cyclization of an alkoxy group with an aromatic nucleus. This type of cyclization also raises some attractive speculations on the biogenetic origin of some "uncommon flavonoid compounds." In view of the present results it should not be difficult to envisage that the biosynthesis of peltogynol[8] (VI), a constituent of the heartwood of *Peltogyne porphyrocardia*, and distemonanthin[9] (VII), a pigment from *Distemonathus benthaminanus*, arise from the well-known uncyclized flavonoid leucofisetinidin and quercetagentin by an analogous process.

VI   VII

VIII   IX
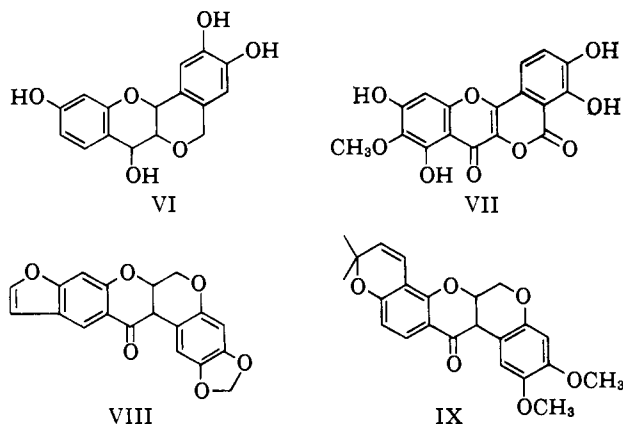
The co-occurrence of 2-methoxyisoflavonoids and rotenoids such as the rotenones dolichone[10] (VIII) and α-toxicarol[11] (IX) is again very interesting from a biosynthetic point of view. Whether isoflavonoids are the precursors of rotenoids, *via* oxidative cyclization, or *vice versa*, is still open to further investigation. Nevertheless, oxidative cyclization presents an alternative possibility to the rotenoid biogenetic scheme offered by Grisebach and Ollis.[12]

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New Synthesis of Phenylcyclopropanes

Sir:

The addition of phenyllithium to allylic chlorides in ether has been found to form phenylcyclopropanes in addition to the allylbenzenes. The ratio of the cyclopropane to the phenyl olefins varies with the structure of the allylic halide. Ratios of cyclopropane to olefins of 13:87, 19:81, and 40:60 were obtained by gas chromatography for the products from allyl chloride, crotyl chloride, and 1-chloro-5,5,7,7-tetramethyloctene-2, respectively. The cyclopropanes can be separated

from the olefins by oxidizing the latter with potassium permanganate. Phenylcyclopropane and 1-phenyl-2-methylcyclopropane were identified by comparing their migration times on a Carbowax column, and infrared and n.m.r. spectra with authentic samples. The structure assignment of 1-phenyl-2-(2,2,4,4-tetramethylpentyl)cyclopropane, which boils at 89–90° (0.29 mm.), depends on analysis (*Anal.* Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.29; H, 11.62), the n.m.r. spectra which showed no vinyl hydrogens, and the infrared spectrum which showed absorption for the cyclopropane ring at 9.72 μ.

This coupling reaction has been studied previously only with crotyl chloride and has been reported to give olefins.[1] Repetition of this work, in which the crotyl chloride was added to excess phenyllithium in ether, and examination of the products by gas chromatography indicated that 1-phenyl-2-methylcyclopropane was also formed under these conditions to the extent of 21%.

The reaction responsible for the formation of the cyclopropanes is probably similar to an SN2' reaction with attack of the phenyl carbanion occurring on the β-carbon atom instead of the γ-carbon. The resulting anion then undergoes an intramolecular reaction with displacement of the halogen. The yields obtained would indicate that steric factors are more important
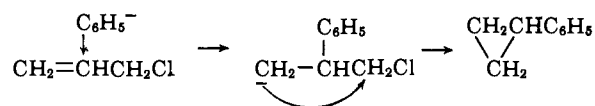
than the type of carbanion formed.

The extent to which this reaction occurs with other basic reagents is being studied further.

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Partial Head-to-Head Polymerization of Propylene Oxide by Stereospecific Catalysts

Sir:

Natta[1] has recently suggested the possibility that noncrystalline polymer chains may arise not only from atactic stereochemistry but from structural irregularities as well. We wish to report here that our investigation of the degradation of amorphous fractions of poly-(propylene oxide) prepared by certain catalysts which simultaneously produce isotactic polymers demonstrates that the irregularities in structure preventing crystallinity are largely, if not entirely, units with head-to-head structure.

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DL-Propylene oxide was polymerized with iron,[2] zinc,[3] and aluminum[4] catalysts. The crystalline and amorphous fractions were separated.[2,5] Each was then separately treated with about 50 mole % of ozone in chloroform[6] followed by lithium aluminum hydride. The dimer glycol fraction was then separated by g.l.c. into the diprimary, primary–secondary, and disecondary isomers[7] corresponding to head-to-head, head-to-tail, and tail-to-tail structural placements in the original polymer chains. The results are summarized in Table I.

Table I. Head-to-Head Structure and Optical Activity[8] of Poly(propylene oxides) from Various Catalysts

Cat.	M.p., deg.	$[\alpha]^{20}$D, deg.	% H–H glycol Exptl.	Calcd.[a]
Zn[3]	Amorph.	−4	39	42
Fe[2]	Amorph.	−10	33	30
Al[4,5]	Amorph.	−18.5	25	13[b]
KOH	56	−20	10	10
Zn	66	−25	<1	0

[a] Calcd. % H–H glycol = $2(25° - [\alpha]^{20}$D). [b] The discrepancy here may arise because the data on optical rotation were from polymer made with aluminum isopropoxide–zinc chloride,[5] the data on head-to-head structure on polymer from triethylaluminum–water.[4]

In addition to the data on head-to-head irregularities, it is possible to obtain data from D-propylene oxide on the extent of inverted centers[8] in the amorphous polymer. On the assumption that every optically inverted center entered the chain structurally inverted (i.e., as a head-to-head unit), we can calculate the number of structural irregularities from the optical rotation. The degree of agreement between head-to-head units found experimentally and calculated by this assumption (Table I) strongly supports the conclusion that optical and structural inversion occurs with a 1:1 correspondence. We may, therefore, conclude that the earlier speculation[5] suggesting that amorphous polymer from optically active monomer arose from racemization of asymmetric centers is incorrect. This also then leads us to reject coordination rearrangement at a single metal atom by an SNi mechanism as a reasonable model for this process, but at least two metals, perhaps adjacent, must be involved, a possibility we had pointed out in 1956.[5] We therefore suggest the following as a partial model for the transition state in coordination-rearrangement polymerization of an epoxide.
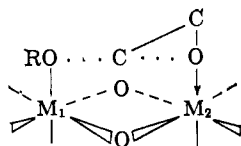
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Tsuruta[9] has presented convincing evidence that the stereoselection for isotactic polymer formation occurs at the coordination step due to asymmetry at the catalyst site, presumably from the nature of the other three ligands at the Lewis acid metal (M).

Vandenberg[4] has concluded that every ring opening in the polymerization of 2-butene oxide occurs with inversion of configuration at one carbon atom. We[10] have found the same to be true for all the catalysts mentioned in Table 1 by using cis- and trans-1,2-dideuterioethylene oxides.

We therefore conclude that every ring-opening step in epoxide polymerization by all catalysts we have so far studied proceeds with inversion of configuration at one of the ring carbons, that catalyst sites producing isotactic propylene oxide rings open by highly selective attack at the primary carbon atom, and that they produce isotactic polymer by stereoselection in the coordination step. The catalyst sites in such catalysts which produce amorphous polymer even from D-monomer must do so by virtue of relatively nonselective ring opening at either the primary carbon (to put in a D-unit) or at the secondary carbon (to put in a unit inverted both in configuration and structure).

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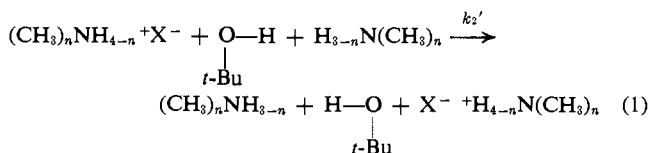
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Hydrogen-Bonded Structure of Ion Pairs of Ammonium Salts as Deduced from Proton-Exchange Rates

Sir:

We have studied the kinetics of the proton-exchange reaction (eq. 1) in t-butyl alcohol, a solvent of fairly

$$(CH_3)_nNH_{4-n}{}^+X^- + O\!-\!H + H_{3-n}N(CH_3)_n \xrightarrow{k_2'}$$
$$\overset{|}{t\text{-Bu}}$$
$$(CH_3)_nNH_{3-n} + H\!-\!O + X^- \ {}^+H_{4-n}N(CH_3)_n \quad (1)$$
$$\overset{|}{t\text{-Bu}}$$

low dielectric constant, at concentrations at which the electrolytes exist largely in the form of ion pairs.[1] This reaction follows second-order kinetics, first order each in ammonium salt and amine. The fact that the rate depends on the first power of the salt concentration precludes a mechanism involving the dissociated ammonium ion because such a mechanism requires that the rate depend on the square root of the salt concentration. The value of the second-order rate constant, k_2', depends on the nature of both the methyl-substituted ammonium ion and the anion and reveals information about the structure of their ion pairs.

Values of k_2' in t-butyl alcohol at 35° are listed in Table I. Second-order rate constants, k_2,[2-5] for the

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