tweezers made it possible to separate needles from a white powder. The needles gave compound VIIIb and the powder compound VIIIa.

Likewise, by chlorination of 2,5-di-*tert*-butylphenol, a mixture of *o*- and *p*-chlorocyclohexadienones was obtained after recrystallizations in hexane. This mixture was composed of yellow plates and small needles.

By manual sorting with tweezers, compound VIa was obtained in the form of colorless needles; the yellow plates were a mixture of VIb and VIc (*o*-chlorocyclohexadienones which we were unable to separate).

We prepared the *p*-chlorocyclohexadienone by another method,[4] only in the case of 3-methyl-5-isopropylphenol taking into account the very low yield (6%) of compound IVb. To a solution of 20 g of 3-methyl-5-isopropylphenol dissolved in 65 g of acetic acid, 250 ml of a sodium hypochlorite solution was added (47–50 chlorometric degrees) so that the temperature did not exceed 50°. Stirring was maintained for 45 min. After washing, 15 g of white crystals was separated and purified by recrystallization in hexane.

2,4,6-Trichloro-4-*tert*-butyl-2,5-cyclohexadien-1-one (I) was colorless needles: mp 116.5–117.5°; uv 252 nm (ϵ 17,200); ir (KBr) 1680 cm^{-1} (C=O); nmr δ 1.21 [s, 9, CH_3 of $C(CH_3)_3$], 7.56 (s, 2, ring vinyl proton).

Anal. Calcd for $C_{10}H_{11}Cl_3O$: C, 47.34; H, 4.34; Cl, 42.01. Found: C, 47.48; H, 4.41; Cl, 42.25.

2,4,6-Trichloro-3-methyl-5-ethylphenol (II) had mp 61.5–62.5°; uv 285 nm (ϵ 1700), 293 (2000); ir (KBr) 3390 cm^{-1} (OH); nmr δ 1.14 (t, J = 7 Hz, 3, CH_3 of CH_2CH_3), 2.43 (s, 3, CH_3), 2.95 (q, J = 7 Hz, 2, CH_2 of CH_2CH_3), 8.3 (s, OH).

Anal. Calcd for $C_9H_9Cl_3O$: C, 45.09; H, 3.75; Cl, 44.46; O, 6.69. Found: C, 45.19; H, 3.68; Cl, 44.29; O, 6.84.

2,4,6-Trichloro-3,5-diethylphenol (III) was white needles: mp 98–99°; uv 285 nm (ϵ 1800), 294 (2100); ir (KBr) 3400 cm^{-1} (OH); nmr δ 1.14 (t, J = 7 Hz, 6, CH_3 of CH_2CH_3), 2.95 (q, J = 7 Hz, 4, CH_2 of CH_2CH_3), 8.68 (s, OH).

Anal. Calcd for $C_{10}H_{11}Cl_3O$: C, 47.34; H, 4.34; Cl, 42.01; O, 6.31. Found: C, 47.14; H, 4.44; Cl, 42.04; O, 6.42.

2,4,6-Trichloro-3-methyl-5-isopropylphenol (IVa) had mp 39.5–40°; uv 286 nm (ϵ 1890), 292 (2090); ir (KBr) 3420 cm^{-1} (OH); nmr δ 1.39 [d, J = 7 Hz, 6, CH_3 of $CH(CH_3)_2$], 2.41 (s, 3, CH_3), 3.94 [m, J = 7 Hz, 1, CH of $CH(CH_3)_2$], 8.52 (s, OH).

Anal. Calcd for $C_{10}H_{11}Cl_3O$: C, 47.34; H, 4.34; Cl, 42.01. Found: C, 47.46; H, 4.41; Cl, 41.83.

Table II

Phenol	Origin	Mp, °C
Phenol	C	40.9
4-Methyl-	C	34.7
4-Ethyl-	C	44.8
4-Isopropyl-	C	63
4-*tert*-Butyl-	C	99.4
2,6-Dimethyl-	C	45.5
3,5-Dimethyl-	C	63.2
3-Methyl-5-ethyl-	C	51
3,5-Diethyl-	P[18]	78
3-Methyl-5-isopropyl-	P[19]	48.5
3-Methyl-2-isopropyl-	P[20]	69.6
2-Methyl-3-isopropyl-	P[21]	81.9
3,5-Diisopropyl-	P[22]	53.1
2,6-Di-*tert*-butyl	C	37
2,5-Di-*tert*-butyl-	C	119.4
2,4-Di-*tert*-butyl-	C	55.8
3,5-Di-*tert*-butyl-	C	91.2
2,4,6-Trimethyl-	C	71.6
2,3,5-Trimethyl-	C	93.7
3,4,5-Trimethyl-	C	107
4-Methyl-3,5-diisopropyl-	P[23]	92.8
4-Methyl-2,5-diisopropyl-	P[23]	52.7
2,6-Dimethyl-4-*tert*-butyl-	C	84
4-Methyl-2,6-di-*tert*-butyl-	C	71
2,4,6-Triisopropyl-	P[22]	19.1
2,4,6-Tri-*tert*-butyl-	C	136

2,4,4,6-Tetrachloro-3-methyl-5-isopropyl-2,5-cyclohexadien-1-one (IVb) had mp 90°; uv 256 nm (ϵ 16,200); ir (KBr) 1700 cm^{-1} (C=O); nmr δ 1.53 [d, J = 7 Hz, 6, CH_3 of $CH(CH_3)_2$], 2.50 (s, 3, CH_3), 3.31 [m, J = 7 Hz, 1, CH of $CH(CH_3)_2$].

Anal. Calcd for $C_{10}H_{10}Cl_4O$: C, 41.66; H, 3.47; Cl, 49.30. Found: C, 41.35; H, 3.41; Cl, 49.59.

2,4,6-Trichloro-3,5-diisopropylphenol (Va) was a white solid: mp 84–85°; uv 286 nm (ϵ 2000), 295 (2500); ir (KBr) 3500 cm^{-1} (OH); nmr δ 1.41 [d, J = 7 Hz, 12, CH_3 of $CH(CH_3)_2$], 4.06 [m, J = 7 Hz, 2, CH of $CH(CH_3)_2$], 8.47 (s, OH).

Anal. Calcd for $C_{12}H_{15}Cl_3O$: C, 51.15; H, 5.33; Cl, 37.83; O, 5.68. Found: C, 51.05; H, 5.38; Cl, 37.70; O, 5.52.

2,4,4,6-Tetrachloro-3,5-diisopropyl-2,5-cyclohexadien-1-one (Vb) was colorless needles: mp 154–155°; uv 254 nm (ϵ 17,500); ir (KBr) 1680 cm^{-1} (C=O); nmr δ 1.54 [d, J = 7 Hz, 12, CH_3 of $CH(CH_3)_2$], 3.32 [m, J = 7 Hz, 2, CH of $CH(CH_3)_2$].

Anal. Calcd for $C_{12}H_{14}Cl_4O$: C, 45.57; H, 4.43; Cl, 44.93. Found: C, 45.95; H, 4.63; Cl, 44.82.

4,4,6-Trichloro-2,5-di-*tert*-butyl-2,5-cyclohexadien-1-one (VIa) was big, colorless needles: mp 119–120°; uv 248 nm (ϵ 13,000); ir (KBr) 1670 cm^{-1} (C=O); nmr δ 1.28 [s, 9, CH_3 of $C(CH_3)_3$ at C-2], 1.73 [s, 9, CH_3 of $C(CH_3)_3$ at C-5], 7.20 (s, 1, ring vinyl proton).

Anal. Calcd for $C_{14}H_{19}Cl_3O$: C, 54.28; H, 6.13; Cl, 34.11; O, 5.17. Found: C, 54.09; H, 6.09; Cl, 34.50; O, 5.27.

VIb and VIc were yellow sheets: mp 120–122°; uv 339 nm (ϵ 3000); ir (KBr) 1690 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{19}Cl_3O$: C, 54.28; H, 6.13; Cl, 34.41; O, 5.17. Found: C, 54.37; H, 6.13; Cl, 34.39; O, 5.22.

4,6,6-Trichloro-2,5-di-*tert*-butyl-2,4-cyclohexadien-1-one (VIb) had nmr δ 1.28 [s, 9, CH_3 of $C(CH_3)_3$ at C-2], 1.65 [s, 9, CH_3 of $C(CH_3)_3$ at C-5], 6.92 (s, 1, ring vinyl proton).

2,4,6-Trichloro-2,5-di-*tert*-butyl-3,5-cyclohexadien-1-one (VIc) had nmr δ 1.12 [s, 9, CH_3 of $C(CH_3)_3$ at C-2], 1.60 [s, 9, CH_3 of $C(CH_3)_3$ at C-5], 6.63 (s, 1, ring vinyl proton).

4,6-Dichloro-2,4-di-*tert*-butyl-2,5-cyclohexadien-1-one (VII) was colorless needles: mp 80–81°; uv 246 nm (ϵ 14,000); ir (KBr) 1680 cm^{-1} (C=O); nmr δ 1.18 [s, 9, CH_3 of $C(CH_3)_3$ at C-4], 1.27 [s, 9, CH_3 of $C(CH_3)_3$ at C-2], 7 (s, 1, ring vinyl proton at C-5), 7.43 (s, 1, ring vinyl proton at C-3).

Anal. Calcd for $C_{14}H_{20}Cl_2O$: C, 61.09; H, 7.27; Cl, 25.82. Found: C, 61.19; H, 7.23; Cl, 25.97.

2,4,4-Trichloro-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-one (VIIIa) was colorless crystals: mp 145–146°; uv 248 nm (ϵ 11,200); ir (KBr) 1670 cm^{-1} (C=O); nmr δ 1.57 [s, 9, CH_3 of $C(CH_3)_3$ at C-5], 1.74 [s, 9, CH_3 of $C(CH_3)_3$ at C-3], 6.48 (s, 1, ring vinyl proton).

Anal. Calcd for $C_{14}H_{19}Cl_3O$: C, 54.28; H, 6.13; Cl, 34.41; O, 5.17. Found: C, 54.42; H, 6.15; Cl, 34.27; O, 5.25.

2,4,4,6-Tetrachloro-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-one (VIIIb) had mp 159–160°; uv 254 nm (ϵ 14,000); ir (KBr) 1680 cm^{-1} (C=O); nmr δ 1.74 [s, CH_3 of $C(CH_3)_3$].

Anal. Calcd for $C_{14}H_{18}Cl_4O$: C, 48.84; H, 5.23; Cl, 41.28; O, 4.65. Found: C, 48.92; H, 5.32; Cl, 41.23; O, 4.56.

2,5,6-Trichloro-2,6-dimethyl-4-*tert*-butyl-3-cyclohexen-1-one (IX) had mp 117-118°; uv 220 nm (ϵ 6000); ir (KBr) 1740 cm^{-1} (C=O); nmr δ 1.23 [s, 9, CH_3 of $C(CH_3)_3$], 1.92-1.94 (6, CH_3), 5.13 (d, J = 0.15 Hz, 1, proton at C-5), 6.03 (d, J = 0.15 Hz, 1, ring vinyl proton at C-3).

Anal. Calcd for $C_{12}H_{17}Cl_3O$: C, 50.79; H, 5.99; Cl, 37.56. Found: C, 50.61; H, 5.61; Cl, 37.86.

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Macrocyclic Diphosphines. Synthesis and Stereoisomerism

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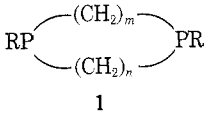
The synthesis of macrocyclic diphosphines is described. Diisopropyl polymethylenediphosphinates were obtained from Michaelis-Arbuzov reaction of diisopropyl phenylphosphonite and polymethylene dibromides. Subsequent reaction of diisopropyl polymethylenediphosphinate with polymethylene dibromide in the presence of sodium bis(2-methoxyethoxy)aluminum hydride under high dilution condition afforded two isomeric macrocyclic bis(phosphine oxides). The relative stereochemistry of the two isomers was established on the basis of their molecular dipole moments. Reduction of the macrocyclic bis(phosphine oxides) with trichlorosilane yielded the diphosphines with overall configuration retenton.

Recently, the syntheses of a number of macrocyclic compounds have been reported. To name a few, there are the macrocyclic polyethers,[1] the macrobicyclic diamines,[2] the macrobicyclic polyoxadiamines,[3] and the polyether sulfides.[4] These synthetic macrocycles typically contain rings or central cavities edged with electronegative binding atoms. They usually exhibit interesting ion-capture and conformational properties. In light of this, the chemistry of macrocyclic polyphosphines should be of potential interest because of the known versatility of phosphines as ligands for transition metals.[5] This paper reports the preparation of polymethylenediphosphines of general structures 1 with m, n > 8, hoping that they might serve as interesting complexing agents on one hand, and as models for stereochemical study on the other hand.



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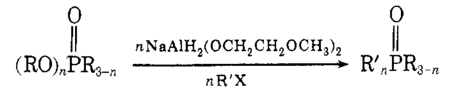
To date, of the cyclic tertiary diphosphines it appears that only 1,4-disubstituted diethylenediphosphines (1, m = n = 2) have been synthesized.[6,7] No investigation on the macrocyclic diphosphine has been reported. This may be due to the inherent difficulty associated with the synthesis of macrocyclic system. In general, the major problem encountered in macrocyclic synthesis is polymerization, arising from the predominance of intermolecular reaction over intramolecular cyclization. While this difficulty can usually be overcome by a high dilution condition, another problem arises as to the efficacy of a particular reaction at high dilution. The latter restriction can sometimes preclude the possibility of obtaining the macrocyclic system by this approach. With these in mind, we feel that, of the many methods of forming carbon-phosphorus bond,[8] the recently reported[9] reaction of phosphorus ester and alkyl halide in the presence of sodium bis(2-methoxyethoxy)aluminum hydride[10] (reaction 1) is the



$$(RO)_nPR_{3-n}\xrightarrow[nR'X]{nNaAlH_2(OCH_2CH_2OCH_3)_2}R'_nPR_{3-n}\qquad(1)$$

most appealing. The reaction has been reported to proceed under mild conditions. It is usually carried out under homogenous condition and is therefore amenable to high dilution.

We envisage therefore the synthesis of macrocyclic diphosphines according to Scheme I. The first step involves Michaelis-Arbuzov reaction of dialkyl phenylphosphonite and polymethylene dibromide and is patterned after our synthesis of linear polymethylene diphosphines.[11]

Scheme I