$C_6H_5F_3N_2O$ 178.0355, found 178.0352. Anal. Calcd for $C_6H_5F_3N_2O$: C, 40.46; H, 2.83; N, 15.73. Found: C, 40.62; H, 2.79; N, 15.98.

A solution of 3.927 g (0.0255 mol) of **1b** and 2.256 g (0.0537 mol) cyanamide in 20 mL of water was allowed to stand at room temperature for 7 days. The crystals which had formed were filtered, giving 3.049 g (68%)[3] of **3b**: mp 119–123 °C (lit.[13] mp 128 °C); NMR ($CDCl_3$) 2.4 (s, 3, CH_3), 5.3–6.0 (s, 2, NH_2), 6.6 ppm (s, 1, CH); IR 3320–3400 (br, NH_2), 3220 (NH_2), 1640 cm^{-1}; MS, M_r calcd for $C_6H_6F_3N_3$ 177.0515, found 177.0514. A 2% yield of **5b**, mp 189–191 °C, was also obtained from this run.

When the same reaction was run with 7.852 g (0.051 mol) of **1b** and 2.250 g (0.0536 mol) of cyanamide in 20 mL of water, 4.892 g of very sticky yellow solid, mp 89–140 °C, was obtained; a second crop of pale yellow crystals, 0.730 g, mp 176–186 °C, was obtained. Several recrystallizations of these solids from ethyl acetate gave 0.749 g of shiny needles, mp 187–191 °C, which were identical (IR, mmp) with **5b** described above. TLC's of the original solid and the residues from recrystallization showed the only major components of the mixture to be **3b** and **5b**.

Cyanamide and 1,1,1-Trifluoro-5-methyl-2,4-hexanedione (1c). A solution of 4.604 g (0.025 mol) of **1c** and 1.145 g (0.027 mol) of cyanamide in 17 mL of methanol was allowed to stand for 8 days at room temperature. The methanol was removed under reduced pressure and, after 1 day, a solid formed. Filtration gave 1.382 g (25%) of 4-(trifluoromethyl)-2-hydroxy-6-isopropylpyrimidine: mp 180–192 °C; recrystallized to analytic purity from methanol, mp 191–191.5 °C; NMR (Me_2SO-d_6) 1.2 (d (J = 7 Hz), 6, CH_3), 2.9 (equintet (J = 7 Hz), 1, CH); IR (KBr) 2500–3300 (br, OH), 1640 cm^{-1}; MS, M_r calcd for $C_8H_9F_3N_2O$: 206.0668, found 206.0656. Anal. Calcd for $C_8H_9F_3N_2O$: C, 46.60; H, 4.40; N, 13.59. Found: C, 46.59; H, 4.17; N, 13.74.

Registry No. **1a**, 123-54-6; **1b**, 367-57-7; **1c**, 30984-28-2; **1d**, 93-91-4; **2a**, 91606-59-6; **3a**, 767-15-7; **3b**, 5734-63-4; **3d**, 15755-15-4; **4**, 1118-66-7; **5a**, 108-79-2; **5b**, 91606-60-9; **5c**, 91606-61-0; **6a**, 91606-62-1; $NCNH_2$, 420-04-2; NH_4OH, 1336-21-6; 1,3-cyclohexanedione, 504-02-9.

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X-ray Crystallographic Structure Determination and Carbon-13 Nuclear Magnetic Resonance Spectrum of 2,2,3,4,5,6,6-Heptachloro-3-(2,3,4,5,6-pentachlorophenoxy)-4-cyclohexenone. An Intermediate in the Synthesis of Nonachloro-3-phenoxyphenol

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Analysis of technical pentachlorophenol (PCP) shows the presence of numerous chlorinated byproducts which arise in the manufacturing process.[1] The potential health hazards from exposure to these chemicals is of some concern. It has been shown, for example, that nonachloro-3-phenoxyphenol, a manufacturing byproduct of PCP,[2] has a hemolytic potency at least a hundred times greater than

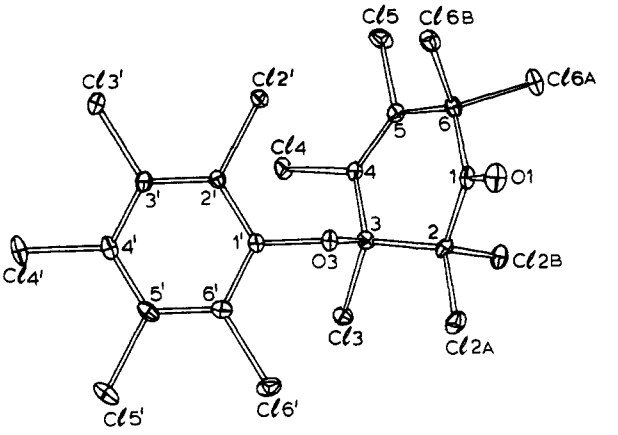

Figure 1. Conformational representation of 2,2,3,4,5,6,6-heptachloro-3-(2,3,4,5,6-pentachlorophenoxy)-4-cyclohexenone (I).

that of PCP.[3] In the synthesis of this contaminant[4] polychlorinated dienone and enone intermediates are produced which subsequently are reduced with sodium iodide to nonachloro-3-phenoxyphenol. Efforts to identify these intermediates depended chiefly on the use of ^{13}C NMR spectroscopy.[4] One of these intermediates, the title compound (I), (V in ref 4) whose structure was not reported, has since been determined by ^{13}C NMR and confirmed by X-ray crystallographic analysis. The results from these studies serve to support the assignments[4] made for the synthetic intermediates reported previously, as well as to provide the spectroscopic information to identify I, another potential contaminant in technical PCP.

Compound I has a molecular ion in the mass spectrum of m/z 596. It also has IR absorptions at 1771 cm^{-1} (carbonyl) and 1582 cm^{-1} (olefin) and a broad absorption around 1350 cm^{-1}. X-ray crystallographic analysis shows that like the crystal structure of the two independent rings of 2,3,4,5,6-pentachloro-4-(pentachlorophenoxy)-2,5-cyclohexadienone,[5] the phenoxy ring of I is planar with a root mean square deviation of the atoms from the plane of only 0.03 Å. The 4-cyclohexenone ring, however, has an envelope conformation with C2 displaced 0.68 Å from the plane formed by the remaining five atoms in the ring. The relative orientation of the two rings about the bonds linking them together is much different from that observed in cyclohexadienone structures. This is a consequence of having a puckered cyclohexenone ring in I rather than the planar cyclohexadienone ring (Figure 1). In the crystal structure of I the O3–C1′ bond is oriented transoid to the C3–Cl3 bond forming a torsion angle, Cl3–C3–O3–C1′, of −172.7°, while the corresponding angles, Cl1–C1–O1–C1′, in the two cyclohexadienone structures are −122.2° and 126.9°. Similarly, the C3–O3 bond is directed nearly perpendicular to the planar phenoxy ring forming torsion angles C3–O3–C1′–C2′ and C3–O3–C1′–C6′ or −92.4 and 94.6°. The corresponding cyclohexadienone torsion angles are C1–O1–C1′–C2 and C1–O1–C1′–C6′. In these two structures, the angles are −166.4° and −122.1° and 73.2° and 77.9°, showing the skewing away from the perpendicular orientation. These crystallographic results also confirm the spectroscopically assigned structure.

The carbon-13 NMR spectrum was obtained by dissolving I in deuteriochloroform. Unlike the enones re-

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Table I. ^{13}C NMR Chemical Shifts for 2,2,3,4,5,6,6-Heptachloro-3-(2,3,4,5,6-pentachlorophenoxy)-4-cyclohexenone (I)

carbon	shift, ppm	carbon	shift, ppm
1	178.87	6	87.51
2	105.80	1′	145.35[a]
3	145.31[a]	2′,6′	130.10
4	135.04	3′,5′	132.48
5	133.31	4′	132.92

[a] C3 and C1′ may be reversed.

ported previously,[4] I is not very soluble and spectra obtained even with 209 000 transients with 1-s acquisition times were poor. However, each peak was clearly visible and assignments could be made (Table I).

The downfield shift of 178.87 ppm was assigned to a carbonyl carbon (C1). Kepone, a hexachlorocyclopentadiene-based pesticide has a carbonyl carbon resonance of 190.87 ppm.[6] Increased shielding of C1 in the title compound by additional α-substitution with chlorine probably is responsible for the upfield shift.[7] The shifts at 145.31 ppm and 145.35 ppm were assigned to the phenyl ether (C1′) and the aliphatic ether (C3) carbons. The absence of a vinyl ether carbon resonance around 154 ppm, as previously observed for the conjugated enones,[4] is a significant difference in these spectra.

Chemical shifts for aromatic nuclei C3′ and C5′ at 132.48 ppm and C2′ and C6′ at 130.10 ppm were more intense than the rest of the signals as expected. A comparison with other compounds containing the pentachlorophenoxy moiety shows that C2′ and C6′ resonances are considerably affected by electron-withdrawing groups through the ether linkage. The C3′, C5′ and C2′, C6′ resonances are 131.3 ppm and 123.9 ppm for decachlorodiphenyl ether,[7] 131.4 ppm and 124.5 ppm for nonachloro-3-phenoxyphenol,[4] and 131.4 and 126.3 ppm for 2,4,4,5,6,6-hexachloro-3-(pentachlorophenoxy)-2-cyclohexenone.[4]

The chlorinated olefinic carbons C4 and C5 were assigned resonances of 135.04 ppm and 133.31 ppm. Chlorinated olefinic resonances typically are found at a somewhat higher field, as, for example, 128.5 ppm and 132.8 ppm for hexachlorocyclopentadiene.[8] However, perturbations from the α chloro ether linkage (C3) should shift these resonances downfield.

A signal at 87.51 ppm is assigned to C6 on the basis of previous results.[4] This compares with a value of 73.92 ppm for the carbons α to the carbonyl of kepone with just one chlorine atom each.[6] Steric compressions in I probably causes the downfield shift.[7] The α carbons of 2,2,6,6-tetrachlorocyclohexanone and of 2,2-dichlorocyclohexanone are observed at 83.9 ppm and 88.5 ppm, respectively,[9] which tend to support our assignment. Finally C2 is found at 105.80 ppm. The effects of C3 and the carbonyl carbon C1 must be additive to produce the large downfield shift for C2.

Experimental Section

Gas chromatographic–mass spectrometric analyses were carried out on a Finnigan 4023 instrument. A Pyrex column (0.32 cm × 4.88 m) packed with 3% OV-101 on 80/100-mesh high performance Chromosorb W (Johns-Manville Co.) was used for separation. Carbon-13 NMR spectra were obtained on a Varian CFT-80 spectrometer. Infrared measurements were made on a Perkin-Elmer 457 instrument. Melting points were determined on a Fisher-Jones melting point apparatus.

The synthesis and isolation of I has been described.[4] The product had a mp of 188–190 °C and a molecular ion cluster in the mass spectrum beginning at m/z 596.

X-ray Crystal Structure. Intensity data for this structure determination were measured on a computer-controlled diffractometer using $\theta/2\theta$ scans. The structure was solved by using the direct methods program MULTAN[10] in conjunction with the NQEST figure of merit program.[11] Refinement of the coordinates of all atoms, anisotropic thermal parameters of the non-hydrogens, and isotropic thermal parameters for the hydrogens using a full-matrix least-squares procedure was based on F with weights based on $1/\sigma^2F$.

Crystal Data. 2,4,4,5,5,6,6-Heptachloro-3-(2,3,4,5,6-pentachlorophenoxy)-4-cyclohexenone, $C_{12}O_2Cl_{12}$, has M_r 601.6, triclinic space group $P\bar{1}$, a = 11.293 (3) Å, b = 12.601 (3) Å, c = 8.340 (2) Å, α = 109.69 (3)°, β = 107.44 (2)° γ = 108.67 (2)°, z = 2, d_c = 2.125 g cm^{-3}, μ(Mo Kα) = 17.56. cm^{-1}, and R = 0.047 for 5109 observed data ($F > 6\sigma_F$) to a $2\theta_{max}$ of 60° using Mo Kα radiation (γ = 0.71069 Å) on a Syntex P_3 diffractometer at lquid N_2 temperature, 90 (4) K, yielding 5522 independent data. The final positional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table II.

Table II. Atomic Coordinates (×10^5) and Equivalent Isotropic Thermal Parameters (×10^2)[a] for I

	x	y	z	B_{iso}
C(1)	128491 (23)	43451 (21)	49877 (33)	103 (7)
C(2)	118767 (24)	37555 (20)	28291 (31)	94 (7)
C(3)	104212 (23)	26953 (20)	22957 (30)	88 (7)
C(4)	106111 (23)	17473 (20)	29550 (30)	82 (6)
C(5)	117923 (23)	20531 (20)	44355 (31)	91 (7)
C(6)	130014 (23)	33795 (21)	56906 (32)	101 (7)
O(1)	134708 (19)	54700 (16)	60466 (27)	155 (6)
O(3)	98649 (17)	34040 (15)	32691 (23)	89 (5)
Cl(2A)	116872 (6)	49467 (5)	23007 (9)	139 (2)
Cl(2B)	127060 (6)	30872 (5)	15790 (8)	120 (2)
Cl(3)	93883 (6)	18827 (5)	−2331 (7)	105 (2)
Cl(4)	92016 (6)	2555 (5)	18018 (8)	113 (2)
Cl(5)	119500 (6)	9406 (5)	50972 (9)	157 (2)
Cl(6A)	131461 (6)	39528 (6)	80428 (8)	135 (2)
Cl(6B)	146240 (6)	34054 (5)	58509 (9)	139 (2)
C(1′)	84842 (23)	27757 (20)	29434 (31)	85 (7)
C(2′)	73956 (25)	27264 (21)	15239 (31)	99 (7)
C(3′)	60068 (24)	20562 (21)	11562 (31)	108 (7)
C(4′)	57135 (23)	15057 (20)	22805 (31)	102 (7)
C(5′)	68174 (23)	16858 (21)	38345 (31)	97 (7)
C(6′)	82003 (23)	23160 (21)	41633 (30)	87 (7)
Cl(2′)	77701 (7)	35690 (6)	3371 (9)	151 (2)
Cl(3′)	46625 (6)	19248 (6)	−6766 (8)	166 (2)
Cl(4′)	40069 (6)	6523 (5)	17988 (9)	145 (2)
Cl(5′)	64752 (6)	11332 (6)	53533 (9)	143 (2)
Cl(6′)	95627 (6)	25941 (6)	61339 (8)	126 (2)

[a] $B_{iso} = {}^4/_3\Sigma_i\Sigma_j\beta_{ij}(a_i \cdot a_j)$. The esd's are given in parentheses.

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Effect of Amines on *O*-Benzyl Group Hydrogenolysis

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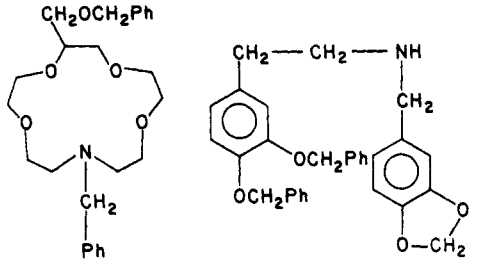
During a recent investigation of preparative routes to functionalized aza crown ethers,[1] we observed exclusive *N*-benzyl group cleavage when monoaza crown **1** reacted with hydrogen in the presence of palladium on activated carbon (Pd/C) catalyst. Since it is generally assumed that O-debenzylation takes place with greater ease than does removal of an *N*-benzyl group,[2,3] this result was totally unexpected. Also, selective cleavage of the *O*-benzyl groups in **2** and **3** has been reported.[4,5] To determine the causative factor for the unusual hydrogenolysis selectivity found with **1**, the present study was undertaken.



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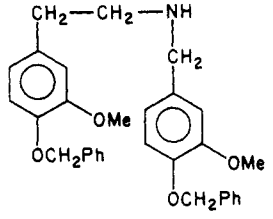

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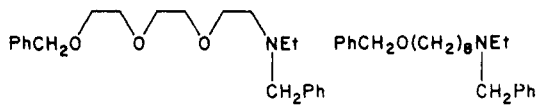
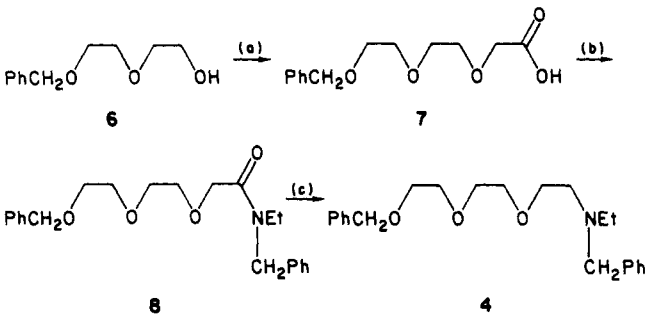
Initially it was thought that the cyclic structure and/or multiethereal linkages of aza crown **1** might be responsible for the unexpected debenzylation selectivity. Therefore, acyclic model compounds **4** and **5** were synthesized (Schemes I and II, respectively). When solutions of **4** and **5** in 95% ethanol were shaken with Pd/C catalyst under



4 **5**

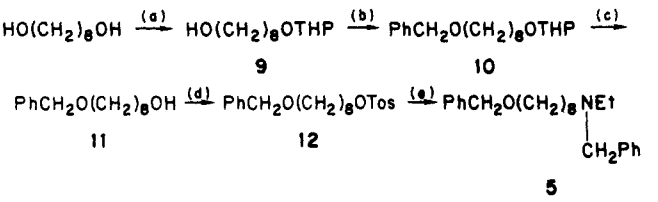
45 psi of hydrogen at room temperature for 20–24 h, only the corresponding products of N-debenzylation **13** and **14** were isolated in yields of 60% and 100%, respectively.

Scheme I[a]

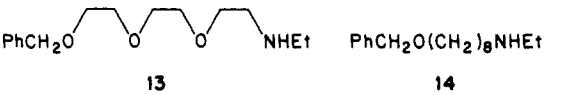


[a] (a) $ClCH_2CO_2H$, *t*-BuOK; (b) $SOCl_2$, then $PhCH_2NHEt$; (c) $LiAlH_4$.

Scheme II[a]



[a] (a) DHP, H^+; (b) $PhCH_2Br$, NaH; (c) H^+; (d) TosCl, pyridine; (e) $PhCH_2NHEt$, Na_2CO_3.



13 **14**

These results suggested that it was not the cyclic polyether structure but the presence of amine functions in **4** and **5** which was inhibiting O-debenzylation under conditions that provided complete cleavage of the *N*-benzyl groups.

To further probe the influence of amines upon potential O-debenzylation processes,[6] benzyl *n*-nonyl ether (**15**) was utilized as the model compound. When a solution of **15** in 95% ethanol was shaken with Pd/C catalyst under 45 psi of hydrogen at room temperature for 20–24 h, complete O-debenzylation was observed. However, when the reaction was conducted under the same conditions but in the presence of 5 mol % of *n*-butylamine or *N*-benzylethylamine, **15** was totally recovered. That such inhibition of O-debenzylation is confined to the more basic nonaromatic amines was established with pyridine. Under the standard conditions, complete cleavage of the *O*-benzyl group in **15** was found in the presence of 5 mol % or even an equimolar amount of pyridine.

The apparent contradiction between our results and the reported O-debenzylations of **2** and **3** which contain amine functions was resolved by studying the reaction of benzyl phenyl ether (**16**) with hydrogen under the standard conditions. In the presence of 5 mol % or 100 mol % of *n*-butylamine, the hydrogenation of **16** proceeded smoothly and gave a quantitative yield of phenol. Thus, the inhibition of O-debenzylation by nonaromatic amines does not extend from alkyl benzyl ethers to aryl benzyl ethers.

We next explored the synthetically attractive possibility that amines might be used to retain an *O*-benzyl group

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