surprisingly, Co(Cap)(1-MeIm) is an even worse dioxygen binder than the simple model complex CoT(p-OCH$_3$)PP(1-MeIm), The presence of oxygen-oxygen stretching bands in the infrared spectra of the Co and Fe dioxygen complexes attributable to $\nu_{^{16}O_2}$ and $\nu_{^{18}O_2}$ confirms that oxygenation has occurred.[12]

There are several possible factors which could produce the lower dioxygen affinities found for the "cap" complexes, and they include the following: (1) unfavorable steric interactions between the bound dioxygen and porphyrin cap, (2) an increase in the conformational strain energy of the "cap" porphyrin upon oxygenation, (3) the absence of stabilizing solvent or environmental interactions for the bound dioxygen, and (4) electronic substituent effects. Previous studies,[13,14] however, have shown that factor 4 has relatively little effect on dioxygen binding to cobalt(II) and manganese(II) para-substituted tetraphenylporphyrins.

In order to further clarify the situation, the "homologous cap" porphyrin complexes were investigated. The unusual properties of Fe(HmCap) are more fully discussed in an accompanying communication, but it should be noted that both Fe(HmCap)B and Co(HmCap)B (B = 1-MeIm or 1,2-Me$_2$Im) are significantly worse dioxygen carriers than the corresponding "cap" compounds. This surprising result then strongly suggests that factor 2 above is primarily responsible for the variation in dioxygen affinities; factors 1 and 3 are less likely explanations, since the environments of the bound dioxygen in both the "cap" and "homologous cap" complexes should be similar, and also the size of the dioxygen binding pocket in the latter should be greater than in the former.

For measurements of base addition constants (K^B), Fe(Cap) has a great advantage over other ferrous porphyrins because K^B can be determined directly, instead of having to be estimated.[15] The data in Table I shows Fe(Cap) to be a poorer base binder compared with Fe(HmCap) and other related model complexes. A similar situation exists for cobalt, although, in this case, both Co(Cap) and Co(HmCap) have comparable K^B values. It is noteworthy that, for 1-MeIm and 1,2-Me$_2$Im binding to Fe(Cap) and Fe(HmCap), the latter sterically hindered base is the better ligand. This has also been noted[7] for another model system. For cobalt porphyrin complexes, however, the reverse is found. These trends may be attributed to the following factors: (a) the greater basicity of 1,2-Me$_2$Im compared with 1-MeIm and (b) the greater porphyrin-axial base steric interactions for the cobalt complexes, which have a shorter P_c to metal distance.[16]

As shown in Figure 1, the "cap" and "homologous cap" porphyrins differ only in that the latter contains an extra methylene group in each of the porphyrin straps. Yet, there are pronounced differences in both the base and dioxygen binding properties of their complexes. These differences appear to be intimately associated with the nature of the cap and with the porphyrin system's ability to accommodate the conformational changes which occur upon addition of base and dioxygen.[19-22]

For the extrapolation to Hb cooperativity, it is apparent that the above discussion is closely related to the porphyrin "doming" concept mentioned[10] earlier. This work strongly supports the viability of such a mechanism, although it does not necessarily require that the porphyrin be constrained to a "domed" configuration. It would be sufficient for the nonbonding protein-heme interactions in T-state Hb to oppose the porphyrin conformational changes which occur upon oxygenation. A more complete understanding of the "cap" and "homologous cap" porphyrin systems must await the elucidation of their respective structures and at present we are attempting to grow suitable crystals for X-ray analysis.

Acknowledgment. This work was supported by grants from the National Institute of Health and the National Science Foundation.

References and Notes

(1) Abbreviations: Hb, hemoglobin; Cap, cap porphyrin; HmCap, homologous cap porphyrin; TPP, *meso*-tetraphenylporphyrinato; TpivPP, *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-$o$-pivalimidophenyl)porphyrinato; Tripiv(4CIm), *meso*-tri(α,α,α-o-pivalimidophenyl)-β-3-(N-imidazolyl)propylamidophenylporphyrinato; T(p-OCH$_3$)PP, *meso*-tetra(p-methoxyphenyl)porphyrlnato; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; 1,2-Me$_2$Im, 1,2-dimethylimidazole; t-BuNH$_2$, *tert*-butylamine; K^B, the equilibrium constant for the base addition, M(porphyrin) + B $\rightleftharpoons$ M(porphyrin)B; $K_B^{O_2}$, the equilibrium constant for the uptake of dioxygen, M(porphyrin)B + O$_2$ $\rightleftharpoons$ M(porphyrin)BO$_2$; $P_{1/2}^{O_2}$, the O$_2$ pressure at half saturation; P_c, the 24-atom porphyrinato plane.

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Optically Active Poly(triphenylmethyl methacrylate) with One-Handed Helical Conformation

Sir:

It has been pointed out that a vinyl polymer obtained from an achiral monomer, CH$_2$=CXY, can not be optically active to a measurable extent even if it is highly isotactic.[1,2] The basis for this reasoning is that, except for the carbon atoms located near the ends of the polymer chain, each asymmetric carbon which is formed in the process of the polymerization becomes "pseudo" asymmetric after the polymer grows to a long chain. This is also recognized in the vinyl polymers which have asymmetric terminal groups deriving from optically active

Table I. Polymerization of TrMA by II and III in Toluene[a]

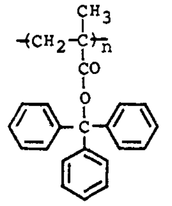
						THF-soluble polymer				THF-insoluble polymer, yield, %
								$[\alpha]^{20}_D$, deg		
run	initiator	solvent	temp, °C	time, h	yield, %	yield, %	$\overline{DP}$[b]	in THF	in toluene	
1	II	toluene	−78	2.9	73	72	62	−70	−85	1
2	II	THF	−78	2.3	93	93	21	−82	−104	0
3	III	toluene	−40	2.0	100	100	42	+262	+363	0
4	III	toluene	−62	0.7	66	61		+278	+380	5
5	III	toluene	−62	2.4	100	49		+334	c	51
6	III	toluene	−78	1.0	25	25	35	+137	+193	0
7	III	toluene	−78	2.0	41	41	48	+190	+258	0
8	III	toluene	−78	3.5	55	54	58	+254	c	1
9	III	toluene	−78	5.2	90	18	43	+245	c	72[d]
10	III	THF	−78	2.4	100	100	21	+7	+10	0

[a] Monomer/solvent, 1/20 (g/mL); [catalyst]/[monomer], 1/20 (mol/mol). [b] Degree of polymerization which was estimated from gel permeation chromatogram of the PMMA derived from poly(TrMA).[16] [c] A part of the polymer was insoluble in toluene. [d] The $\overline{DP}$ estimated by GPC was 74.

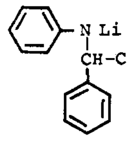
initiators.[3-7] However, there will be a possibility of yielding an optically active polymer when a polymerization proceeds with forming a tightly coiled helix of polymer and the helix is sufficiently stable in solutions.[8] The only example of the polymer of this type so far reported is poly(*tert*-butyl isocyanide) $[{>}C{=}NC(CH_3)_3]_n$,[9] though it is not a vinyl polymer.

We have reported that the copolymer of triphenylmethyl methacrylate (TrMA) with a small amount of (*S*)-1-phenylethyl methacrylate showed a large positive optical rotation which was opposite in sign to that of poly[(*S*)-1-phenylethyl methacrylate].[10,11] This abnormal optical rotation was attributed to the helical conformation of the isotactic TrMA sequence preferential in one screw sense which was formed in the process of the polymerization. TrMA yields a highly isotactic polymer even in tetrahydrofuran (THF) by butyllithium (*n*-BuLi), because the bulky triphenylmethyl group prevents the addition of the monomer to the growing chain end in a syndiotactic manner.[12]

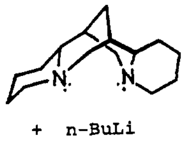
In this communication, we describe the preparation of optically active polymers (I) of TrMA. We used lithium (*R*)-*N*-(1-phenylethyl)anilide (II)[13] and (−)-sparteine-*n*-BuLi(III) complex[14] as chiral catalysts. The former catalyst gave a polymer whose chirality was induced by the catalyst fragment attached to the polymer end, and the latter produced the polymer which contained no chiral component but had a chirality caused only by helicity.



I



II



III

The results of the polymerization of TrMA are shown in Table I. During the polymerization, generally the reaction mixture was homogeneous in appearance, although it formed gel at the final stage of the polymerization under the conditions employed. However, it became turbid when the mixture was warmed to room temperature after the complete conversion of the monomer, and after the precipitation in methanol a part of the polymer was insoluble in THF and toluene. Poly(TrMA) of high molecular weight was insoluble in common organic solvents. Therefore, the polymer was separated into THF-soluble and -insoluble parts and the optical rotation was measured in THF and in toluene. Optically active polymers were obtained with both the initiators. The polymers prepared with initiator II showed negative specific rotations which were much greater than the rotation expected from the chiral fragment of II probably attached to the polymer as an end group. On the other hand, the polymers obtained with catalyst III in toluene showed very large positive rotations in spite of the absence of asymmetric components in the molecules. The polymer produced with catalyst III in THF exhibited only low specific rotation, probably because the sparteine moiety of the catalyst did not affect the polymerization as much in the polar solvent. Poly(methyl methacrylate)s (PMMAs) derived from these poly(TrMA)s showed very small rotation ($[\alpha]^{20}_D$ 0 ± 2° in toluene).[15]

The polymerization was carried out in a 1.0-cm cell with III in toluene under the conditions shown in runs 4 and 5, and the change of the optical rotation of the reaction mixture was followed along with the progress of the polymerization. The rotation was approximately zero at first, but began to increase gradually after ~10 min and reached a constant value in 2 h. It was found that the optical rotation α^{-62}_D of the reaction mixture was +1.66° at 66% conversion and +2.75° at complete conversion. These values correspond to the specific rotations $[\alpha]^{-62}_D$ +444 and +490°, respectively, indicating that the $[\alpha]^{-62}_D$ of the polymer yielded after 66% conversion amounted to about +580°.

The ^1H NMR spectra of the PMMAs derived from the THF-soluble and -insoluble poly(TrMA)s were identical with the spectrum of typical isotactic PMMA. One exception was the existence of a very small peak due to the terminal butyl group in the spectrum of the lower molecular weight polymer. The values of isotactic triad fractions were very high and appeared to be nearly 100%.

The large optical rotations of these poly(TrMA)s must be attributed to the helicity of the rigid isotactic TrMA sequence, because the PMMAs derived from these polymers showed almost no optical rotation. The specific rotation of poly(TrMA) seems to increase with increasing molecular weight of the polymer, if the polymer is prepared by III in toluene, and the rotation of the THF-insoluble part may be greater than that of the THF-soluble one. In the polymerization with II, the content of the prevailing helix may be determined only in the initiation reaction. Therefore, it is expected that the content will not increase as the polymerization proceeds. On the other hand, in the polymerization with III, the content of the prevailing helix may increase with the progress of the reaction because chiral (−)-sparteine always exists around the growing end. This may be one of reasons why III gave the polymer of higher optical rotation.

The polymer of high molecular weight showed very clear polarization under a polarized microscope. Probably the polymer has high crystallinity.

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Onium Ions. 19.[1] Chloromethylhalonium Ions

Sir:

In our search for nonvolatile and, therefore, safer chloromethylating agents, we report here the first preparation and study of previously unknown chloromethylhalonium ions.

When dichloromethane is dissolved in a twofold molar excess of antimony pentafluoride in sulfuryl chloride fluoride solution at −130 °C, the bis(chloromethyl)chloronium ion (**1**) is formed. The NMR parameters of **1** are given in Table I.

$$[ClCH_2\overset{+}{Cl}CH_2Cl]\,Sb_2F_{10}Cl^-$$

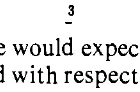
1

When sulfur dioxide is added to a solution of **1**, it forms chloromethylated sulfur dioxide **2**, whose ^1H and ^{13}C NMR

$$[ClCH_2\text{-}\overset{+}{O}=S=O]\,Sb_2F_{10}Cl^-$$

2

shifts are δ_H 7.0 (s) and δ_C 88.8 (t), $J_{C\text{-}H}$ = 102.1 Hz. That no chloromethylated SO_2ClF (**3**) is formed in the solution of **1** in SO_2ClF is apparent from the fact that, if **3** were the ob-



$$ClCH_2\text{-}\overset{+}{O}=\underset{F}{\overset{Cl}{S}}=O$$

3

served species, then one would expect its ^{13}C chemical shift to be ~15 ppm deshielded with respect to the ^{13}C shift of **2**, as is the case in the $CH_3F\text{-}SbF_5$ system in SO_2 and SO_2ClF.[2] Since the opposite trend is noted, **1** must be the observed species, in accord with the fact that CH_2Cl_2 is a better nucleophile than SO_2ClF.

Table I. ^1H and ^{13}C Parameters of Chloromethylmethyl- and Bis(chloromethyl) Halonium Ions

	δ—CH_2—		δ—CH_3	
ion	^1H	^{13}C ($J_{C\text{-}H}$)[b]	^1H	^{13}C ($J_{C\text{-}H}$)
1	7.0	78.5 (194.0, t)		
4	6.8	69.0 (193.6, t)		
5	6.3	37.8 (186.8, t)		
6	6.3	80.4 (191.2, t)	4.3	50.7 (162.3, q)
7	6.2	69.4 (190.8, t)	4.1	39.3 (162.0, q)
8	6.0	38.6 (185.2, t)	3.8	12.2 (158.5, q)

[a] In parts per million from external Me_4Si capillary in SO_2ClF at −90 to −100 °C. [b] t = triplet, q = quartet. $J_{C\text{-}H}$ in Hz.

Ions **1** and **2** are stable up to −85 °C in $SbF_5\text{-}SO_2ClF$ solution, above which temperature they form difluoromethane.

A series of additional chloromethylhalonium ions were prepared by treating ion **1** with several monohalo- and dihaloalkanes. The ^1H and ^{13}C NMR parameters of the chloromethylhalonium ions formed are given in Table I. Halonium ions **4** and **5** were formed by treating **1** with bromochloromethane and chloroiodomethane, respectively (reaction 1). The bis(chloromethyl)iodonium ion **5** could also be prepared from $ClCH_2I$ and $HF\text{-}SbF_5$ in SO_2 solution at −50 °C, but attempts to prepare the related bromonium ion **4** in a similar way gave a complex mixture of products.

$$\underset{\sim}{1} + ClCH_2X \xrightarrow[-130°C]{SO_2ClF} ClCH_2\overset{+}{X}CH_2Cl \qquad (1)$$

4, X = Br
5, X = I

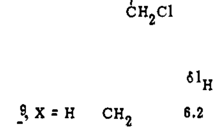
Chloromethylmethylhalonium ions **6**, **7**, and **8** were also prepared by similar methods (reaction 2). It is interesting to note that the difference between J_{CH} in bis(chloromethyl)halonium ions and the coresponding dimethylhalonium ions is uniformly 30 Hz.[3] The same trend is also observed in the chloromethylmethyl halonium ions **6**, **7**, and **8** and between **2** and $[CH_3O{=}S{=}O]^+$.

$$\underset{\sim}{1} + CH_3X \xrightarrow[-130°C]{SO_2ClF} CH_3\overset{+}{X}CH_2Cl \xleftarrow[-130°C]{SO_2ClF} CH_3F{:}SbF_5 + ClCH_2X \qquad (2)$$

6, X = Cl
7, X = Br
8, X = I

X = Cl,Br,I

When dimethyl or chloromethylmethyl ether was added to a solution of **1**, oxonium ions **9** and **10** were formed (reaction 3). Attempts to prepare ions **9** and **10** by methylating[4] chloromethylmethyl ether or bis(chloromethyl) ether (eq 4) gave complex mixtures of ions, which did not include either **9** or **10**. Ions **11** and **12** were the major products obtained in each reaction.[5] Ion **11** was also a byproduct in reaction 3.



(3)

		δ^1H	$\delta^{13}C$	J_{CH}
9, X = H	CH_2	6.2	94.9	188.4 Hz
	CH_3	4.6	77.0	158.1
10, X = Cl	CH_2	6.5	92.7	188.0
	CH_3	4.9	76.0	159.2

$$CH_3F{:}SbF_5 + XCH_2OCH_2Y \xrightarrow[-78°C\ \text{to}\ -120°C]{SO_2\ \text{or}\ SO_2ClF} CH_2{=}\overset{+}{O}\text{-}CH_2Y \qquad (4)$$

X = Cl, Y = H
X = Y = Cl

11, Y = H
12, Y = Cl

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