under the conditions used here. $F_2PPF_2 \cdot BH_3(g)$ is relatively stable but undergoes slow decomposition involving both cleavage of the P–P bond and shift of a fluorine. The equation describing the process is

$$F_2PPF_2 \cdot BH_3 \longrightarrow F_3PBH_3(g) + PF(s)$$

The solid yellow $(PF)_n$ is presumably polymeric. No evidence for decomposition to $P_2F_4(g)$ and $B_2H_6(g)$ was observed. It is also significant that F_2PPF_2, in sharp contrast to the related fluorides of nitrogen,[3] reacts smoothly and nonexplosively with diborane.

A 1.03-mmole sample of B_2H_6 (Callery Chemical Co.) was frozen into a 50-ml bulb on the vacuum line. A 1.04-mmole sample of P_2F_4[1] was frozen into a second evacuated 250-ml bulb, connected to the first bulb through a stopcock. With the stopcock closed between the two, the P_2F_4 and B_2H_6 were allowed to vaporize and warm to room temperature. The vapors were then allowed to mix by opening the stopcock between the units. After 3–4 hr at 25°, the gaseous mixture was passed through traps held at -85, -100, and $-196°$. The $P_2F_4 \cdot BH_3$ retained in the $-100°$ trap was further purified by opening the $-100°$ trap to a $-196°$ trap for 20–36 hr. The product, a white crystalline solid at $-100°$, represented a 30% conversion of P_2F_4 to $P_2F_4 \cdot BH_3$. The molecular weight as determined by vapor density was 155 (calculated for $F_4P_2 \cdot BH_3$: 152); H^- (by hydrolysis in acid solution): $3.1 H^-/P_2F_4 \cdot BH_3$. Vapor pressure data were not obtained because of decomposition in the liquid phase to PF_3BH_3 and its decomposition products, but the product is sufficiently volatile to pass through a trap at $-85°$.

Major mass spectrometer peaks given as mass number (tentative assignment) and relative abundance are: 152 $(P_2F_4 \cdot BH_3^+)$, 1.67; 138 *$(P_2F_4^+)$, 8.15; 119 *$(P_2F_3^+)$, 5.71; 83 $(F_2PBH_3^+)$, 8.05; 82 $(F_2PBH_2^+)$, 11.0; 81 $(F_2P^{10}BH_2^+$ and $F_2P^{11}BH^+)$, 3.43; 80 $(F_2P^{10}BH^+)$, 1.55; 69 *(F_2P^+), 100; 50 *(PF^+), 24.5; and 31 *(P^+), 25.6. Much of the pattern (marked by an asterisk) is identical with that for P_2F_4. The over-all pattern is consistent with the formula assigned. Infrared absorptions are listed as [frequency, cm^{-1} (probable assignment), and intensity]: 2432 (ν_{B-H}), m br; 1102 (δ_{B-H}), w; 1042 (δ_{B-H}), m; 902 $(\nu_{as, P-F})$, vvs br; 850 $(\nu_{sym,P-F})$, s; 727 (ρ_{BH_3}) m; 670–680 (?), w, br; 598 $(\nu_{P-B}?)$, w; 442 (δ_{F-PF}), vw, 395 (τ_{B-P}), w; 370 (δ_{F-P-F}), wm. The spectrum of the solid shows resolution of the B–H stretching region near 2400 cm^{-1} into two distinct peaks as expected. (The symbols used above are defined as follows: ν = stretch, δ = deformation, ρ = rocking, τ = torsional.) The ^{11}B nmr taken at $-80°$ on the neat liquid shows a quartet with $J_{B-H} = 101$ cps and δ (relative to B-(OCH$_3$)$_3$) equal to 60 ppm.

No splitting of the ^{11}B signal by phosphorus is observed, whereas other compounds containing a B–P bond of comparable stability show a definite doublet pattern.[2] Broadening of the ^{11}B signal suggests that rapid exchange of the BH$_3$ moiety between phosphorus atoms might be occurring. More detailed analysis of the ^1H, ^{19}F, and ^{31}P spectra is currently being carried out.

(3) T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, 78, 1524 (1956). No reaction of N_2F_4 with B_2H_6 is reported in the literature, but the above reference indicates an explosive reaction of NF_3 and B_2H_6.

P_2F_4 appears to be stronger as a Lewis base toward BH$_3$ than is PF$_3$; slow decomposition of $P_2F_4 \cdot BH_3$ by fluoride shift and cleavage of the P–P bond gives F_3PBH_3 which then decomposes to give significant concentrations of F$_3$P and B_2H_6. On the other hand, no P_2F_4 was ever detected in the system during decomposition, and B_2H_6 appeared only after the appearance of F_3PBH_3. These observations suggest that the B–P interaction in the adduct may be enhanced by partial double-bond interaction between phosphorus atoms in the parent P_2F_4. Such interaction would enhance the basicity of one phosphorus atom at the expense of the other and in a manner which contrasts sharply with the basicity toward BH$_3$ of other bidentate ligands such as hydrazine.

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Crystalline Catalysts Containing Al–O–Al or Zn–N–Zn Groups for Stereospecific Polymerization of Propylene Oxide

Sir:

Since the pioneering work by Price on the stereospecific polymerization of propylene oxide,[1] a large number of papers dealing with the mechanism of the polymerization as well as with the nature of catalysts have been published.[2] But, unfortunately, the ill-defined nature of catalysts and the rather low stereospecificity of polymerization make the detailed interpretation of the stereoregulating mechanism difficult. We now wish to report two types of crystalline catalyst for stereospecific polymerization of propylene oxide.[3] These catalysts are the organometallic compounds, one containing aluminum and oxygen and another zinc and nitrogen.

Bis(diethylaluminum) oxide (Et$_2$AlOAlEt$_2$, II) has been mentioned as one of the reaction products of triethylaluminum with carbon dioxide[4] or with water,[5] but has not been isolated in a pure form. It was found, by a new route according to eq 2, that exactly equimolar amounts of lithium diethylaluminate (Et$_2$AlOLi, I)[6] reacted in toluene at low temperature with diethylaluminum chloride to give bis(diethylaluminum) oxide (Et$_2$AlOAlEt$_2$, II) accompanied by the precipitation of lithium chloride in a quantitative amount.[7] This oily product disproportionated to

(1) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, 78, 690, 4787 (1956).

(2) J. Furukawa and T. Saegusa, "Polymerization of Aldehydes and Oxides," Interscience Publishers, Inc., New York, N. Y., 1963, pp 125–208; A. E. Gurgiolo, *Rev. Macromol. Chem.*, 1, 76 (1966).

(3) All experiments described in this paper were done under an atmosphere of nitrogen or argon.

(4) K. Ziegler, *Angew. Chem.*, 68, 721 (1956); K. Ziegler, F. Krupp, K. Weyer, and W. Larbig, *Ann.*, 629, 251 (1960).

(5) S. Ishida, *J. Polymer Sci.*, 62, 10 (1962); T. Saegusa, Y. Fujii, H. Fujii, and J. Furukawa, *Makromol. Chem.*, 55, 232 (1962); G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, E. I. Larikov, and A. F. Zhigach, *Zh. Obshch. Khim.*, 34, 3435 (1964).

(6) H. Tani, T. Araki, N. Oguni, and T. Aoyagi, *J. Polymer Sci.*, B4, 97 (1966).

(7) H. Tani, T. Araki, and T. Aoyagi, presented at the 13th Annual Meeting of the Society of High Polymers, Japan, May 2, 1965, Tokyo.

give a mixture of its higher homologs and triethyl-aluminum under distillation conditions, so its isolation by usual purification methods was difficult. Nevertheless, the analytical data (Anal. Calcd for $C_8H_{20}O$-Al_2: Al, 29.0; C_2H_5:Al, 2.0. Found: Al, 26.5; C_2H_5: Al, 1.9) approximate the expected values. Product II is quite similar in chemical properties and in distillation behavior to the reaction product of triethylaluminum and water in a molar ratio of 1:0.5.

$$Et_3Al + LiOH \longrightarrow Et_2AlOLi + EtH \quad (1)$$
$$\text{I}$$

$$Et_2AlOLi + Et_2AlCl \longrightarrow Et_2AlOAlEt_2 + LiCl \quad (2)$$
$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$

The 5,6-benzoquinolinate (IV) of bis(diethylaluminum) oxide was obtained in crystalline state (90% yield) when the 5,6-benzoquinolinate (III) of diethylaluminum chloride was used at room temperature instead of diethylaluminum chloride. Compound III was recrystallized from n-hexane, colorless needles, mp 43°. Anal. Calcd for $C_{17}H_{19}NClAl$: Al, 9.0. Found: Al, 9.1. Product IV was recrystallized from n-hexane, pale yellow needles, mp 75° dec. The structure of IV was confirmed by analysis (Anal. Calcd for $C_{21}H_{29}ONAl_2$: Al, 14.80; C_2H_5:Al, 2.0. Found: Al, 14.82; C_2H_5:Al, 1.9), cryoscopic molecular weight determination (benzene) (Anal. Calcd for $C_{21}H_{29}ONAl_2$: mol wt, 365. Found: mol wt, 531.4 (5.272 moles $1.^{-1}$), 475.3 (2.636 moles $1.^{-1}$), 380.4 (1.318 moles $1.^{-1}$), and 350 (extrapolated value to zero concentration)), and nmr spectra [$\delta_{C_6D_6}$ (ppm):[8] 1.69 (12.16 methyl H, triplet), 0.77 (8.00 methylene H, quartet), and 6.83–9.17 (8.91 ring H, multiplet)]. The equivalency of four ethyl groups observed by nmr study corresponds to a rapid migration of a donor between two aluminum atoms in solution. The isolation of compound IV is of value as an evidence for the actual existence of $Et_2AlOAlEt_2$ and for its acceptor property for coordination.

$$Et_2AlOLi + [Et_2AlCl]\cdot[5,6\text{-benzoquinoline}] \longrightarrow$$
$$\text{I} \qquad\qquad \text{III}$$
$$[Et_2AlOAlEt_2]\cdot[5,6\text{-benzoquinoline}] + LiCl \quad (3)$$
$$\text{IV}$$

N,N-Bis(ethylzinc)-t-butylamine (EtZnN(t-Bu)ZnEt, V) was obtained in about 35% yield by allowing 2 moles of diethylzinc and 1 mole of t-butylamine in toluene to react at 80° for 10 hr,[9] giving, recrystallized from n-heptane, colorless needles, mp 67–69°. The structure of V was confirmed by analysis (Anal. Calcd for $C_8H_{19}NZn_2$: Zn, 50.4; C_2H_5:Zn, 1.00. Found: Zn, 51.7; C_2H_5:Zn, 0.84), cryoscopic molecular weight determination (benzene) (Anal. Calcd for $C_8H_{19}NZn_2$: mol wt, 260. Found: mol wt, 264 (0.624 mole $1.^{-1}$), 260 (0.312 mole $1.^{-1}$)), and nmr spectra [$\delta_{C_6H_6}$ (ppm):[8] 1.50 (5.75 methyl H, triplet), 0.53 (4.00 methylene H, quartet), and 1.32 (9.30 t-butyl H, singlet)].

$$2Et_2Zn + t\text{-BuNH}_2 \longrightarrow EtZnN(t\text{-Bu})ZnEt + 2EtH \quad (4)$$
$$\text{V}$$

Preliminary results of the polymerization of propylene oxide by using compounds I–V are summarized in

(8) Chemical shifts (δ values) are internally standardized to benzene (7.37 ppm).
(9) This reaction is the extension of that of the aluminum analogs to the zinc compound; see H. Tani and N. Oguni, J. Polymer Sci., B3, 123 (1965).

Table I. Acetone-insoluble fractions of the polymer are confirmed to be isotactic crystalline polyethers by their infrared spectra and X-ray diffraction patterns. From this table it appears that the compounds IV and V are crystalline stereospecific catalysts and that the Zn–N–Zn compound V has a stereoregulating power far higher than that reported earlier. In addition, these compounds have well-defined structures, are soluble in hydrocarbon solvents, and therefore act as homogeneous catalysts. All these properties make these catalysts particularly suitable for mechanism studies.[10,11] Details of the polymerization mechanism concerned with the real active species are now in progress.

Table I. Polymerization of Propylene Oxide[a]

Catalyst	Rate of polymerization	Polymer Yield, %	Acetone-insoluble fraction, %[b]	[η]
I	....	0	..	....
II	Very high[c]	95	40	2.1[d]
III	....	0	..	....
IV	Low	79	45	2.6[d]
V	Low	39	81	8.3[e]

[a] Polymerization conditions: temperature, 30°; time, 7 days; solvent, toluene; catalyst, 3 mole % of monomer. [b] Fractionation was done at room temperature. [c] Spontaneous exothermic reaction. [d] 0.1–0.30 g/100 ml of benzene at 25.0 ± 0.1°. [e] 0.1–0.25 g/100 ml of benzene at 25.0 ± 0.1°.

(10) In view of the facile disproportionation of II, it may be questioned if the actual active species is II or not.
(11) The disproportionation

$$2[Et_2AlOAlEt_2]\cdot[5,6\text{-benzoquinoline}] \rightleftharpoons Et_2AlOAlEt_2 +$$
$$\text{IV} \qquad\qquad\qquad\qquad \text{II}$$
$$[Et_2AlOAlEt_2]\cdot2[5,6\text{-benzoquinoline}]$$
$$\text{VI}$$

may be assumed to exist in the polymerization system, but, in view of catalytic activity of VI (extremely low) and of II (very high), it is reasonable to conclude that the results reported in Table I may be mainly due to IV.

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Intramolecular, Long-Range Oxidations at Saturated Carbon Centers

Sir:

The past 7 years have witnessed the development of powerful new methods of organochemical synthesis by the utilization of intramolecular, free-radical decompositions of certain alcohol derivatives. Lead tetraacetate oxidation of alcohols,[1] photolysis of nitrites,[2] and thermolysis or photolysis of hypohalites[3]

(1) (a) G. Cainelli, M. L. Mihailović, D. Arigoni, and O. Jeger, Helv. Chim. Acta, 42, 1124 (1959), and subsequent papers; (b) see review by K. Heusler and J. Kalvoda, Angew. Chem., 76, 518 (1964).
(2) (a) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. Pechet, J. Am. Chem. Soc., 82, 2640 (1960), and subsequent publications; (b) see review by M. Akhtar, Advan. Photochem., 2, 263 (1964).
(3) (a) C. Meystre, K. Heusler, J. Kalvoda, P. Wieland, G. Anner, and A. Wettstein, Experientia, 17, 475 (1961), and subsequent papers; (b) see also ref 1b and 2b.