SCHEME II

(A)[a] $\mathbf{1} + SeO_2 \longrightarrow$ Hydrocarbons and Polymers

(B)[b] $\mathbf{1} + t\text{-}BuO_2COPh \longrightarrow \xrightarrow{OH^-}$ Seven Alcohols

(C) $\mathbf{1} + Pd(OAc)_2 \longrightarrow \xrightarrow{LiAlH_4}$ Hydrocarbons

(D)[c] $\mathbf{1} + NBS \longrightarrow \xrightarrow{AgOAc} \xrightarrow{OH^-}$ Polymers

(E) $\mathbf{1} + Hg(OAc)_2 \longrightarrow$ Recovered **1**

(F)[d] $\mathbf{1} + CrO_3\text{–}Py_2 \longrightarrow$ Recovered **1**

[a] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959). [b] H. L. Goering and U. Mayer, *J. Amer. Chem. Soc.*, **86**, 3753 (1964). [c] A. C. Cope, M. Brown, and H.-H. Lee, *ibid.*, **80**, 2855 (1958). [d] W. G. Dauben, personal communication.

Experimental Section

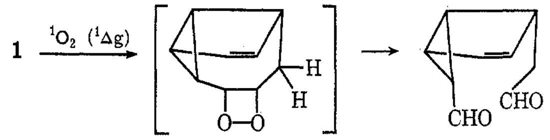
Melting points were taken in capillaries and are uncorrected.

exo-**Tricyclo[6.1.0.0^{4,9}]nona-2,5-dien-7-ol (2a)**.—A solution of 2.0 g of **1** and 15 mg of rose bengal in 100 ml of anhydrous methanol was bubbled with oxygen and irradiated with a tungsten-iodine lamp until the absorption of oxygen ceased (calcd 200 ml, obsd 350 ml). The reaction mixture was reduced with 10 g of $NaBH_4$ at room temperature, quenched with 100 ml of 20% KOH solution, and then extracted with ether. The ether layer was dried over K_2CO_3 and evaporation of ether gave a viscous oil. This oil was chromatographed on a column of 100 ml of Silica AR with 10% ether–pentane, and divided into 20 fractions of 150 ml each. After evaporation of the solvent, fractions 6, 7, and 8 gradually crystallized on standing at room temperature to give white needles, mp 87.0–88.0°. These were recrystallized from pentane to give 800 mg (35%) of white needles: mp 88.5–89.5°; nmr, see text; ir (CCl_4) 3601 (m), 3360 (s), 3050 (s), 2915 (m), 2840 (w), 1586 (w), 1376 (m), 1341 (m), 1265 (m), 1038 (s), 997 (s), 970 (m), 956 (m), 942 (w), 919 (m), 910 (m), 892 (m), 853 (w), 727 (m) and 693 cm^{-1} (s); mass spectrum, parent peak at *m/e* 134 ($C_9H_{10}O^+$) and a base peak at *m/e* 43; R_f 0.31 (5 × 20 alumina coated plate eluted with 25% ether–pentane).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.45; H, 7.56.

Fractions 1 and 2 consisted of a mixture of hydrocarbons (0.1 g). Combination of fractions 3, 4, and 5 yielded a viscous oil (0.5 g). The ir spectrum of this oil showed a characteristic aldehyde absorption at 2710 and 1730 cm^{-1}, a double bond absorption at 1650 cm^{-1}, and a cyclopropyl absorption at 3050 cm^{-1} (neat). We believe that this component is dialdehyde **5**. A possible explanation for the unusual formation of this aldehyde is presented in Scheme III. $^1\Delta g$ oxygen reacts with **1** to form a 1,2-dioxetane intermediate[11] which cleaves to **5**. A more detailed report on further chemistry of **5** is forthcoming.

SCHEME III



5

Fractions 9–15 consisted of viscous polymers (1.0 g). Fractions 16–20 consisted of small amounts of polymers and inorganic materials (0.1 g).

exo-**Tricyclo[6.1.0.0^{4,9}]nona-2,5-dien-7-yl *p*-Nitrobenzoate (2b)**.—To a solution of 100 mg of **2a** in 3 ml of dry pyridine was added 270 mg of *p*-nitrobenzoyl chloride at 0°. The solution was stirred for 0.5 hr at this temperature and then allowed to stand in the freezer for 6 hr. The mixture was decomposed with five drops of water at 0° and extracted with ether. The ether layer was washed with cold dilute HCl and saturated $NaHCO_3$, and then saturated NaCl. After drying over K_2CO_3, evaporation of the solvent gave a yellow solid, which was recrystallized from ether–pentane to give 190 mg of pale yellow leaflets, mp 138.5–139.5°, 91% yield.

Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63. Found: C, 67.69; H, 4.67.

Tricyclo[6.1.0.0^{4,9}]nona-2,5-dien-7-one (3).—To a solution of 50 mg of **2a** in 10 ml of ether was added 0.5 g of CrO_3 in 6 ml of water. The mixture was stirred at room temperature for 3.5 hr. After usual work-up, the ketone **3** was collected by preparative tlc (Silica AR) with 25% ether–pentane (detected with uv lamp), ir (CCl_4) 1715 cm^{-1}, R_f 0.81.

Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.85; H, 6.01.

endo-**Tricyclo[6.1.0.0^{4,9}]nona-2,5-dien-7-ol (4)**.—A solution of 28 mg of **3** in 2 ml of methanol was added to stirred $NaBH_4$ (80 mg) in 2 ml of methanol at room temperature. After the mixture had been stirred for 2 hr, the excess hydride was destroyed with 1 ml of 20% KOH solution. The aqueous layer was extracted with ether and the ether solution was washed with water and dried over K_2CO_3. Evaporation of the ether yielded a residue which was purified by preparative tlc (Silica AR) with 25% ether–pentane (detected with uv lamp): mp 111–112°; ir (CCl_4) 3550 cm^{-1} (OH); nmr ($CDCl_3$) τ 4.0–5.0 (4 H, multiplet, olefinic), 5.5 (1 H, narrow multiplet, α H), 6.70 (1 H, narrow multiplet, bisallylic), and 8.0–9.0 (3 H, multiplet, cyclopropyl); mass spectrum *m/e* 134 ($C_9H_{10}O^+$); R_f 0.54.

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.41; H, 7.52.

Registry No.—**1**, 30767-78-3; **2a**, 34886-41-4; **2b**, 34886-42-5; **3**, 34886-43-6; **4**, 34886-44-7.

Acknowledgment.—The authors gratefully acknowledge the help of Professor C. S. Foote, of the University of California at Los Angeles, with whom many fruitful discussions of this work were held.

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Twofold Redox Addition of Carbon Tetrachloride to Olefins

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Received December 20, 1971

The addition of haloalkanes to olefins, first described by Kharasch, has been known for a long time.[1] One of the drawbacks has been that with less reactive carbon halogen compounds, telomerization is observed rather than simple 1:1 addition. This difficulty has been overcome by a technique utilizing copper or iron salts as catalysts.[2-4] Even under these conditions some byproducts of telomeric 2:1 structures have been reported.

We now show that under proper conditions products of "twofold" addition (not telomeric) can be obtained.

$$\begin{tikzcd} CCl_4 + 2CH_2{=}CHR \arrow[r] \arrow[dr] & RCHClCH_2CCl_2CH_2CHClR \\ & CCl_3CH_2CHRCH_2CHClR \end{tikzcd}$$

twofold addition

2:1 telomer

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[1] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 957, pp 239–289.

[2] S. Murai, N. Sonoda, and S. Tsutsumi, *J. Org. Chem.*, **29**, 2104 (1964).

[3] R. K. Freidlina, E. T. Chukovskaya, and B. A. Englin, *Dokl. Akad. Nauk SSSR*, **159**, 1346 (1964).

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This has now been demonstrated for methyl acrylate, ethylene, octene, and allyl alcohol. In addition, the possibility of combining two different functional groups by using two steps in the reaction has been shown. The yields are generally low, but that of dimethyl 2,4,4,6-tetrachloroheptanedioate (15%) is synthetically interesting. No effort has been made yet to optimize the yields.

The twofold addition products formed from carbon tetrachloride with ethylene and 1-octene were unsaturated, apparently from the loss of hydrogen chloride. This was even more noteworthy in that the products formed from carbon tetrachloride and allyl alcohol and methyl acrylate were saturated. One possible cause of this difference is the solvent, which was isopropyl alcohol for the addition to ethylene, but acetonitrile for the addition to allyl alcohol, methyl acrylate, and octene. The loss of hydrogen chloride from the product derived from 1-octene could be thermal dehydrochlorination.

$$\mathrm{CCl_4 + 2C_2H_4 \longrightarrow CH_2ClCH{=}CClCH_2CH_2Cl + HCl}$$

Products which are formed from isopropyl alcohol include isopropyl chloride, isopropyl ether, acetone, and propylene, which is converted to 1,1,1,3-tetrachlorobutane.

The nature of the solvent apparently plays a role in the reduction of carbon tetrachloride to chloroform,[5] since chloroform was not observed in experiments with allyl alcohol and methyl acrylate in acetonitrile,[6,7] but was isolated in the reactions of ethylene with carbon tetrachloride in isopropyl alcohol.

Twofold additions of carbon tetrachloride to allyl alcohol and methyl acrylate were carried out in acetonitrile to avoid some of the above-mentioned side reactions. The yields were low, 15% for methyl acrylate and 6.5% for allyl alcohol, but no effort was made to optimize them.

$$\mathrm{CCl_4 + CH_2{=}CHCH_2OH \longrightarrow HOCH_2CHClCH_2CCl_2CH_2CHClCH_2OH}$$

$$\mathrm{CCl_4 + CH_2{=}CHCOOCH_3 \longrightarrow CH_3OCOCHClCH_2CCl_2CH_2CHClCOOCH_3}$$

The reaction of 1-octene with carbon tetrachloride was also carried out in acetonitrile. The yield of twofold addition product was only 4%, and, similar to the results with ethylene, it was unsaturated. This, however, may have been due to thermal dehydrochlorination during isolation.

In order to show that products from two different olefins with carbon tetrachloride could be made, 1,1,1,3-tetrachloropropane was treated with octene in isopropyl alcohol. The desired mixed twofold addition product was formed, but loss of hydrogen chloride was extensive.[8]

$$\mathrm{CCl_3CH_2CH_2Cl + CH_2{=}CH(CH_2)_5CH_3 \longrightarrow \underset{2.8\%}{CH_3(CH_2)_5CHClCH_2CCl_2CH_2CH_2Cl} + \underset{8.4\%}{C_{11}H_{19}Cl_3} + \underset{18\%}{C_{11}H_{18}Cl_2}}$$

Nmr Spectra.—Most characteristics of the nmr spectra are as expected. The notable characteristic is the separation of two methylene protons adjacent to an asymmetric center.[9] This is observed in all of the products derived from olefins $\mathrm{CH_2{=}CHR}$ where R is not H. The most striking effect is observed in the nmr spectra of methyl 2,4,4,4-tetrachlorobutyrate and dimethyl 2,4,4,6-tetrachloroheptanedioate, where the nmr signals for the two methylene protons are not only well separated but couple with each other with J = 15 and 3 Hz, respectively.

Experimental Section

Addition of Carbon Tetrachloride to Ethylene.—A mixture of 1083 g of carbon tetrachloride, 871 g of isopropyl alcohol, 18.9 g of $\mathrm{FeCl_3 \cdot 6H_2O}$, 15.75 g of benzoin, and 11.2 g of diethylamine hydrochloride was heated to 125° in a 1-gallon 316 stainless steel Parr Magnedash autoclave. The reactor was pressured to 2500 psig with ethylene and held at 125° for 4 hr. Distillation was used to separate 80 g of chloroform, 925 g of 1,1,1,3-tetrachloropropane,[3,4] nmr ($\mathrm{CCl_4}$) δ 3.84 (t, 2), 3.18 (t, 2, J = 7.5 Hz), and 38 g of 1,1,1,3-tetrachlorobutane, bp 50–55° (10 mm), $n^{20}\mathrm{D}$ 1.4795, nmr ($\mathrm{CCl_4}$) δ 3.20 (2 d, 2, J = 5.5 Hz), 4.40 (m, 1), 1.70 (d, 3, J = 6.5 Hz). *Anal.* Calcd for $\mathrm{C_4H_6Cl_4}$: C, 24.52; H, 3.09; Cl, 72.09. Found: C, 24.63; H, 3.11; Cl, 72.26.

The last part of the distillation provided a mixture of 18 g of 1,1,5-trichloro-1-pentene, 9 g of 1,3,5-trichloro-2-pentene, 17 g of 1,1,1,5-tetrachloropentane, and 7 g of 1,3,3,5-tetrachloropentane which were separated by gas chromatography for analysis.

1,1,5-Trichloro-1-pentene had nmr ($\mathrm{CCl_4}$) δ 5.89 (t, 1, =CH–, J = 3.8 Hz), 2.35 (2 t, 2, J = 3.8 and 4.0 Hz), 1.88 (m, 2, J = 4.0, 3.1 Hz), 2.53 (t, 2, J = 3.1 Hz). *Anal.* Calcd for $\mathrm{C_5H_7Cl_3}$: C, 34.62; H, 4.07; Cl, 61.31. Found: C, 34.52; H, 4.11; Cl, 61.40.

1,3,5-Trichloro-2-pentene had nmr ($\mathrm{CCl_4}$) δ 4.20 (d, 2, $\mathrm{{=}CHCH_2Cl}$, J = 3.6 Hz), 5.88 (t, 1, =CH–, J = 3.6 Hz), 2.80 (t, 2, $\mathrm{{=}CClCH_2}$–, J = 3.3 Hz), 3.70 (t, 2, –$\mathrm{CH_2Cl}$, J = 3.3 Hz). *Anal.* Calcd for $\mathrm{C_5H_7Cl_3}$: C, 34.62; H, 4.07; Cl, 61.31. Found: C, 34.73; H, 4.13; Cl, 61.03.

1,1,1,5-Tetrachloropentane had nmr ($\mathrm{CCl_4}$) δ 2.71 (t, 2, $\mathrm{CCl_3CH_2}$–, J = 3.5 Hz), 1.92 (m, 4), 3.59 (t, 2, –$\mathrm{CH_2Cl}$, J = 3.0 Hz).

1,3,3,5-Tetrachloropentane had nmr ($\mathrm{CCl_4}$) δ 3.85 (t, 4, –$\mathrm{CH_2Cl}$), 2.70 (t, 4, J = 4.0 Hz). *Anal.* Calcd for $\mathrm{C_5H_8Cl_4}$: C, 28.61; H, 3.84; Cl, 67.55. Found: C, 28.45; H, 3.40; Cl, 66.98.

Addition of Carbon Tetrachloride to Methyl Acrylate.—A mixture of 30.8 g of carbon tetrachloride, 34.4 g of methyl acrylate, 8.2 g of acetonitrile, 0.21 g of benzoin, 0.22 g of diethylamine hydrochloride, and 0.17 g of $\mathrm{CuCl_2 \cdot 2H_2O}$ was divided into three portions and charged to 45 ml polymerization tubes. The tubes were heated at 150° for 17 hr and cooled. Three water washes and steam distillation were used to separate 9 g (20%) of methyl 2,4,4,4-tetrachlorobutyrate, bp 46–53° (0.1–0.2 mm), $n^{20}\mathrm{D}$ 1.4812,[4,10] nmr ($\mathrm{CCl_4}$) δ 3.86 (s, 3), 4.61 (2 d, 1), 3.22 (2 d, 1), 3.83 (2 d, 1), and 10 g (15%) of dimethyl 2,4,4,6-tetrachloroheptanedioate, bp 140–141° (2.0 mm), $n^{20}\mathrm{D}$ 1.4928, nmr ($\mathrm{CCl_4}$) δ 3.82 (s, 3), 4.68 (t, 1), 2.92 (2d, 2). *Anal.* Calcd for $\mathrm{C_9H_{12}Cl_4O_4}$: C, 33.16; H, 3.71; Cl, 43.50. Found: C, 33.42; H, 3.67; Cl, 43.28.

Addition of Carbon Tetrachloride to Allyl Alcohol.—This reaction was carried out as described above, except that 23.2 g of allyl alcohol was substituted for the methyl acrylate. The products were 10 g (24%) of 2,4,4,4-tetrachlorobutan-1-ol, bp 60–61° (0.15 mm), $n^{20}\mathrm{D}$ 1.5042, nmr ($\mathrm{CCl_4}$) δ 3.66 (s, 3, –OH), 3.29 (2 d, 2, $\mathrm{CCl_3CH_2}$–), 4.39 (m, 1, –CHCl–), 3.9 (d, 2, –$\mathrm{CH_2O}$–), and 3.5 g (6.5%) of 2,4,4,6-tetrachloroheptane-1,7-diol, bp 100–110° (4–7 mm), $n^{20}\mathrm{D}$ 1.5113, nmr ($\mathrm{CCl_4}$) δ 3.6 (s, 1, –OH), 3.26 (2 d, 2, –$\mathrm{CCl_2CH_2}$–), 4.35 (m, 1, –CHCl–), 3.7 (d, 2, –$\mathrm{CH_2O}$–). *Anal.* Calcd for $\mathrm{C_7H_{12}Cl_4O_2}$: C, 31.15; H, 4.48; Cl, 52.53. Found: C, 30.81; H, 4.21; Cl, 53.05.

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Addition of Carbon Tetrachloride to 1-Octene.—This reaction was carried out as described above except that all reagents were doubled and 89.6 g of 1-octene was used in place of allyl alcohol. The mixture was heated in six 45-ml polymerization tubes. The products were 41 g (38.5%) of 1,1,1,3-tetrachlorononane,[4,11,12] bp 95–98° (1.7–2.0 mm), $n^{20}\mathrm{D}$ 1.4768, nmr (CCl_4) δ 3.2 (2 d, 2, $-CH_2CCl_3$), 4.2 (m, 1, $-CHCl-$), 1.85 (m, 2, $-CH_2CHCl-$), 1.36 (m, 8, $-CH_2-$), 0.9 (t, 3, $-CH_3$), and 5.5 g (4%) of 9,9,11-trichloro-7-heptadecene, bp 170° (2.0 mm), $n^{20}\mathrm{D}$ 1.4766, nmr (CCl_4) δ 0.9 (t, 3, $-CH_3$), 1.2–1.8 (m, 10, $-CH_2-$), 4 (m, 1, $-CHCl-$), 5.5 (d, 1, $-CH{=}$), 2.7 (d, 2, $=CClCH_2-$). *Anal.* Calcd for $C_{17}H_{31}Cl_3$: C, 59.74; H, 9.14; Cl, 31.12. Found: 59.37; H, 9.28; Cl, 31.11.

Addition of 1,1,1,3-Tetrachloropropane to 1-Octene.—A mixture of 42 g of 1-octene, 68 g of 1,1,1,3-tetrachloropropane, 40 ml of isopropyl alcohol, 0.9 g of $FeCl_3 \cdot 6H_2O$, 0.7 g of benzoin, and 0.5 g of diethylamine hydrochloride was refluxed at 85° for 20 hr. The mixture was washed twice with water and steam distilled. The residue was fractionated but the distillation cuts were mixtures as indicated by gas chromatography. Mass spectroscopy coupled to a gas chromatograph indicated that the three major components were 14.0% of $C_{11}H_{18}Cl_2$, 8.4% of $C_{11}H_{19}Cl_3$, and 2.8% of $C_{11}H_{20}Cl_4$.

Registry No.—Carbon tetrachloride, 56-23-5; ethylene, 74-85-1; 1,1,1,3-tetrachloropropane, 1070-78-6; 1,1,1,3-tetrachlorobutane, 13275-19-9; 1,1,5-trichloro-1-pentene, 2677-33-0; 1,3,5-trichloro-2-pentene, 34909-84-7; 1,1,1,5-tetrachloropentane; 2467-10-9; 1,3,3,5-tetrachloropentane, 24616-07-7, methyl methacrylate, 80-62-6; methyl 2,4,4,4-tetrachlorobutyrate, 25335-11-9; dimethyl 2,4,4,6-tetrachloroheptanedioate, 34909-87-0; allyl alcohol, 107-18-6; 2,4,4,4-tetrachlorobutan-1-ol, 3290-70-8; 2,4,4,6-tetrachloroheptane-1,7-diol, 34909-89-2; 1-octene, 111-66-0; 1,1,1,3-tetrachlorononane, 1070-27-5; 9,9,11-trichloro-7-heptadecene, 34909-90-5.

Acknowledgment.—Thanks are expressed to Dr. W. T. Pace for running the nmr spectra, to B. W. Wilkes for the mass spectra, and to Drs. J. P. Henry and J. T. Fitzpatrick for helpful discussions.

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Deoxygenations of 2-(D-*arabino*-Tetrahydroxybutyl)pyrazine 4-*N*-Oxide and 1-*N*-Oxide

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Received August 23, 1971

Deoxygenations of aromatic *N*-oxides[1] have been carried out with sulfur dioxide,[2] sulfurous acid,[3] phosphorus trichloride,[4] or phosphorus oxychloride[5] or by catalytic reduction over Raney nickel[6] or palladium carbon.[7] The reactions of pyrazine 1-*N*-oxide and pyrazine 1,4-di-*N*-oxide with phosphorus oxychloride have been reported to give 2-chloropyrazine and 2,6-dichloropyrazine in 25 and 40% yield, respectively.[8]

During the course of an investigation of heterocyclic compounds derived from carbohydrates, it was shown[9] that 2-amino-2-deoxy-D-glucose oxime (**1**) reacted with glyoxal to yield 2-(D-*arabino*-tetrahydroxybutyl)pyrazine 4-*N*-oxide (**2**) identical with that derived from 2-amino-2-deoxy-D-mannose oxime and glyoxal. The present report describes an investigation of the deoxygenations of carbohydrate-derived pyrazine *N*-oxides. The deoxygenation of 2-(D-*arabino*-tetraacetoxybutyl)-pyrazine 4-*N*-oxide (**3**) with phosphorus oxychloride yields the monochloropyrazine derivative **4**. In this case, the possible substitution position of chlorine is 3 or 5 on the pyrazine ring. The nmr spectrum of the crystalline monochloro tetraacetyl derivative **4** showed two singlets at τ 1.47 and 1.54 due to the uncoupled protons at C-3 and C-6 of the pyrazine ring. Thus it may be concluded that the position of chlorination is C-5 of the pyrazine ring (Scheme I).

On the other hand, the catalytic deoxygenation of 2-(D-*arabino*-tetrahydroxybutyl)pyrazine 4-*N*-oxide (**2**) was performed in methanol with palladium/carbon at room temperature by using a slightly positive pressure of hydrogen. The deoxygenated product **6** was oxidized with potassium permanganate to yield the pyrazinemonocarboxylic acid **7**, which showed an identical infrared spectrum, paper chromatographic R_f value,[10,11] and melting point with the authentic pyrazine-2-carboxylic acid. This fact shows that the 4-*N*-oxide **2** has been completely deoxygenated to 2-(D-*arabino*-tetrahydroxybutyl)pyrazine (**6**).

1-Amino-1-deoxy-D-fructose oxime (D-isoglucosamine oxime) (**9**) is an isomer of 2-amino-2-deoxy-D-glucose oxime (**1**) and can form a pyrazine 1-*N*-oxide derivative by the reaction with glyoxal. Little has been known of this sugar oxime and it was synthesized according to the procedure described by Breuer[12] from 1-amino-1-deoxy-D-fructose acetate (**8**)[13] and hydroxylamine. The condensation product **10** of this sugar oxime and glyoxal showed the identical molecular formula, ultraviolet maximum, and ultraviolet molecular absorption coefficient with those of 2-(D-*arabino*-tetrahydroxybutyl)pyrazine 4-*N*-oxide (**2**), but showed a quite different melting point and infrared spectrum from those of the latter. The deoxygenation by catalytic reduction of **10** was carried out according to the method used for the 4-*N*-oxide **2** and yielded the deoxygenated product **6**, which had identical physical constants and infrared spectrum with those of the deoxygenated product

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