Experimental Section

10-Chloro-9-phenanthrol and the chloro dimer **2** were prepared by the method of Müller, *et al.*[1]

10-Ethoxy-9-phenanthrol was prepared by a modification of the procedure of Forneau and Matti.[9]

A slurry of 45 g (0.217 mol) of phenanthrenequinone in a mixture of 375 ml of 95% ethanol and 45 ml of H_2O was stirred and heated to reflux. Then, with *vigorous* stirring and refluxing, SO_2 was passed into the reaction mixture for 8 hr, and the dark reddish-brown solution was filtered and cooled to −20° for several hours to crystallize the product. Additional material can be obtained by diluting the filtrate with 10–20 ml of H_2O and cooling overnight at −20°. *It is essential to protect the product from air*, as it is very easily oxidized, especially when impurities are present. It is best purified by several recrystallizations from warm 95% ethanol with rapid cooling to −20°, followed by crystallization from hexane and then again from ethanol. The product is colorless, mp 76–77°. The yield (of pure material) is 8–10 g.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.68; H, 5.88. Found: C, 80.62; H, 5.88.

The ethoxy dimer **3** was prepared using both Müller's procedure[1] and that of Goldschmidt,[10] the properties of the product being the same. Recrystallization from a mixture of chloroform and ethanol gave material melting at 137–138° and with less included solvent of crystallization than recrystallization from the solvent recommended previously.[1,10]

Equilibrium Studies.—All epr spectra were measured in degassed solutions in the same quartz sample tube. The output from the overmodulated first derivative signal was digitized using a Dymec digital voltmeter and a Hewlett-Packard digital recorder. The data were then transferred to punch cards and doubly integrated by means of DINGRT,[11] a program which includes automatic base-line correction after the first integration. The integrated absorptions were then converted to concentrations using a calibration curve based on galvinoxyl.

Registry No.—**3**, 35099-79-7; 10-ethoxy-9-phenanthrol, 35099-80-0.

Acknowledgment.—The authors wish to acknowledge support of this research by the Army Research Office (Durham) and by the National Science Foundation.

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[9] E. Forneau and J. Matti, *Bull. Soc. Chim. Fr.*, **9**, 633 (1942).

[10] S. Goldschmidt and C. Steigerwald, *Chem. Ber.*, **55**, 3197 (1922).

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The Induced Decomposition of *tert*-Butyl Peroxide by Ether Radicals. A Nuclear Magnetic Resonance Study

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An examination of the products of the decomposition of *tert*-butyl peroxide in 4-chlorobenzyl ethyl ether and 3,4-dichlorobenzyl phenyl ether shows that the formed mixed acetals of the type ArCH(OR)O-*t*-Bu partially decomposed. The formation of the mixed acetal PhCH(OMe)O-*t*-Bu in the decomposition of *tert*-butyl peroxide in benzyl methyl ether was found to be promoted in the presence of added chlorinated solvents. *o*-Dichlorobenzene was found to promote the induced decomposition of the peroxide by several ether radicals; the mixed acetal $CH_3CH(OEt)O$-*t*-Bu was also isolated from a reaction in diethyl ether.

Although for a long time it was commonly believed that *tert*-butyl peroxide is inert to radical-induced decomposition, a property which has made it superior to other organic peroxides, evidence recently obtained indicates that in a number of solvents induced decomposition does in fact occur.[1] In certain primary and secondary alcohols and amines Huyser[2,3] has reported that induced decomposition of the peroxide occurs by hydrogen transfer. In alkyl benzyl ethers $ArCH_2OR$, however, a direct attack of the ether radical on the peroxo linkage has been postulated.[4]

The present paper reports a further study of the reaction products of these systems by nmr spectroscopy and discusses the nature of the induced decomposition reaction.

Results and Discussion

α-Alkoxybenzyl radicals $Ar\dot{C}HOR$, generated by the decomposition of *tert*-butyl peroxide in alkyl benzyl ethers, are known to undergo the following reactions (eq 1–4). Earlier work[1] has shown that for the series

$$2Ar\dot{C}HOR \longrightarrow (Ar\overset{|}{C}HOR)_2 \quad (1)$$

$$Ar\dot{C}HOR \longrightarrow ArCHO + R\cdot \quad (2)$$

$$Ar\dot{C}HOR + t\text{-}Bu_2O_2 \longrightarrow ArCH(OR)O\text{-}t\text{-}Bu + t\text{-}BuO\cdot \quad (3)$$

$$Ar\dot{C}HOR + t\text{-}BuO\cdot \longrightarrow ArCH(OR)O\text{-}t\text{-}Bu \quad (4)$$

of ethers $PhCH_2OR$ (R = Me, Et, *i*-Pr, *t*-Bu, and Ph) the radical $Ph\dot{C}HOR$ only undergoes dimerization and fragmentation reactions (eq 1 and 2). However in chloro substituted benzyl ethers, $ClC_6H_4CH_2OR$ and $3,4\text{-}Cl_2C_6H_3CH_2OR$, kinetic results and the isolation of mixed acetals ArCH(OR)O-*t*-Bu have provided evidence for the induced decomposition and cross-dimerization pathways (eq 3 and 4).[4,5]

4-Chlorobenzyl Ethyl Ether.—In the decomposition of *tert*-butyl peroxide in several alkyl 3,4-dichlorobenzyl ethers it was found that 3,4-dichlorobenzaldehyde was produced in surprisingly high yields (44–88%).[1] Since this is much greater than that expected from simple radical fragmentation (*e.g.*, $Ph\dot{C}HOMe$ gives only 10% benzaldehyde), it was suspected that the aldehyde must have originated from another source.

An examination of the reaction products from the decomposition of *tert*-butyl peroxide in 4-chlorobenzyl ethyl ether by nmr spectroscopy revealed that in addition to the expected products, *viz.*, 4-chlorobenzaldehyde, the dimer $(4\text{-}ClC_6H_4\overset{|}{C}HOEt)_2$ and the mixed acetal $4\text{-}ClC_6H_4CH(OEt)O$-*t*-Bu, smaller quantities of 4-chlorobenzaldehyde diethyl acetal $4\text{-}ClC_6H_4CH$-

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[1] S. H. Goh, R. L. Huang, S. H. Ong, and I. Sieh, *J. Chem. Soc., C*, 2282 (1971).

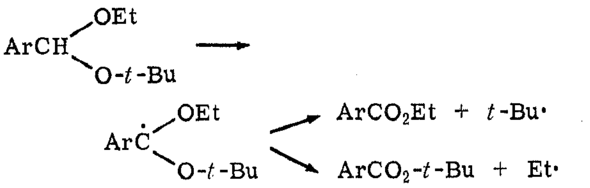
[2] E. S. Huyser and A. A. Kahl, *Chem. Commun.*, 1238 (1969).

[3] E. S. Huyser, C. J. Bredeweg, and R. M. Vanscoy, *J. Amer. Chem. Soc.*, **86**, 4148 (1964).

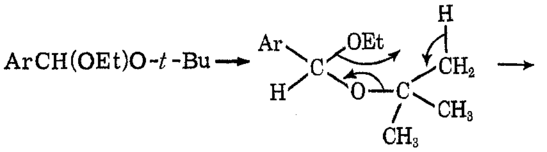
[4] R. L. Huang, T.-W. Lee, and S. H. Ong, *J. Chem. Soc., C*, 2522 (1969).

[5] S. H. Goh and S. H. Ong, *J. Chem. Soc., B*, 870 (1970).

$(OEt)_2$, ethyl 4-chlorobenzoate, *tert*-butyl 4-chlorobenzoate, and isobutylene were also formed. The esters are probably derived from the hydrogen abstraction of the mixed acetal[6] as shown.


(5)

Isobutylene and 4-chlorobenzaldehyde diethyl acetal were found to arise *via* the thermal decomposition of the mixed acetal probably by the following mechanism (eq 6 and 7).



$$ArCHO + EtOH + CH_2{=}C(CH_3)_2 \quad (6)$$

$$ArCH(OEt)O\text{-}t\text{-}Bu + EtOH \longrightarrow ArCH(OEt)_2 + t\text{-}BuOH \quad (7)$$

Since aldehyde is produced by these reactions, its formation in high yields can be accounted for in cases where the mixed acetals are thermally unstable.

3,4-Dichlorobenzyl Phenyl Ether.—The reaction of *tert*-butyl peroxide with this ether gave mainly 3,4-dichlorobenzaldehyde but none of the mixed acetal. This is rather surprising for two reasons. Firstly, it is unlikely that the radical $Ar\dot{C}HOPh$ generated would undergo fragmentation to give the highly unstable phenyl radical.[1,7] Secondly, the relative rate of decomposition of *tert*-butyl peroxide in this ether is very rapid and indicates that induced decomposition of the peroxide has occurred.[1] An examination of the products by nmr spectroscopy however revealed that the formation of aldehyde was accompanied by an approximately similar quantity of isobutylene. This observation could be accounted for as being due to the thermal decomposition of an initially formed mixed acetal product (analogous to eq 6). These findings indicate that the induced decomposition of the peroxide occurs readily in alkyl 3,4-dichlorobenzyl ethers; changes in the alkyl group (Me, Et, *i*-Pr, and Ph) do not significantly affect the extent of induced decomposition.

Effect of *o*-Dichlorobenzene.—An examination of the previous results[1,4] of the decomposition of *tert*-butyl peroxide in a number of alkyl benzyl ethers $ArCH_2OR$ reveals the fact that the chloro substituted ethers are the most significant in causing induced decomposition of the peroxide. This suggests that the medium, *i.e.* the chloro-substituted benzyl ethers, may at least in part be responsible for the induced decomposition pathway. Experiments to verify this possibility were conducted with benzyl methyl ether and an added solvent, and the results are given in Table I. The formation of the mixed acetal $PhCH(OMe)O\text{-}t\text{-}Bu$ product was found to be dependent on the solvent used; the chloro substituted benzene solvents in particular show a dramatic effect in promoting induced decomposition but other solvents including dimethylformamide, acetonitrile, benzonitrile, and diphenyl ether fail to do so.

TABLE I

DECOMPOSITION OF *tert*-BUTYL PEROXIDE IN BENZYL METHYL ETHER WITH ADDED SOLVENT[a]

Solvent	% PhCH-(OMe)O-*t*-Bu	% PhCHO
None[b]	3	10
o-Dichlorobenzene[c]	19	8
o-Dichlorobenzene	42	13
Chlorobenzene	16	7
p-Dichlorobenzene	13	6
1,2,3-Trichlorobenzene	39	12
m-Bromochlorobenzene	26	10
Dichloromethane	21	5
Benzonitrile	0	1
Others[d]	0	1

[a] Reactions of benzyl methyl ether (10 mmol), *tert*-butyl peroxide (2.5 mmol), and the solvent (6 mmol) at 110° for 72 hr. Percentage yields are based on *tert*-butyl peroxide. [b] Reference 1. [c] Only 3 mmol of solvent was used. [d] Includes acetonitrile, dimethylformamide, diphenyl ether, and bromobenzene.

The effect of added *o*-dichlorobenzene in promoting the induced decomposition of *tert*-butyl peroxide was also examined for the series of benzyl alkyl ethers $ArCH_2OR$ and the results are summarized in Table II.

TABLE II

DECOMPOSITION OF *tert*-BUTYL PEROXIDE IN BENZYL ALKYL ETHERS IN THE PRESENCE OF *o*-DICHLOROBENZENE[a]

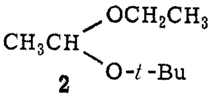
$ArCH_2OR$	Registry no.	% ArCH-(OR)O-*t*-Bu (δ)[b]	ArCHO
$4\text{-}ClC_6H_4CH_2OMe$		45 (5.67)	10
$4\text{-}ClC_6H_4CH_2OMe$	1195-44-4	36[c]	11
$PhCH_2OMe$		42 (5.73)	12
$PhCH_2OMe$	538-86-3	40 (5.69)	9
$PhCH_2O\text{-}i\text{-}Pr$	937-54-2	25 (5.70)	10
$PhCH_2O\text{-}t\text{-}Bu$	3459-80-1	40 (5.69)	12
$PhCH_2O\text{-}c\text{-}C_6H_{11}$	16224-09-2	32 (5.68)	7
$p\text{-}MeC_6H_4CH_2OMe$	3395-88-8	50 (5.71)	12

[a] Reactions of the ether $ArCH_2OR$ (10 mmol), *tert*-butyl peroxide (2.5 mmol), and *o*-dichlorobenzene (6 mmol) at 110° for 72 hr. Percentage yields are based on *tert*-butyl peroxide. [b] Chemical shift of the benzylic proton in ppm downfield from TMS in the reaction mixture. [c] Without *o*-dichlorobenzene (ref 4); the other ethers yield no or negligible amounts of mixed acetal without added dichlorobenzene.

Mixed acetals $ArCH(OR)O\text{-}t\text{-}Bu$, estimated by their characteristic absorptions at $\delta \sim 5.7$, were obtained in all cases. In the case of 4-chlorobenzyl methyl ether, which gives the mixed acetal without added dichlorobenzene, the yield of the mixed acetal was increased by the solvent added. Interestingly, despite the high tendency of α-*tert*-butoxybenzyl radical $Ph\dot{C}HO\text{-}t\text{-}Bu$ to undergo fragmentation[1] and the steric restriction imposed by the *tert*-butoxy group, a 40% yield of benzaldehyde di-*tert*-butyl acetal (1) could be isolated.

$PhCH(O\text{-}t\text{-}Bu)_2$

1



$$CH_3CH\begin{matrix}\nearrow OCH_2CH_3\\ \searrow O\text{-}t\text{-}Bu\end{matrix}$$

2

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[6] E. S. Huyser and D. T. Wang, *J. Org. Chem.*, **29**, 2720 (1964).

[7] M. S. Kharasch, A. Fono, and W. Nudenberg, *ibid.*, **16**, 113 (1951).

Further, it was found that the reaction could be extended to diethyl ether which gave 43% of the mixed acetal (**2**). It may be noted that decomposition of the peroxide in the pure ether does not give this product.[3]

Mechanism of the Induced Decomposition Reaction.—The mechanism of the induced decomposition of *tert*-butyl peroxide by ether radicals may be discussed in the light of the new findings. It may be noted that other cases of radical-induced decomposition of the peroxide occurs by hydrogen transfer.[3,8] In the decomposition of *tert*-butyl peroxide in 1-butanol, for example, a kinetic deuterium isotope effect has been observed. In the case of ether radicals induced decomposition can take place by electron transfer or by direct attack on the peroxo linkage. The former mechanism has been suggested to be a key step in many induced decomposition reactions of acyl peroxides.[9] This mechanism is probably important for the induced decomposition of benzoyl peroxide by ether radicals.[10,11] Although *tert*-butyl peroxide may be expected to be a much poorer electron acceptor compared to benzoyl peroxide, recent evidence has shown the possibility of a *tert*-butyl peroxide radical anion species.[12]

The present results show that chlorinated solvents play an important role in promoting the formation of mixed acetals; medium polarity[13] or a simple dilution effect of the added solvent does not appear to be important. Further, chloride ion was not detectable in the reaction products by silver nitrate solution and only a negligible amount of *o*-dichlorobenzene was consumed at the end of each reaction. These results may be attributed to a complexing of the ether radical to *o*-dichlorobenzene (**3**), which should be favorable in view

$$\mathrm{Ph\dot{C}HOR\ C_6H_4Cl_2} \longleftrightarrow \mathrm{Ph\overset{+}{C}HOR\ C_6H_4Cl_2{}^{\cdot -}}$$

3

of the donor property of the radical.[14] (This, however, may not be the complete explanation since in the case of dichloromethane it is difficult to see how complexing could occur.) The direct effect of complexing would be the inhibition, by polar and steric effects, of radical dimerization (which is the major reaction of $\mathrm{Ph\dot{C}HOR}$ radicals in the absence of dichlorobenzene) and thus allowing pathways leading to mixed acetal formation to compete favorably. Since the preliminary kinetic data indicate that the formation of mixed acetal is accompanied by enhanced rate of decomposition of the peroxide, the induced decomposition reaction must be important. This can occur by direct interaction of the peroxide with **3** but the possibility of electron transfer as important step(s) in the mechanism, however, cannot be excluded; such electron transfers through chlorine atom as bridges are better known in inorganic systems.[15]

Experimental Section

Nmr spectra were obtained with a Hitachi Perkin-Elmer R20B spectrometer (60 MHz) and are given in δ (ppm) with TMS as internal standard. Gas chromatography (glc) was performed on a Varian-Aerograph 1520 instrument using 6-ft QF-1 or 6-ft SE-30 columns.

tert-Butyl peroxide was purified by distillation under reduced pressure before use. Benzyl alkyl ethers were prepared and purified as reported previously.[1,4] Other solvents were redistilled and dried over 4-Å molecular sieves.

4-Chlorobenzyl Ethyl Ether.—A mixture of the ether (17.1 g, 100 mmol) and *tert*-butyl peroxide (2.92 g, 20 mmol) was heated in a sealed Carius tube at 110° for 96 hr. The reaction mixture was fractionally distilled under reduced pressure to give three fractions: mainly unreacted ether (12 g), impure mixed acetal (2.5 g), and a residue (2.5 g). Preparative glc afforded the following products (yields are based on ether consumed): (a) **the mixed acetal** $\mathrm{4\text{-}ClC_6H_4CH(OEt)O\text{-}\mathit{t}\text{-}Bu}$ (33%), δ ($\mathrm{CCl_4}$) 7.25 (4 H, broad s), 5.66 (1 H, s), 2.9–3.6 (2 H, m), 1.30 (9 H, s), and 1.07 (3 H, t, 7 Hz), hydrolysis by dilute $\mathrm{H_2SO_4}$ gave $\mathrm{4\text{-}ClC_6H_4CHO}$, EtOH, and *t*-BuOH; (b) **4-chlorobenzaldehyde diethyl acetal** (14%), δ ($\mathrm{CCl_4}$) 7.28 (4 H, broad s), 5.41 (1 H, s), 3.46 (4 H, q, 7 Hz), and 1.19 (6 H, t, 7 Hz), hydrolysis by dilute $\mathrm{H_2SO_4}$ gave 4-chlorobenzaldehyde and ethanol; (c) **ethyl 4-chlorobenzoate** (2%), δ ($\mathrm{CCl_4}$) 7.93 (2 H, d, 9 Hz), 7.33 (2 H, d, 9 Hz), 4.33 (2 H, q, 7 Hz), and 1.40 (3 H, t, 7 Hz); (d) ***tert*-butyl 4-chlorobenzoate** (1%), δ ($\mathrm{CCl_4}$) 7.86 (2 H, d, 9 Hz), 7.29 (2 H, d, 9 Hz), and 1.57 (9 H, s); and (e) **4-chlorobenzaldehyde** (10%). *meso*-α,α′-Diethoxy-4,4′-dichlorobibenzyl (10%), δ ($\mathrm{CCl_4}$) 7.17 (2 × 4 H, s), 4.10 (2 × 1 H, s), 2.9–3.5 (2 × 2 H, m), and 1.10 (2 × 3 H, t, 7 Hz), crystallized out from the residue.

A pure sample of the mixed acetal (50 mg) on heating in a sealed tube at 110° for 96 hr gave 4-chlorobenzaldehyde diethyl acetal, 4-chlorobenzaldehyde, and isobutylene.

3,4-Dichlorobenzyl Phenyl Ether.—The reaction of the ether (4.4 mmol) with *tert*-butyl peroxide (1.8 mmol) at 130° for 48 hr gave upon distillation and glc the following products (yields are based on ether consumed): (a) 3,4-dichlorobenzaldehyde (41%), (b) phenol (3%), and (c) a mixture of *o*-*tert*-butoxy- and *p*-*tert*-butoxyphenols (4%), δ ($\mathrm{CCl_4}$) 6.5–7.2 (total 9 H, both s, O-*t*-Bu), ν_{OH}($\mathrm{CCl_4}$) 3600 and 3200 $\mathrm{cm^{-1}}$. Isobutylene (50%) could also be detected in the crude reaction mixture.

Reaction of Benzyl Methyl Ether with *tert*-Butyl Peroxide in Different Solvents.—Reactions were carried out using the ether (10 mmol), *tert*-butyl peroxide (2.5 mmol), and the solvent (6 mmol) in tubes (sealed under nitrogen) heated at 110° for 72 hr. The following reaction products PhCH(OMe)O-*t*-Bu, $\mathrm{PhCH(OMe)_2}$, PhCOOMe, and PhCHO can be estimated by nmr after an addition of known quantity of trichloroethylene or tetrachloroethane as standard to the reaction mixture (Table I). Using authentic samples in *o*-dichlorobenzene solvent the characteristic chemical shifts 5.73, 3.04, and 1.19 ppm for the mixed acetal PhCH(OMe)O-*t*-Bu, 5.23 and 3.21 ppm for the acetal $\mathrm{PhCH(OMe)_2}$, 3.72 ppm for methyl benzoate, and 9.77 ppm for benzaldehyde can be distinguished. When shaken with 1 drop of 0.5 *M* sulfuric acid the absorptions of the mixed acetal PhCH(OMe)O-*t*-Bu immediately vanish, those of the acetal $\mathrm{PhCH(OMe)_2}$ also disappear after a few minutes, and corresponding increases in the aldehyde absorption were observed.

Mixed acetals can be isolated as described previously by fractional distillation under reduced pressure.[4] Benzaldehyde di-*tert*-butyl acetal was isolated and purified by glc, δ ($\mathrm{CCl_4}$) 7.1–7.3 (5 H, m), 5.62 (1 H, s), and 1.17 (18 H, s); hydrolysis by water gave benzaldehyde and *tert*-butyl alcohol.

In all the reactions using *o*-dichlorobenzene and dichloromethane as solvents no free chloride ion in the products was detectable by silver nitrate solution. Glc showed that only a negligible amount of *o*-dichlorobenzene was consumed after the reaction.

Reactions of Benzyl Alkyl Ethers with *tert*-Butyl Peroxide in the Presence of *o*-Dichlorobenzene.—Reactions were carried out as described above using the ether (10 mmol), *tert*-butyl peroxide (2.5 mmol), and *o*-dichlorobenzene (6 mmol), and the reaction products, *viz.*, ArCH(OR)O-*t*-Bu, $\mathrm{ArCH(OR)_2}$, and ArCHO, were estimated by their characteristic nmr absorption peaks; the mixed acetal when shaken with 1 drop of dilute acid gave the aldehyde. The results are given in Table II. In cases where the

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[8] E. R. Bell, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **72**, 337 (1950).

[9] K. Tokumaru and O. Simamura, *Bull. Chem. Soc. Jap.*, **36**, 333 (1963).

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[11] (a) K. Rubsamen, W. P. Neumann, R. Sommer, and U. Frommer, *Chem. Ber.*, **102**, 1290 (1969); (b) W. F. Smith and B. W. Rossiter, *Tetrahedron*, **25**, 2059 (1969).

[12] T. Shida, *J. Phys. Chem.*, **72**, 723 (1968).

[13] E. S. Huyser in "Advances in Free-Radical Chemistry," Vol. 1, G. H. Williams, Ed., Logos, 1965, Chapter 3.

[14] R. L. Huang, T.-W. Lee, and S. H. Ong, *J. Chem. Soc., C*, 40 (1969).

[15] H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970.

mixed acetals were relatively unstable, isobutylene could be detected from its characteristic nmr signals, *i.e.*, δ 4.63 (septet, 1.1 Hz) and 1.64 (t, 1.1 Hz).

Diethyl Ether.—The reaction of ether under the same conditions as above gave a 43% yield of the mixed acetal MeCH(OEt)O-*t*-Bu. The crude product was short path distilled at 100° (bath) and 150-mm pressure and purified by preparative glc, δ (CCl_4) 1.11 (3 H, t, 7 Hz), 1.17 (3 H, d, 5 Hz), 1.19 (9 H, s), 3.43 (2 H, q, 7 Hz), and 4.84 (1 H, q, 5 Hz). Hydrolysis by dilute sulfuric acid gave acetaldehyde, ethanol, and *tert*-butyl alcohol.

Registry No.—3,4-Dichlorobenzyl phenyl ether, 33598-40-2; *tert*-butyl peroxide, 75-91-2.

Acknowledgments.—I thank Yap Chuan Hoe, Ong Lam Eng, and Miss Tan Chear Eng for some preliminary experiments.

Naphthyridine Chemistry. XIV.
The Meisenheimer Reaction of the 1,X-Naphthyridine 1-Oxides

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The treatment of the 1,X-naphthyridine 1-oxides with phosphorus oxychloride affords the 2-, 3-, and 4-chloro-1,X-naphthyridines in varying amounts depending upon the position of the nonoxidized nitrogen atom. The 2-chloro compounds formed decrease from 0.60 to 0.13 mol ratio in the sequence 1,7-, 1,5-, 1,8-, 1,6-naphthyridine 1-oxide, while, in the same sequence, the 3-chloro isomers increases from 0.03 to 0.02 and the 4-chloro isomers from 0.37 to 0.67 mol ratio. Possible mechanisms to account for these changes are discussed.

Several recent papers[1-3] have described the results of studies of the Meisenheimer reaction on various naphthyridine *N*-oxides. In order to further delineate the effect that the position of the nonoxidized nitrogen atom has upon the product distribution in the naphthyridine 1-oxides when they are treated with phosphorus oxychloride, we have examined the behavior of the 1-oxides of 1,7- (**1**) and 1,8-naphthyridine (**2**).

When 1,7-naphthyridine 1-oxide (**1**) is treated with phosphorus oxychloride, a four-component mixture (as established by tlc and vpc) is obtained. Preparative scale vpc allows the separation of this mixture into three components. The compound with the shortest retention time is 1,7-naphthyridine (4% of the total reaction mixture); the second component (35% of the total reaction mixture) has a molecular formula of $C_8H_5N_2Cl$. The melting point of this material, as collected from the gas chromatograph, is 108–110°. Since the melting point for this compound, whose nmr spectrum is that expected for 4-chloro-1,7-naphthyridine, is 121–122°,[4] it appeared that we were dealing with a mixture. When this substance was twice sublimed and finally recrystallized from cyclohexane, its melting point was raised to that reported for the 4-chloro-1,7-naphthyridine (**3**). Thus, the material collected from the gas chromatograph is a mixture. In order to identify the component which "contaminated" the vpc peak, a sample of the crude reaction products was hydrolyzed with aqueous base in the anticipation that any 2- or 4-chloro-1,7-naphthyridine would be converted to the corresponding dihydro-oxo compounds, while any 3-chloro-1,7-naphthyridine that might be present would not be affected by these conditions.

In this fashion we obtained a two-component mixture consisting of 1,7-naphthyridine and 3-chloro-1,7-naphthyridine (**5**). The identity of these two products was established by comparison with authentic samples. It is of interest to note that the 3-chloro- and the 4-chloro-1,7-naphthyridines have the same retention times on several vpc columns and, consequently, the very minor amount of 3-chloro-1,7-naphthyridines formed in this reaction is not detectable in the presence of the substantial amounts of 4-chloro-1,7-naphthyridine formed. The amount of 3-chloro-1,7-naphthyridine obtained from this reaction could, consequently, not be directly calculated by an analysis of the vpc traces alone. The data presented in Table I are those obtained by taking this fact into account.

The third component (56% of the total reaction mixture) has a molecular formula of $C_8H_5N_2Cl$ and is identified as 2-chloro-1,7-naphthyridine (**4**) by an analysis of its nmr spectrum. This spectrum (Table II) shows the presence of one deshielded singlet (τ 0.61) and two AB patterns. The sizes of the coupling constants of the AB patterns (9.0 and 6.0 Hz, respectively) require that both of the systems involve coupling of protons on vicinal carbon atoms, thus establishing structure **4** as the correct one.

The fourth component, which appears as a very minor shoulder on the trailing edge of the peak due to the 2-chloro-1,7-naphthyridine, is estimated to correspond to 2% of the total reaction mixture. This material is neither 5-chloro-[5] nor 8-chloro-1,7-naphthyridine[6] by gc comparisons of these compounds with the unknown, and has not yet been identified.

In order to assure ourselves that neither the 2-chloro- (**4**) nor the 4-chloro-1,7-naphthyridine (**3**) is hydrolyzed during the aqueous work-up, we modified the usual procedure by utilizing methanol in place of water. When this was done, and the methanolic solution was heated with sodium methoxide until tlc no longer showed the presence of either the 2-chloro- or 4-chloro-1,7-naphthyridine (a total of 12 hr), we isolated a mixture of the 2- (**6**) and 4-methoxy-1,7-naphthyridines (**7**). An analysis of the nmr spectrum of this mixture showed that the ratio of 2- to 4-methoxy derivatives is

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[5] Prepared by Eisch chlorination of 1,7-naphthyridine: unpublished results.

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