Noncatalytic Chlorination of Diphenyl Ether

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The chlorination of diphenyl ether employing conventional chlorination catalysts proceeds by well-established aromatic electrophilic substitution rules, i.e., chlorine substitution at the ortho and para positions relative to the phenoxy substituent. Furthermore, the presence of a chloro substituent deactivates the ring toward further electrophilic substitution, and one would anticipate the predominant dichlorodiphenyl ether isomers to contain one chloro substituent on each ring. Chlorination with equimolar quantities of chlorine in the absence of catalyst gave a totally unexpected product mixture. The most striking anomaly was a preponderance of 2,4-dichlorodiphenyl ether (GC analysis) over the anticipated other dichlorinated species. It has been established that the 2,4-dichlorodiphenyl ether is a GC thermally decomposed artifact of phenyl 3,4,5,6-tetrachloro-1-cyclohexen-1-yl ether, a tetrachloro adduct of diphenyl ether. Although the tetrachloro adduct was too unstable to permit isolation and characterization, the spectral data and chemical reactions of the adduct srongly support the proposed structure. Higher molecular weight products (tar) are the results of the facile alkylation properties of the tetrachloro adduct.

Although numerous references describe the chlorination of diphenyl ether,[2-9] only a few give detailed product distribution data. For example, Brewster[9] showed that the equimolar chlorination of diphenyl ether in acetic acid yielded primarily 4-chlorodiphenyl ether and further chlorination gave mixtures of 4,4′-dichlorodiphenyl ether and 3,4′-dichlorodiphenyl ether. Sloane and Bradley[8] reported that neat chlorination of diphenyl ether produced monochlorodiphenyl ethers with a para/ortho ratio of 11. The dichlorinated phenyl ethers were not identified. Weingarten and Schisla[6] chlorinated diphenyl ether, 2-chlorodiphenyl ether, and 4-chlorodiphenyl ether in acetic acid and carbon tetrachloride in the presence and absence of metal halide catalysts. Their results indicated that 4-chlorodiphenyl ether is the predominate product from the chlorination of diphenyl ether at 33% conversion. No mention is made of any dichlorinated species. The chlorination of 2- and 4-chlorodiphenyl ether produced only 2- and 4-substituted products, and there was no indication of the previously reported 3,4′-dichlorodiphenyl ether.[9] They did, however, obtain minor amounts of 2,4-dichlorodiphenyl ether, an unexpected product.

Results

We wish to report the results concerning the neat noncatalytic chlorination of diphenyl ether at greater than 30% conversions to show the formation of an unusual nonaromatic product.

The chlorination of diphenyl ether at room temperature would be expected to follow normal electrophilic substitution

Scheme I

rules (Scheme I), i.e., substituion at the 2 and 4 positions. The introduction of chlorine in one of the phenyl rings would not significantly deactivate the unsubstitued phenyl ring; therefore bis(chlorophenyl) ethers would be readily obtained.

The catalytic chlorination of diphenyl ether did indeed yield the anticipated products as illustrated in Figure 1. All product compositions were determined by GC (internal standard) and are expressed in weight percent.

An entirely different reaction profile is observed when diphenyl ether is chlorinated in the absence of a catalyst at room temperature. This product was also analyzed via GC (internal standard), and the reaction profile is illustrated in Figure 2. 2,4-Dichlorodiphenyl ether (7) appears to form very early in
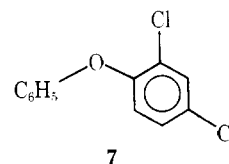

the reaction and accounts for the majority of the dichlorinated species. Formation of 7 ceases after the extinction of diphenyl ether. Also, a large amount of "unaccountables" is formed, i.e., components that do not elute from the GC but are measured by difference between accounted material and 100%. The 4-Cl/2-Cl ratio is greater than 10, and 2,4,4′-trichlorodiphenyl ether also appears to form early in the reaction. Table I further illustrates the product distribution differences between the catalyzed and noncatalyzed reactions.

It was initially presumed that 2,4-dichlorodiphenyl ether was formed by the chlorination of monochlorodiphenyl ether. However, the chlorination of 2- and 4-chlorodiphenyl ether produced less than 0.5% 2,4-dichlorodiphenyl ether (7). Therefore, 7 cannot be formed from diphenyl ether by an aromatic substitution reaction. The fact that the amount of 7 does not increase after the extinction of diphenyl ether adds further evidence to this conclusion.

The key to the formation of 7 is found in the proton NMR spectrum (T-60, CDCl$_3$) of the crude reaction product (Figure 3). In addition to the expected aromatic protons (6.5–7.2 ppm), there are nonaromatic protons appearing as a doublet at 4.73 ppm and as a complex multiplet at 4.20–4.58 ppm. Integration at 4.73 ppm indicates one proton compared to four protons in the 4.20–4.58 ppm region.

Various attempts were made to isolate the nonaromatic product by column chromatography. Aluminas (basic, neutral, acidic) with Brockman activities of I–IV, Florisil, and silica gel caused the product to decompose. However, the nonaromatic product was enriched to about 50% purity by passage through a falling film still (toluene, 2–3 mm). The IR spectrum
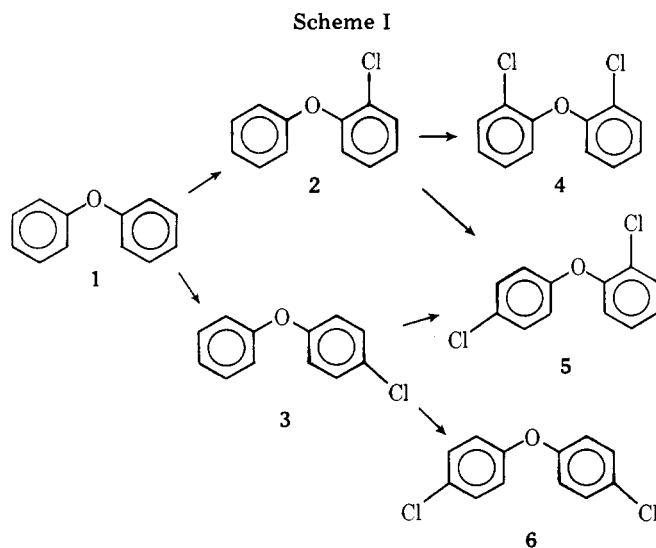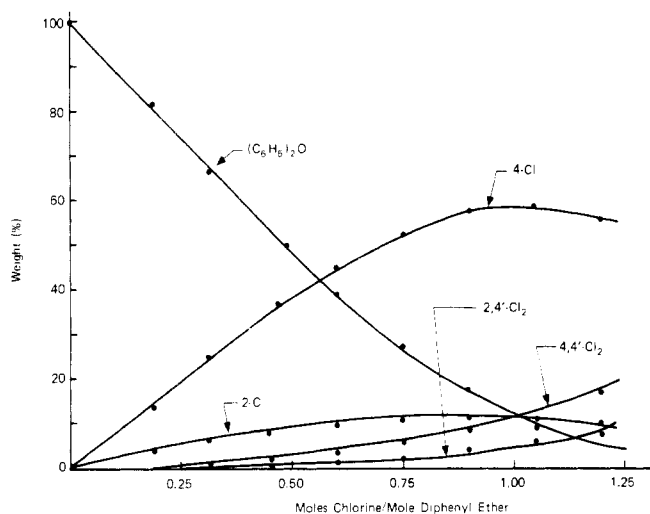
Figure 1. Reaction profile of the stannic chloride catalyzed chlorination of diphenyl ether.
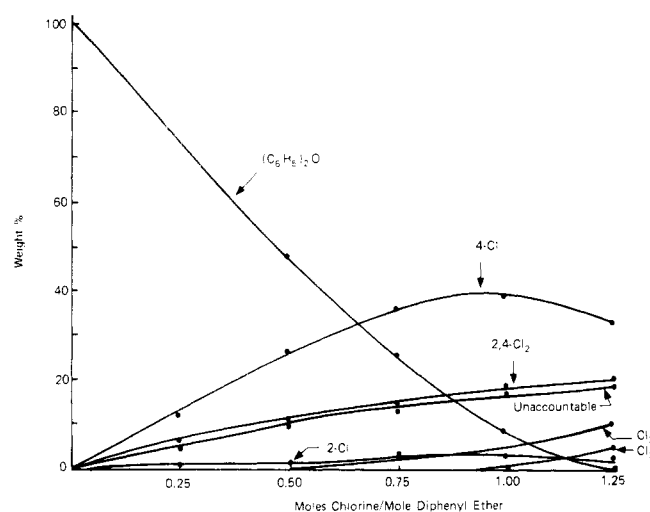

Figure 2. Reaction profile of the noncatalyzed chlorination of diphenyl ether.

Table I. Chlorination of Diphenyl Ether with ~1 equiv of Chlorine

component[a]	registry no.	catalyzed	noncata-lyzed
diphenyl ether	101-84-8	17.8	9.9
2-chlorodiphenyl ether	2689-07-8	11.6	3.0
4-chlorodiphenyl ether	7005-72-3	57.2	39.8
3,5-dichlorodiphenyl ether	24910-68-7	0.0	1.7
2,4-dichlorodiphenyl ether	51892-26-3	0.3	19.1
2,2'-dichlorodiphenyl ether	7024-98-8	0.2	0.0
2,4'-dichlorodiphenyl ether	6903-65-7	3.7	1.6
4,4'-dichlorodiphenyl ether	2444-89-5	8.4	3.9
2,4,4'-trichlorodiphenyl ether	59039-21-3	0.0	2.6
unaccounted		0.2	16.9

[a] Weight percent.

(film) had absorbances at 2960 and 2980 cm^{-1}, representing aliphatic carbon–hydrogen stretching frequency. In addition, the ^{13}C NMR spectrum (Jeol FX-60, acetone) had four peaks of equal intensity at chemical shifts of 63.0, 61.2, 58,6, and 57.1 ppm.

The above spectral data strongly support the structure of the nonaromatic product as phenyl 3,4,5,6-tetrachloro-1-cylcohexen-1-yl ether (8). Based on the integration of the
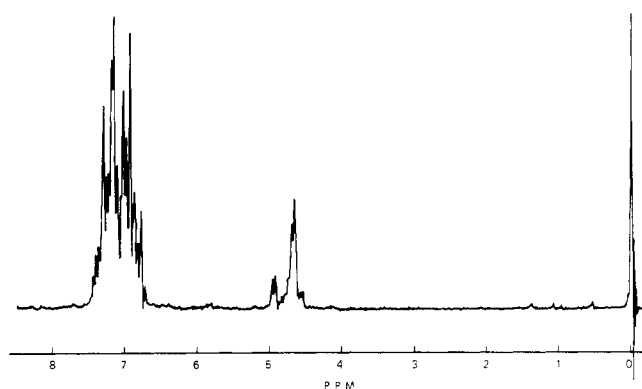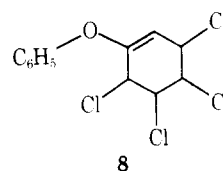

**Figure 3.** Proton NMR spectrum of the crude reaction mixture from the noncatalyzed chlorination of diphenyl ether.

8

nonaromatic and aromatic protons in the NMR, 8 is formed in about 35% yield. Structure 8 is clearly consistent with all of the spectral data. Compound 8, however, is decomposed to 2,4-dichlorodiphenyl ether (7) during the GC analysis. Thus, 7 is actually an analytical artifact of 8.

To determine with certainty that 8 was decomposing to 2,4-dichlorodiphenyl ether (7) during the GC analyses, a large amount of crude chlorinated phenyl ether was thermally decomposed (30–275 °C for 5 h). Copious hydrogen chloride evolution was observed between 100 and 150 °C. The product of the thermal treatment was void of nonaromatic protons (NMR) and contained 20.0% 7 (GC). Careful distillation of this sample permitted the isolation of 58% of the amount of 7 present (98% pure via GC). This fraction had identical IR and NMR spectra with an authentic sample prepared by the reaction of potassium 2,4-dichlorophenate and bromobenzene.

Additional data were obtained from the decomposition of enriched 8. A crude product containing ~35% 8 was decomposed isothermally at 150 °C (neat) and chemically at room temperature with pyridine and sodium ethoxide in ethanol. Analysis (GC) after the disappearance of nonaromatic proton absorption indicated that the predominate product was 7.


8
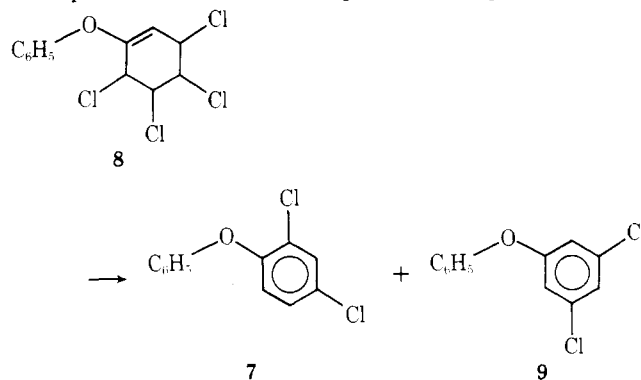
7 **9**

Small amounts of 3,5-dichlorodiphenyl ether (9) were also formed. 2,5-Dichlorodiphenyl ether was absent, and trace quantities, at best, of 3,4-dichlorodiphenyl ether were detected. It appears, therefore, that the predominant product is 7 with minor amounts of 9 formed by either an E1 or an E2 elimination. The formation of 7 and 9 adds further proof to structure 8 because structural isomers of 8 would not yield both 7 and 9.

Products similar to **8** were also formed in the chlorination of 2-, 3-, and 4-chlorodiphenyl ethers as indicated by NMR; however, complete characterization was not attempted. The tetrachloro adducts of 2- and 4-chlorodiphenyl ethers decompose during GC analyses to 2,2',4- and 2,4,4'-trichlorodiphenyl ethers, respectively. The products from the chlorination of 3-chlorodiphenyl ether were not identified due to the lack of analytical standards, but two trichlorodiphenyl ethers were formed based on GC retention times. An attempt to extend this reaction to 4,4'-dichlorodiphenyl ether was not successful. This chemical is inert to chlorine under the normal reaction conditions of this study.

Discussion

The mechanism of the formation of **8** appears to be an electrophilic addition rather than a free-radical process. Reaction conditions were mild, and in general free-radical chlorination of aromatic compounds produces completely saturated products.[10] The reaction was insensitive to the presence or absence of light.

We propose that the major mechanistic pathway is the 1,2 addition of chlorine to the 3 and 4 positions of diphenyl ether to yield **10** followed by a 1,4 addition to the 2 and 5 positions to produce **8**.
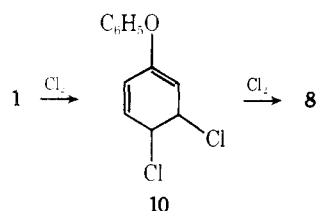

Initial 1,4 addition of chlorine at either the 2,5 or the 1,4 positions would yield a 1,4-cyclohexadiene. Further chlorination of the cyclohexadiene derived from the 2,5 addition to yield **8** would require complete inertness of the double bond adjacent to the phenoxy group to chlorine addition. The 1,4 addition to the 1,4 positions would produce an α-chloro ether, an intermediate incapable of forming **8**. The 1,2-chlorine addition to the 1,2 positions would also form an α-chloro ether intermediate. Therefore, the proposed sequence is the only rational path to **8**. The initial 1,2 addition can be either cis or trans. Beavin et al.[11] proposed the initial 1,2-chlorine addition to biphenyl as cis. Recently, Heasley et al.[12] have shown that 1,2 addition of chlorine to conjugated cyclodienes is primarily trans. Certainly, the diphenyl ether structure is more closely related to biphenyl than to a conjugated cyclodiene and one would anticipate a cis-1,2 addition to diphenyl ether, also.

The second mole of chlorine is proposed to proceed primarily by a cis-1,4 addition. Fairly extensive prior work has established that bromination gives almost exclusively cis-1,4 addition to 1,3-cyclohexadiene,[13] and the primary 1,4-chlorine addition is also cis.[12]

Without any direct experimental evidence to confirm which possible stereoisomer of the diphenyl ether tetrachloro adduct (**8**) is predominant, and hence the course of the reaction, we have proposed the scheme that agrees best with the published literature. However, it must be recognized that the aromatization of biphenyl tetrachloro adduct with sodium methoxide gave a mixture of 3,5- and 3,4-dichlorobiphenyl and only a trace of 2,4-dichlorobiphenyl.[11] The diphenyl ether tetrachloro adduct (**8**) gave almost exclusively 2,4-dichlorodiphenyl ether. Therefore, the stereostructures of the biphenyl and diphenyl ether tetrachloro adducts may differ.

The thermal decomposition of **7** from **8** should proceed by an E1 mechanism since no base is present.[14] Two allylic carbocations are possible intermediates. However, since the loss of a chloride anion adjacent to the phenoxy group cannot lead to **7**, the first dehydrochlorination is specific.
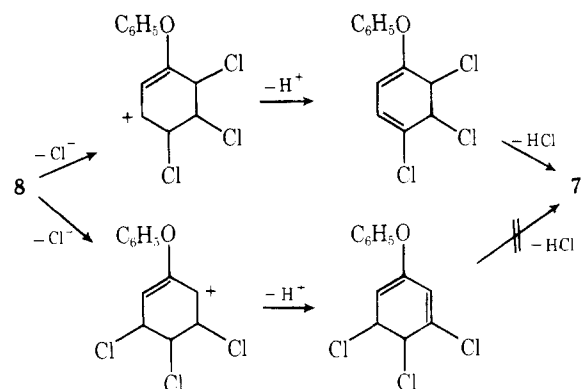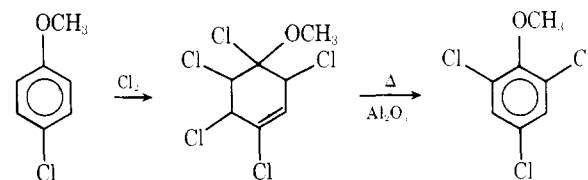

The proposed chlorination intermediates, dehydrochlorination intermediates, and the tetrachloro adduct itself account for the relatively large amounts of high molecular weight products that do not elute during the GC analysis. These structures are reactive alkylation reagents. Direct probe mass spectrometry of the thermally decomposed products verifies the presence of compounds represented by the general structure **11**.

11, $X = 2, 3, 4$
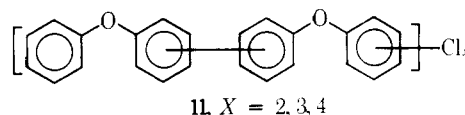
The formation of unusual nonaromatic products from the halogenation of aromatic compounds has been the subject of a recent review.[15] The chlorination of ethers such as 3,4-dimethylanisole yielded cyclohexenones **12** and **13**.[16] No such
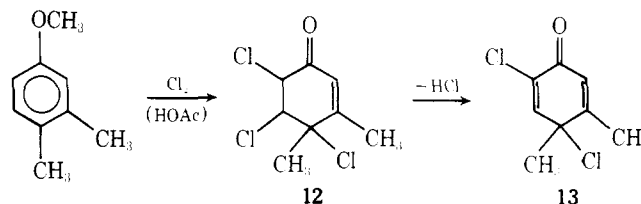
keto products were detected in the diphenyl ether chlorination. The only work related to this subject was the neat chlorination of 4-chloroanisole, which gave 1,3,4,5,6-penta-

chloro-4-methoxycyclohexene in 35% yield.[17] The reason for the structural differences of the 4-chloroanisole and the diphenyl ether chlorinations is not known. There must, however, be obvious similarities since both compounds gave tetrachloro adducts in reasonable yields.

Experimental Section

General. The GC analyses of the chlorinated diphenyl ethers were determined with a Hewlett Packard 5750 dual column chromatograph equipped with a thermal conductivity detector. The column used was 20 ft × 0.125 in. o.d. packed with 8% apiezon L and 8% FFAP mixed on Gas Chrom Q (60–80 mesh). Operating conditions were 275 °C isothermal, He flow of 30–40 mL/min, and 1,2-diphenylethane as an internal standard. Analytical standards of chlorinated diphenyl ether were prepared in high purity. The chromatographic data were analyzed on a Varian chromatograph data system 240 L using the appropriate computer programs. The elution order and times(s) are the following: diphenyl ether, 555; 1,2-diphenylethane, 800; 2-chlorodiphenyl ether, 936; 3-chlorodiphenyl ether, 936; 4-chlorodiphenyl ether, 1008; 3,5-dichlorodiphenyl ether, 1348; 2,5-dichlorodiphenyl ether, 1400; 2,4-dichlorodiphenyl ether, 1524; 2,2'-dichlorodiphenyl ether, 1579; 2,4'-dichlorodiphenyl ether, 1709; 3,4-dichlorodiphenyl

ether, 1709; 4,4'-dichlorodiphenyl ether, 1898; 2,4,2'-trichlorodiphenyl ether, 2650; and 2,4,4'-trichlorodiphenyl ether, 2863.

Infrared spectra were determined on a Perkin-Elmer 457 grating spectrophotometer and proton NMR on a Varian T-60.

Technical grade diphenyl ether (>99%, The Dow Chemical Co.) and chlorine (99.5%, Matheson Corp.) were used.

Catalytic Chlorination of Diphenyl Ether. A mixture of diphenyl ether (340.2 g, 2.00 mol) and stannic chloride (0.68 g, 2.6 mmol) was heated to 70 ± 1 °C, and chlorine (130 g, 1.83 mol) was sparged into the mixture for 3.0 h. Samples were withdrawn and analyzed every 0.5 h. The results are plotted in Figure 1 and tabulated in Table I.

Noncatalytic Chlorination of Diphenyl Ether. Diphenyl ether (17.02 g, 0.10 mol) was chlorinated at 25 ± 5 °C with chlorine (8.9 g, 0.25 mol) sparged in during 2.5 h. Samples were withdrawn every 0.5 h for GC analysis. The results are plotted in Figure 2 and tabulated in Table I.

Noncatalytic Chlorination of 2-Chlorophenyl Ether. 2-Chlorodiphenyl ether (20.45 g, 0.100 mol) was chlorinated with chlorine (8.9 g, 0.125 mol) at 30 ± 5 °C for 2.5 h. The final product (26.7 g) was analyzed via GC. The composition (wt %) was the following: 2-chlorodiphenyl ether. 6.5; 2,4-dichlorodiphenyl ether, 0.5; 2,2'-dichlorodiphenyl ether, 2.5; 2,4'-dichlorodiphenyl ether, 33.1; 2,4,2'-trichlorodiphenyl ether, 23.6; 2,4,4'-trichlorodiphenyl ether, 2.0; eluting but not identified, 4.4; unaccounted, 27.3. NMR (T-60, benzene-d_6) showed a complex aromatic multiplet at 6.2–7.35 ppm and a complex nonaromatic multiplet at 4.2–4.7 ppm. Integration of the protons showed ∼31.6% of a nonaromatic product.

Noncatalytic Chlorination of 3-Chlorodiphenyl Ether. 3-Chlorodiphenyl ether (20.45 g, 0.100 mol) was chlorinated with chlorine (8.9 g, 0.125 mol) at 30 ± 5 °C for 2.5 h. The final product (26.7 g) was analyzed by GC. However, no standards were available, so the isomer content was done by elution time and factors were assumed based on previous samples. The composition (wt %) was the following: 3-chlorodiphenyl ether, 6.1; dichlorodiphenyl ethers (four isomers), 40.4; trichlorodiphenyl ethers, 22.9; others eluting, 3.1; unaccounted, 14.9. The NMR (T-60, benzene-d_6) showed complex aromatic and nonaromatic multiplets at 6.2–7.3 and 4.2–4.8 ppm, respectively. Integration of the protons showed that ∼25.7% of a nonaromatic product was produced.

Noncatalytic Chlorination of 4-Chlorodiphenyl Ether. 4-Chlorodiphenyl ether (20.45 g, 0.100 mol) was chlorinated with chlorine (8.9 g, 0.125 mol) at 30 ± 5 °C for 2.5 h. The final product (27.5 g) was analyzed by GC. The composition (wt %) showed the following: 4-chlorodiphenyl ether, 5.8; 2,4-dichlorodiphenyl ether, 0.2; 2,4'-dichlorodiphenyl ether, 1.9; 4,4'-dichlorodiphenyl ether, 29.5; 2,4,4'-trichlorodiphenyl ether, 34.2; others eluting, 5.8; unaccounted, 22.3. NMR (T-60, benzene-d_6) showed complex aromatic and nonaromatic multiplets at 6.35–7.3 and 4.2–4.8 ppm, respectively. Integration of the protons showed that ∼38.0% of the nonaromatic product was produced.

Thermal Decomposition of Crude Noncatalyzed Chlorinated Diphenyl Ether. Crude noncatalyzed chlorinated diphenyl ether (862.8 g) was slowly heated from room temperature to 275 °C during a 5-h period. Hydrogen chloride evolution began at 100 °C and essentially ceased during the heating period. The final product weight of 827 g represented a hydrogen chloride loss of 0.98 mol or the formation of ∼13.5% of 7. Analyses (GC) prior to and after the heat treatment indicated the following change in composition (wt %): diphenyl ether, 35.7, 38.7; 2-chlorodiphenyl ether, 2.9, 2.8; 4-chlorodiphenyl ether, 26.2, 27.3; 3,5-dichlorodiphenyl ether, 0.2, 0.1; 2,4-dichlorodiphenyl ether, 14.8, 20.0; 2,4'-dichlorodiphenyl ether, 1.2, 0.5; 4,4'-dichlorodiphenyl ether, 1.9, 2.7; unaccounted, 16.8, 7.8.

The crude thermally decomposed product was distilled in a 30 plate Oldershaw column. Diphenyl ether and monochlorodiphenyl ethers were removed at a 5–10:1 reflux ratio. The 2,4-dichlorodiphenyl ether (95.6 g, 58% recovery) was collected at a 20:1 reflux ratio, bp 200–202 °C (50 mm). The IR spectrum (carbon tetrachloride) showed major absorbances at 6.25, 6.30, 6.70, 6.80, 8.00, 8.36, 9.12, 9.50, 11.52, 12.00, 14.50, and 15.18 μm. The NMR (carbon tetrachloride) had complex splitting at 6.70–7.38 ppm. These spectral properties were identical with authentic 2,4-dichlorodiphenyl ether synthesized from the reaction of potassium 2,4-dichlorophenate and bromobenzene.

Thermal and Chemical Dehydrochlorinations of Enriched Diphenyl Ether Tetrachloro Adduct. Crude noncatalyzed chlorinated diphenyl ether was subjected to a falling film distillation (toluene, bp 110 °C, 2–3 mm). The diphenyl ether tetrachloro adduct, which was enriched to ∼50% by this operation, served as starting material for experiments A and B.

A. Thermal. Material enriched in the tetrachloro adduct (2.00 g) was heated at 150 °C for 24 h. No evidence of aliphatic proton absorption was observed in the NMR spectrum. GC analysis of the product (1.84 g, a light yellow oil) indicated the following composition (wt %): diphenyl ether, 1.1; 2-chlorodiphenyl ether, 2.8; 4-chlorodiphenyl ether, 34.9; 3,5-dichlorodiphenyl ether, 2.2; 2,4-dichlorodiphenyl ether, 25.6; 2,4'-dichlorodiphenyl ether, 0.9; 4,4'-dichlorodiphenyl ether, 9.4; trichlorodiphenyl ether, 9.4; unaccounted, 11.4.

B. Pyridine. The same distilled diphenyl ether (1.00 g) and 10 g of pyridine were heated at 50 °C for 24 h. Removal of pyridine by evaporation under diminished pressure left a semisolid residue which was mixed with benzene. Undissolved solid residue (pyridine hydrochloride) was removed by filtration, and the benzene was removed by evaporation. The proton NMR spectrum of the residue indicated that aliphatic protons were still present. Another treatment with fresh pyridine (10 g) and the same isolation technique yielded 0.83 g of a liquid product with no aliphatic proton absorption. GC analysis indicated the following composition (wt %): diphenyl ether, 7.7; 2-chlorodiphenyl ether, 3.4; 4-chlorodiphenyl ether, 42.0; 3,5-dichlorodiphenyl ether, 1.8; 2,4-dichlorodiphenyl ether, 15.4; 2,4'-dichlorodiphenyl ether, 1.9; 4,4'-dichlorodiphenyl ether, 6.1; 2,4,4'-trichlorodiphenyl ether, 2.8; unaccounted, 17.0.

C. Sodium Ethoxide. Crude noncatalyzed chlorinated diphenyl ether (1.00 g) was mixed with 5 mL of absolute ethanol. The addition of 0.707 g of 20.4% sodium ethoxide in absolute ethanol caused an immediate color change (green) and precipitation of a white solid. After standing for 4.5 h at room temperature, the precipitate (0.10 g of NaCl) was removed by filtration. The filtrate was evaporated to dryness. The residue (yellow liquid, 0.96 g) had some small extraneous absorbances in the proton NMR spectrum, indicating a small degree of reaction other than dehydrochlorination. The GC also had a number of minor small peaks not characteristic of the previous reactions. The identified peaks were (wt %) as follows: diphenyl ether, 1.9; 2-chlorodiphenyl ether, 2.4; 4-chlorodiphenyl ether, 34.5; 3,5-dichlorodiphenyl ether, 1.7; 2,4-dichlorodiphenyl ether, 10.6; 2,4'-dichlorodiphenyl ether, 1.6; 4,4'-dichlorodiphenyl ether, 10.9; 2,4,4'-trichlorodiphenyl ether, 5.3.

Preparation of 2,4-Dichlorodiphenyl Ether. To a stirred mixture of 94.2 g (0.60 mol) of bromobenzene, 2 g of copper powder, and 200 mL of dimethylformamide was added 92.5 g (0.50 mol) of potassium 2,4-dichlorophenate. The mixture was stirred and heated at the reflux temperature for 16 h, cooled, and poured into ice water. The mixture was extracted with toluene. The toluene was removed by distillation, and the product was purified by fractional distillation to obtain 30.0 g (29%) of 2,4-dichlorodiphenyl ether: bp 116–124 °C (0.8 mm); n^{25}_D 1.5983 (lit.[18] n^{25}_D 1.5892).

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