

TABLE I
 ETHYLENE-BUTENE-2 COPOLYMERIZATION

Experimental conditions: ethylene partial pressure maintained constant during the copolymerization = 100 mm.; initial partial pressure (nitrogen + butene-2 + solvent) = 750 mm.; butene-2 employed, 10 g.

Butene-2 employed	Catalyst employed		Moles butene-2/ moles transition metal	Solvent, cc.	T, °C.	Time, min.	Co-polymer obtained, g.	[η] at 135° in tetralin	Molar content butene % ^a
	Type	Moles transition metal/moles aluminum							
<i>cis</i>	VCl ₄ /Al(hexyl) ₃	1:2.5	50	<i>n</i> -Heptane, 35	-30	500	3.83	1.44	38
<i>trans</i>	VCl ₄ /Al(hexyl) ₃	1:2.5	50	<i>n</i> -Heptane, 35	-30	500	2.44	2.04	16
<i>cis</i>	V(acetylacetonate) ₃ / Al(C ₂ H ₅) ₂ Cl	1:5	64	Toluene, 30	-30	500	2.91	1.27	20
<i>trans</i>	V(acetylacetonate) ₃ / Al(C ₂ H ₅) ₂ Cl	1:5	64	Toluene, 30	-30	500	1.74	1.92	6
<i>cis</i>	δ -TiCl ₃ /Al(C ₂ H ₅) ₃	1:1	29	Toluene, 18	0	1200	0.4	n.d.	4

^a Mean values of radiochemical and infrared spectrophotometric analyses.

 TABLE II
 FRACTIONATION OF A RAW ETHYLENE-*cis*-BUTENE-2 COPOLYMER BY BOILING SOLVENTS EXTRACTION
 Molar content of *cis*-butene-2 in the raw copolymer, 41%; [η] at 135° in tetralin 1.68

	Diethyl ether extract (37.8 weight %)	<i>n</i> -Hexane extract (45.3 weight %)	<i>n</i> -Heptane extract (6.6 weight %)	Extraction residue (10.3 weight %)
Butene-2 content % per moles	50	49	12	2.5
[η] at 135° in tetralin	0.21	0.41	1.2	3.3
Crystallinity by X-rays	Low of the alternating type	High of the alternating type	Low of the polyethylene type	High of the polyethylene type

bands between 13.6 and 13.9 μ , from longer sequences of methylenic groups, are practically absent. (3) By fractionating the crude products, prepared with suitable catalytic systems, such as those prepared from vanadium tetrachloride and aluminum trialkyls, we isolated ethylene-*cis*-butene-2 alternating crystalline copolymers having a density of 0.90. They show a characteristic X-ray spectrum (see Table II and Fig. 1). The identity period along the chain axis, determined on oriented fibers, is about 9.15 Å., and the melting temperature is 130–135° (as determined by X-rays).

The high crystallinity of some alternating ethylene-butene-2 copolymers confirms the regularity of the chemical structure, and also demonstrates a high regularity of steric structure. In fact, in each monomeric unit of butene-2 two tertiary carbon atoms are present, and therefore stereoregular structures of the di-isotactic or di-syndiotactic type can be foreseen. Accurate investigations on the configurations of these crystalline polymers are in progress and will be described in other communications.

A great number of catalytic systems, and also some systems that are stereospecific only to a limited extent in the homopolymerization of α -olefins, may promote, when employed under suitable conditions, the formation of ethylene-*cis*-butene-2 alternating copolymers rich in crystallizable fractions.

Catalytic systems, which are not stereospecific in the polymerization of α -olefins, e.g., systems yielding, under the same operating conditions, completely atactic polymers of propylene (e.g., vanadium-triacetylacetonate/aluminum-diethylmonochloride) are not stereospecific in the ethylene-*cis*-butene-2 copolymerization. In fact, they promote the formation of alternating copolymers that

are either completely amorphous ($d = 0.87$) or exhibit a very low crystallinity by X-rays.

The ethylene-*trans*-butene-2 alternating copolymers, produced up to now with all the catalysts examined, are not crystalline when examined by X-rays at room temperature. This proves that steric factors may exert a remarkable influence not only on the rate of this copolymerization, but also on the steric structure of the polymer.

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 THE PHENOL OXIDATION OF A LIGAND BY
 COPPER(II)

Sir:

We have obtained evidence for rapid oxidation of the phenolic ligand 4-hydroxybenzoxazole by copper(II) in the presence of a specific complexing agent for the reduced form of the metal, copper(I). Observations which originally prompted the work reported here include (1) discrepancies between the formation constants of copper(II)-4-hydroxybenzoxazole chelates determined potentiometrically by Lane, *et al.*,² and the values which we have obtained by an identical method (Table I) and (2) the purple-brown color, characteristic of mixed

(1) This work has been supported by the U. S. Atomic Energy Commission.

 (2) T. J. Lane, A. Sam and A. J. Kandathil, *J. Am. Chem. Soc.*, **82**, 4462 (1960).

valence complexes,^{3,4} accompanied by precipitate formation, which develops when copper(II) and 4-hydroxybenzoxazole are mixed and allowed to stand for several hours.⁵ If some oxidation of the phenolic ligand occurs under these conditions, it is certainly not extensive as indicated below. However, in the presence of a copper(I) chelating agent, such oxidation is strongly promoted. This can be demonstrated by extracting an aqueous solution of the chloroform insoluble copper(II) complex of 4-hydroxybenzoxazole with a chloroform solution of 2,9-dimethyl-1,10-phenanthroline (neocuproine), a specific chelating agent for this ion.⁶ When this extraction is carried out, practically all of the copper originally present in the aqueous layer is converted into the yellow complex of copper(I) and neocuproine. It can be shown by the method of Nilsson⁷ using bis-cyclohexanone-dioxaldihydrazone that the copper was present very predominantly as copper(II) before this extraction.

Convincing evidence for the participation of 4-hydroxybenzoxazole in this oxidation-reduction reaction can be obtained by extracting aqueous solutions containing various ratios of 4-hydroxybenzoxazole:copper(II), with chloroform solutions of neocuproine. The percentage of the total copper obtained in the extract as the copper(I) chelate increases in a linear manner with increasing molar ratio of 4-hydroxybenzoxazole:copper(II) and reaches a maximum of about 90% when this ratio is unity. It is therefore clear that equimolar proportions of 4-hydroxybenzoxazole and copper(II) are involved in the oxidation-reduction reaction.

To our knowledge this is the first example of the oxidation of a phenol by a metal ion, "catalyzed" by a specific chelating agent for the reduced form of the metal ion. Because of the importance of phenol oxidation in biogenesis⁸ and the widespread occurrence of copper(II) in phenol oxidases,⁹ this type of oxidation-reduction reaction might have important biological implications.

TABLE I

CHELATE FORMATION CONSTANTS FOR COPPER(II)-4-HYDROXYBENZOXAZOLE IN 50% DIOXANE-WATER AT 25°

	Ligand: Metal Ratio		
	8:1	6:1	4:1
Log K_1	7.05	7.05	7.16
Log K_2	6.49	6.44	6.62
Log K_1 (Lane, <i>et al.</i>) ²	6.40	...	6.56
Log K_2 (Lane, <i>et al.</i>) ²	5.85	...	6.18

The neocuproine could promote this phenol oxidation (1) by chelating copper(I) and thereby

(3) I. M. Klotz, G. H. Czerlinski and H. A. Fiess, *J. Am. Chem. Soc.*, **80**, 2920 (1958).

(4) H. M. McConnell and N. Davidson, *ibid.*, **72**, 3168 (1950).

(5) Due to the high dilution, these changes, although they apparently occur, are difficult to perceive during the potentiometric titration.

(6) G. F. Smith and W. H. McCurdy, Jr., *Anal. Chem.*, **24**, 371 (1952).

(7) G. Nilsson, *Acta Chem. Scand.*, **4**, 205 (1950).

(8) D. H. R. Barton and T. Cohen, "Festschrift Arthur Stoll," Birkhauser AG., Basle, 1957, p. 117.

(9) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelates," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1952, pp. 387-392.

displacing an equilibrium involving weak complexes of copper(I) and copper(II), or (2) by removing copper ions, as copper(I), from the 4-hydroxybenzoxazole-copper(II) complex leaving behind the oxidized form of the phenolic ligand. The electron transfer in the latter process would presumably occur *via* a homolytic cleavage of the metal-oxygen bond similar to that thought to occur in the copper ion catalyzed oxidations of ascorbic acid and pyrocatechol.⁹ Taube¹⁰ has cited examples of the catalysis of oxidation-reduction reactions by ligands which stabilize preferentially the oxidized or reduced form of the metal ion.

It is unlikely that a true equilibrium is being displaced because the oxidized form of the 4-hydroxybenzoxazole, presumably a phenol free radical, would be expected to have a very short half-life and to couple readily with another such radical.⁸ For this reason we favor the latter reaction path although it is evident that the detailed mechanism remains to be elucidated.

(10) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).

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1,3,5,7-TETRACHLORO-1,3,5,7-TETRASILA-ADAMANTANE

Sir:

We have recently characterized a chlorosilane of unusual properties which tends to confirm the mechanism of chlorosilane hydrolysis postulated by Sommer, *et al.*¹ The material is believed to be a bridgehead compound of adamantane structure containing four potentially reactive sites as shown in Fig. 1. The substance was produced in a high pressure reaction of SiCl₄ and (CH₃)₃SiCl in the presence of AlCl₃. During the course of the reaction the reactor became overheated and probably reached 500° or higher. Formation of other cyclic materials under similar conditions has been reported.^{2,3} The 1,3,5,7-tetrachloro-1,3,5,7-tetrasiladamantane was isolated as impure tabular crystals showing bipyramids, with the top face well developed. The crystals appeared during the distillation of the residue between cuts of the cyclics [(CH₃)₂SiCH₂]₃ and [(CH₃)₂SiCH₂]₄. The yield was about 0.1%. The crystals were sublimed and recrystallized from toluene. The presence of one or more persistent impurities was noted, however, and tend to minimize the value of the analytical data in proving the structure.

Anal. Calcd. for Si₄C₆H₁₂Cl₄: C, 21; H, 3.5; Si, 33; Cl, 42; mol. wt., 338.4. Found: C, 24.1; H, 4.6; Si, 27.7; Cl, 43.6; mol. wt., 348.

(1) L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya and R. Pepinsky, *J. Am. Chem. Soc.*, **83**, 2210 (1961).

(2) G. Fritz, *Z. Naturforsch.*, **12b**, 123 (1957).

(3) G. Fritz, D. Habel, K. Kummer and G. Teichmann, *Z. anorg. u. allgem. Chem.*, **302**, 60 (1959).