

shown in Figure 1. This consists of a triangle of osmium atoms bridged on the longest edge by an acetyl group and a hydrogen atom.<sup>11</sup> The carbene group is terminally bonded to Os(1), to which is also coordinated the oxygen of the bridging acetyl group. The bond distances from C(25), the carbenoid carbon atom, to Os(1) and to the methoxy oxygen and the methyl carbon atoms as well as the angles about C(25) are all typical of those found in Fischer-type carbene complexes<sup>2</sup> (see caption to Figure 1).

Our work clarifies for the first time the rarity of the Fischer carbene groups on metal clusters. This derives from the chemical properties of the  $\eta^1\text{-C(O)R}$  group formed in the attack of nucleophile on the cluster. In the medium needed to form such a group, alkylation is very slow; in attempts to exchange solvent, the labilizing influence of the  $\eta^1\text{-C(O)R}$  group leads to loss of CO and formation of the bridged  $\mu\text{-O}=\text{C(R)}$  complex. It is ironic that synthesis of the Fischer carbene takes place on a hydrido-cluster complex, which gives some idea of the relative tendencies for competing processes such as attack by nucleophile on coordinated CO as opposed to removal of bridging hydrogen as proton.

**Acknowledgment.** This work has been supported by a grant from the National Science Foundation (No. CHE 79-08406).

**Registry No.** 4, 65908-54-5; 5, 82390-92-9;  $\text{CH}_3\text{Li}$ , 917-54-4;  $\text{CH}_3\text{S-O}_3\text{CF}_3$ , 333-27-7.

(10) Orange crystals are monoclinic, space group  $P2_1/n$ ,  $a = 9.578$  (4) Å,  $b = 13.494$  (4) Å,  $c = 15.187$  (6) Å,  $\beta = 96.30$  (3)°;  $V = 1951$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 3.15$  g cm<sup>-3</sup> ( $\text{MoK}\alpha = 0.71069$  Å<sup>3</sup>). The structure was solved and refined by using 2728 observed ( $I > 3\sigma(I)$ ) independent reflections measured on a Syntex PI automated diffractometer in the range  $0^\circ < 2\theta < 50^\circ$ . An absorption correction was applied ( $\mu = 195.66$  cm<sup>-1</sup>). Refinement converged at  $R = 0.050$  and  $R_w = 0.061$ .

(11) After all non-hydrogen atoms were refined anisotropically, the metal hydride was located and refined.

## Dichlorine Monoxide: A Powerful and Selective Chlorinating Reagent†

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Dichlorine monoxide ( $\text{Cl}_2\text{O}$ ) has long been known<sup>1</sup> and has been the subject of some modern mechanistic<sup>2</sup> and physical<sup>3</sup> studies, but it has not been shown to be a useful reagent in synthetic chemistry. We have found that  $\text{Cl}_2\text{O}$  is a powerful and selective reagent for either side-chain or ring chlorination of deactivated aromatic substrates, and it gives excellent yields under mild conditions where conventional reagents fail or require harsh conditions.

The free-radical, side-chain chlorinations of deactivated alkyl aromatic compounds such as *p*-nitrotoluene normally require high temperatures and give largely benzyl chlorides and hydrochloric acid.<sup>4</sup> Only small amounts of benzal chlorides and little or no benzotrichlorides are produced.<sup>5</sup> More forcing conditions lead

**Table I.** Chlorination of Deactivated Alkyl Aromatic Compounds with  $\text{Cl}_2\text{O}$  in  $\text{CCl}_4$

substrate	product	yield, %
		99
		89
		99
		96
		100
		97

<sup>a</sup> Reaction temperature 25 °C. <sup>b</sup> Reaction temperature 75 °C.

**Table II.** Pseudo-First-Order Rate Constants for

$\text{X}-\text{C}_6\text{H}_4-\text{CHCl}_2 + \text{Cl}_2\text{O}$  in  $\text{CCl}_4$  at 25.0 °C

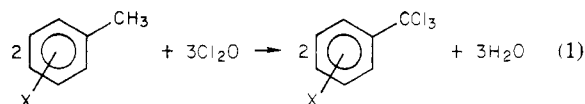
X	$10^4 k, \text{s}^{-1}$
$\text{NO}_2$	1.05
$\text{CF}_3$	1.42
Cl	2.70

**Table III.** Relative Rate Constants for

$\text{X}-\text{C}_6\text{H}_4-\text{CH}_3 + \text{Cl}_2\text{O}$  in  $\text{CCl}_4$  at 25.0 °C

X	$k_{\text{rel}}$
Cl	3.44
$\text{CO}_2\text{CH}_3$	1.76
$\text{CF}_3$	2.28
$\text{NO}_2$	1.00

to excessive byproducts via the ipso reaction.<sup>6</sup> In marked contrast, chlorinations with  $\text{Cl}_2\text{O}$  at 25 °C can lead exclusively to trichloromethyl derivatives in high yields with water as the only byproduct (eq 1). Representative examples are shown in Table I. Mono- and dichloro products also can be produced in useful



yields by adjusting the  $\text{Cl}_2\text{O}$ /arene ratio, but the chief utility of this chemistry is the direct synthesis of relatively inaccessible, negatively substituted trichloromethyl arenes, which are convenient precursors to other functionalized arenes such as the corresponding trifluoromethyl derivatives or carboxylic acids.

In a typical reaction,<sup>7,8</sup>  $\text{Cl}_2\text{O}$  (42.4 g, 0.49 mol) in  $\text{CCl}_4$  (750

(5) We found, for example, the chlorination of *p*-nitrotoluene with excess  $\text{Cl}_2$  at 165–170 °C for 9–14 h gave <1% *p*-nitrobenzotrichloride. Free-radical initiators or UV light had little or no effect. Catalysts such as  $\text{I}_2$ ,  $\text{SbI}_3$ ,  $\text{C}_6\text{H}_5\text{I}$ ,  $\text{C}_6\text{H}_5\text{IO}$ , or  $\text{SbCl}_3$  in some cases reduced the required reaction temperature to 135 °C but did not increase the yield of benzotrichloride. Other chlorinating agents including  $\text{SO}_2\text{Cl}_2$  or *t*-BuOCl also failed to trichlorinate *p*-nitrotoluene.

(6) Traynham, J. G. *Chem. Rev.* 1979, 79, 323.

(7) Marsh, F. D. (to Du Pont) U.S. Patent 4 226 783.

(8) Solutions of  $\text{Cl}_2\text{O}$  in  $\text{CCl}_4$  (ca. 1.0 M), prepared by passing a mixture of chlorine and air over yellow mercuric oxide,<sup>9</sup> were used in this work, but in situ generation has given overall better yields for some large-scale preparations. **Caution:** Neat  $\text{Cl}_2\text{O}$  is toxic, explosive, and a strong oxidizing agent, but solutions in  $\text{CCl}_4$  (ca. 1 M) can be handled safely and stored at -15 to 0 °C.

† Contribution No. 3058.


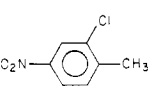

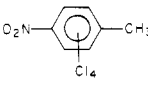
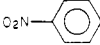
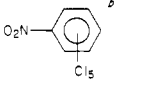

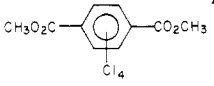
(1) (a) Balard, A. *J. Ann. Chim. Phys., Ser. 2* 1834, 57, 225. (b) Balard, A. *J. Taylor's Sci. Mem.* 1837, 1, 269. (c) Gay-Lussac, J. L. *C. R. Acad. Sci.* 1842, 14, 927.

(2) Tanner, D. D.; Nychka, N. *J. Am. Chem. Soc.* 1967, 89, 121.

(3) See, for example: Renard, J. J.; Bolker, H. I. *Chem. Rev.* 1976, 76, 487.

(4) (a) Hoch, P. E. In "Chlorine, Its Manufacture, Properties, and Uses"; Sconce, J. S., Ed.; Reinhold: New York, 1962; pp 834–863. (b) Russell, G. A. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, pp 293–311. (c) Poutsma, M. L. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 2, pp 181–185.

**Table IV.** Chlorination of Deactivated Aromatic Rings with  $\text{Cl}_2\text{O}$ /Acid at 20–40 °C

substrate	product	acid	yield, %
		$\text{H}_2\text{SO}_4$	99
		$\text{CF}_3\text{SO}_3\text{H}$	97
		$\text{H}_2\text{SO}_4$	94
		$\text{CF}_3\text{SO}_3\text{H}$	99

<sup>a</sup> 0.5 equiv of  $\text{Cl}_2\text{O}$ . <sup>b</sup>  $\geq 2.5$  equiv of  $\text{Cl}_2\text{O}$ .

mL) was added to *p*-nitrotoluene (33.3 g, 0.243 mol) in  $\text{CCl}_4$  (30 mL). After 96 h at room temperature, water and solvent were removed to give *p*-nitrobenzotrithloride (58.8 g, 99% purity, yield 99.8%). At 75 °C the reaction affords an equivalent yield in about 3 h.

The relative rate constants for introducing the first, second, and third chlorines into *p*-nitrotoluene at 30 °C are 1.0, 1.35, and 0.9, respectively. These nearly equivalent rates sharply contrast with the normal decreasing order of benzylic hydrogen reactivities toward electrophilic radicals:  $\text{CH}_3 > \text{CH}_2\text{Cl} \gg \text{CHCl}_2$ .<sup>4</sup> Although  $\text{Cl}_2\text{O}$  is exceptionally reactive, the chlorinations of *p*-nitroethylbenzene and 5-nitroindan (Table I) illustrate its remarkable selectivity for the replacement of benzylic hydrogens.

We have probed the mechanistic aspects of the  $\text{Cl}_2\text{O}$  reactions using isotope effects, free-energy relationships, and related kinetic studies. The kinetic deuterium isotope effect determined with 4-nitrobenzyl chloride- $\alpha$ - $d_1$  is substantial ( $k_{\text{H}}/k_{\text{D}} = 9.1$  at 55 °C in  $\text{CCl}_4$ ). Although the comparative isotope effect for the reaction with  $\text{Cl}_2$  in  $\text{CCl}_4$  could not be determined at 55 °C because of unreactivity, our value at 165 °C ( $k_{\text{H}}/k_{\text{D}} = 1.7$ ) compares favorably with literature data for the chlorinations of toluene- $d_1$  ( $k_{\text{H}}/k_{\text{D}} = 1.30$ ) and *p*-chlorotoluene- $d_1$  ( $k_{\text{H}}/k_{\text{D}} = 1.44$ ) with  $\text{Cl}_2$  in  $\text{CCl}_4$ .<sup>10</sup> The linear free energy relationships found for the chlorination of 4-substituted benzal chlorides and toluenes by  $\text{Cl}_2\text{O}$  ( $\rho = -0.76$  and  $-0.9$ , respectively; cf. Tables II and III) reveal a polar effect similar in magnitude to that reported for hydrogen abstraction from toluenes by chlorine radical in  $\text{CCl}_4$  at 40 °C ( $\rho = -0.7$ ).<sup>11</sup>

These results are consistent with a free-radical process involving hydrogen abstraction by  $\text{ClO}\cdot$  radical. The comparative isotope effects indicate more bond breaking and a more symmetrical transition state for hydrogen abstraction by  $\text{ClO}\cdot$  than by  $\text{Cl}\cdot$ .<sup>12</sup> The transition state for attack by  $\text{ClO}\cdot$  therefore has appreciably more benzylic free radical character than that for attack by  $\text{Cl}\cdot$ . (The apparent anomaly of similar  $\rho$  values yet widely different isotope effects for benzylic chlorinations is explained at least in part by the significantly greater electronegativity of  $\text{Cl}\cdot$  vs.  $\text{ClO}\cdot$ .<sup>13</sup>) The similar reactivity of the benzylic hydrogens in *p*-nitrotoluene and *p*-nitrobenzyl and -benzal chlorides toward  $\text{ClO}\cdot$  in fact indicates that radical stability effects can be at least as important as polar effects. This contrasts with attack by  $\text{Cl}\cdot$ , which is dominated by polar effects.<sup>4</sup>

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(12) The assumption that transition-state symmetry and large isotope effects are related, however, has been challenged. See, for example: Motell, E. L.; Boone, A. W.; Fink, W. H. *Tetrahedron* **1978**, 34, 1619.

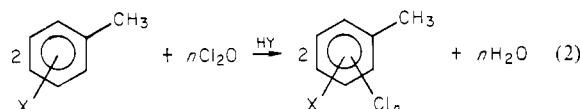
(13) Lee, L. C.; Smith, G. P.; Moseley, J. T.; Cosby, P. C.; Guest, J. A. *J. Chem. Phys.* **1979**, 70, 3237.

**Table V.** Chlorination of Toluene

reagent	chlorotoluene, %		
	ortho	para	meta
$\text{Cl}_2\text{O}/\text{TFA}^a$	71	29	ca. 0.1
$\text{Cl}_2/\text{HClO}_4/\text{AgClO}_4^b$	75	23	2.2
$\text{Cl}_2/\text{HOAc}^c$	60	40	0.5

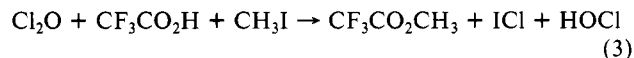
<sup>a</sup> This work. <sup>b</sup> Reference 14. <sup>c</sup> Reference 18.

A new and powerful reagent that gives exclusive ring chlorination of deactivated aromatics in high yields at 0–50 °C is produced if a strong protic acid ( $\text{p}K_{\text{a}}(\text{HY}) \leq \text{p}K_{\text{a}}(\text{CF}_3\text{CO}_2\text{H})$ ) is added to the  $\text{Cl}_2\text{O}$  reaction medium (eq 2).



In comparison with known reagents<sup>14–18</sup> and from the representative chlorinations shown in Table IV, this reagent is among the most reactive and selective known for chlorination of deactivated ring systems. The degree of chlorination is controlled by the quantity of  $\text{Cl}_2\text{O}$  employed, although mono- and perchlorinated products are normally the most easily isolated and purified.<sup>19</sup> The large  $\rho$  value of  $-7.8$  obtained for monochlorination of a series of 4-substituted toluenes by  $\text{Cl}_2\text{O}$  in  $\text{CF}_3\text{CO}_2\text{H}$  at 25.0 °C and the observed regioselectivity (Table V) are consistent with electrophilic aromatic substitution.

The electrophilic species produced from  $\text{Cl}_2\text{O}$  and strong acids has limited stability at room temperature and has not been characterized. The “substitutive electrophilic dehalogenations” we have observed with alkyl halides (eq 3) are similar to those reported for perfluoroalkylsulfonyl hypohalites.<sup>20</sup> This suggests the possible intermediacy of acid hypohalites in the electrophilic chlorinations (eq 4).<sup>21</sup>



We are continuing to investigate this possibility as well as the scope, limitations, and further mechanistic aspects of these new reactions.

**Registry No.** *p*-Nitrotoluene, 99-99-0; 3,4-dinitrotoluene, 610-39-9; *p*-cyanotoluene, 104-85-8; methyl *p*-tolyl sulfone, 3185-99-7; *p*-nitroethylbenzene, 100-12-9; 5-nitroindan, 7436-07-9; nitrobenzene, 98-95-3; dimethyl terephthalate, 120-61-6; dichlorine monoxide, 7791-21-1; *p*-nitrobenzo trichloride, 3284-64-8; 3,4-dinitrobenzo trichloride, 76213-13-3; *p*-cyanobenzo trichloride, 2179-45-5; 1-(trichloromethyl)-4-(methylsulfonyl)benzene, 76213-17-7; 1-(1,1-dichloroethyl)-4-nitrobenzene, 76213-14-4; 1,1,3,3-tetrachloro-5-nitroindan, 76213-19-9; 2-chloro-4-

(14) Norman, R. O. C.; Radda, G. K. *J. Chem. Soc.* **1961**, 3610.

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(17) Ballester, M.; Molinet, C.; Castaner, J. *J. Am. Chem. Soc.* **1960**, 82, 4254.

(18) Brown, H. C.; Stock, L. M. *J. Am. Chem. Soc.* **1957**, 79, 5175.

(19) In a representative experiment,  $\text{Cl}_2\text{O}$  (6.3 g, 0.073 mol) in  $\text{CCl}_4$  (68 mL) was added dropwise to *p*-nitrotoluene (2.5 g, 0.018 mol) in  $\text{CF}_3\text{SO}_3\text{H}$  (10.9 g, 0.072 mol) with cooling to maintain the reaction at 35–45 °C. After being stirred for 3 h at room temperature, the mixture was poured onto ice and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic extract was washed with 5% aqueous  $\text{NaHCO}_3$ , dried, and concentrated to give a white solid which was recrystallized from acetone–water to give 4.8 g (97% yield) of pure 2,3,5,6-tetrachloro-4-nitrotoluene.

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nitrotoluene, 121-86-8; 2,3,5,6-tetrachloro-4-nitrotoluene, 22490-21-7; pentachloronitrobenzene, 82-68-8; dimethyl tetrachlorophthalate, 20098-41-3; *p*-chlorotoluene, 106-43-4; methyl *p*-toluate, 99-75-2; *p*-(trifluoromethyl)toluene, 6140-17-6;  $\alpha,\alpha$ -dichloro-*p*-nitrotoluene, 619-78-3; 1-(dichloromethyl)-4-(trifluoromethyl)benzene, 82510-98-3; *p*, $\alpha$ , $\alpha$ -trichlorotoluene, 13940-94-8; toluene, 108-88-3; *o*-chlorotoluene, 95-49-8.

## Phospholipids Chiral at Phosphorus. 2. Preparation, Property, and Application of Chiral Thiophospholipids<sup>1</sup>

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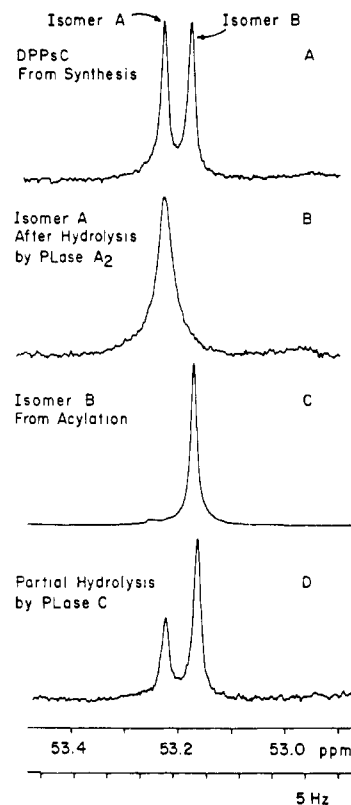
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Recently we have reported the synthesis of chiral [<sup>18</sup>O]<sub>1</sub>1,2-dipalmitoyl-*sn*-glycero-3-phosphorylcholine (DPPC) and its application in studying the stereochemistry of transphosphatidyl transfer catalyzed by phospholipase D.<sup>2</sup> By similar procedures, we have synthesized chiral [<sup>17</sup>O]<sub>1</sub>DPPC (as separate diastereomers and mixture), which are potentially useful in the chemical and physical study of the conformation and the motion of the phosphate head group of phospholipids in different phases and in protein-lipid interactions.<sup>3-5</sup>

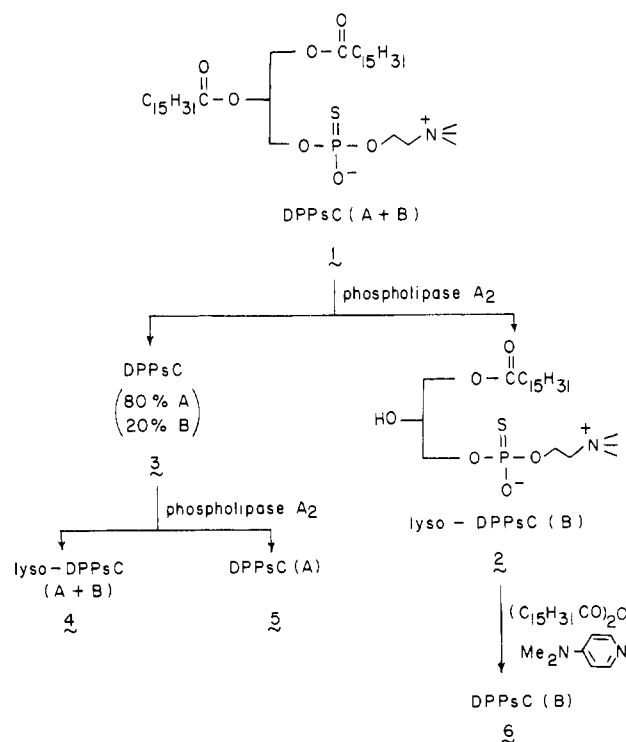
However, [<sup>18</sup>O]<sub>1</sub>DPPC is useful only for phospholipases C and D and not for other phospholipases. Also, the <sup>17</sup>O NMR study of [<sup>17</sup>O]<sub>1</sub>DPPC is difficult in vesicles or lipid bilayers<sup>7</sup> due to large line widths and quadrupolar splittings. As an alternative and complementary approach, we now report synthesis and application of separate diastereomers of 1,2-dipalmitoyl-*sn*-glycero-3-thiophosphorylcholine (DPPsC).

The diastereomeric mixture of thiophospholipids (random configuration at both C-2 and P) has been synthesized recently<sup>8</sup> but has not been resolved into separate diastereomers either chemically or spectroscopically. Following the procedure of Nifant'ev et al.,<sup>8a</sup> we have synthesized DPPsC (**1**) from (*S*)-(-)-1,2-dipalmitin (synthesized from D-mannitol<sup>9</sup>). The structures of synthetic intermediates and the final DPPsC have been characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and TLC, which are consistent with literature data.<sup>8</sup> <sup>31</sup>P NMR analysis of **1** in CDCl<sub>3</sub> (Figure 1A) showed two separate peaks due to two diastereomers (isomer A, lower field; isomer B, higher field). It was found that phospholipase A<sub>2</sub> (bee venom, Sigma, 1500 units/mg) preferentially hydrolyzes isomer B of DPPsC, which provides a convenient



**Figure 1.** <sup>31</sup>P NMR spectra (81.0 MHz) of DPPsC (10 mM in CDCl<sub>3</sub>): (A) mixture of diastereomers from chemical synthesis; (B) pure isomer A recovered from hydrolysis by phospholipase A<sub>2</sub>; (C) pure isomer B (containing 3% isomer A) obtained from acylation of the product of phospholipase A<sub>2</sub> hydrolysis, lyso-DPPsC; (D) DPPsC after partial hydrolysis by phospholipase C. NMR parameters: spectral width 1000 Hz; acquisition time 4.1 s; <sup>1</sup>H decoupling; line broadening 0.1 Hz; pulse width 12  $\mu$ s (90° pulse at 20  $\mu$ s); number of scans 500 (A, D), 1000 (B), 2600 (C); temperature 30 °C. Chemical shifts are referenced to external 1 M H<sub>3</sub>PO<sub>4</sub>, with + indicating a downfield shift.

### Scheme I. Separation of Diastereomers of DPPsC



way to separate the two diastereomers, as outlined in Scheme I. Hydrolysis of DPPsC(A + B) in a mixture of 0.1 M Tris buffer

(1) Supported by a grant from NIH (GM30327) and in part by a grant from NSF (PCM 8140443). The NMR spectrometers used were funded by NIH GM 27431 and NSF CHE 7910019. The <sup>14</sup>N NMR was obtained with the help of Dr. C. Cottrell. Abbreviations used: NMR, nuclear magnetic resonance; DPPC, 1,2-dipalmitoyl-*sn*-glycero-3-phosphorylcholine; DPPsC, 1,2-dipalmitoyl-*sn*-glycero-3-thiophosphorylcholine; MOPS, 3-[N-morpholino]propanesulfonic acid; Tris, 2-amino-2-hydroxymethyl-1,3-propanediol; Pi, inorganic phosphate; IR, infrared spectrum; TLC, thin-layer chromatography.

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(4) The <sup>17</sup>O NMR signal of [<sup>17</sup>O]<sub>1</sub>DPPC broadens from 440 Hz in CH<sub>3</sub>OD (100 mg in 1.5 ml) to 3250 Hz in CDCl<sub>3</sub> (at 33 °C) (ref 5) as a result of the micelle formation in chloroform (ref 6). This can best be explained by a 7.4-fold increase in the rotational correlation time  $\tau_r$  of phosphoryl oxygens, which suggests a restriction in the motion of the phosphate group upon aggregation, which is consistent with the recent finding in the restricted motion of the choline side chain due to aggregation (ref 6a).

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(7) We have so far not been able to observe any <sup>17</sup>O NMR signal of a sonicated or unsonicated dispersion of [<sup>17</sup>O]<sub>1</sub>DPPC in water. A possible solution would be to prepare oriented lipid bilayers.

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