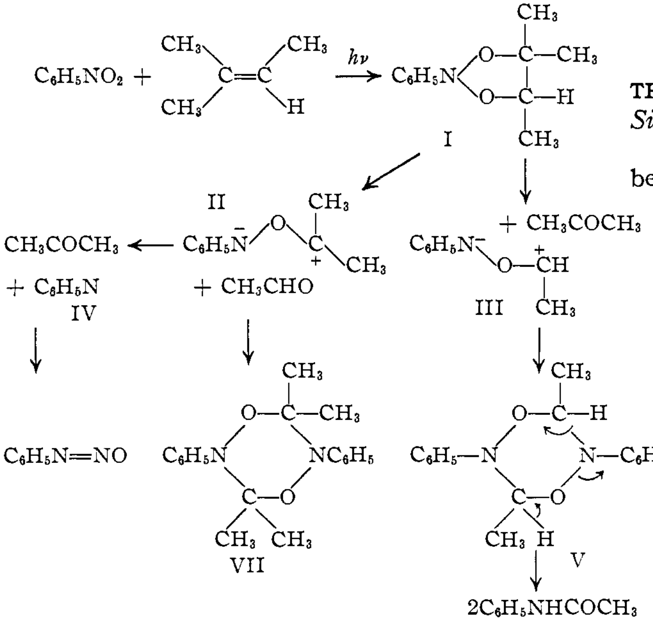
olefins as a possible synthetic route to the unknown 1,3,2-dioxazolidines (I). The reactions outlined below demonstrate that addition of nitrobenzene does indeed occur, but that the expected primary products decompose mainly to carbonyl compounds and azobenzene.

A 1:4-mixture of nitrobenzene and 2-methyl-2-butene was irradiated at room temperature with a mercury resonance arc.[3] From the volatile portion of the reaction products, acetone (2,4-DNP, m.p. 124.5–125°) and acetaldehyde (dimedone derivative, m.p. 142–143°) were isolated (12%). After removal of starting material the following compounds were isolated by chromatography of the residue: N-phenylacetamide (VI), m.p. 114–115°; azobenzene, m.p. 66° and a neutral material (VII), m.p. 169–170°, $\lambda_{\max.}$ 246 mμ (ϵ 10,600) infrared, no OH, no C=O, no C=N (*Anal.* Calcd. for $C_{18}H_{22}O_2N_2$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.40; H, 7.41; N, 9.37); mol. wt. calcd. 298, found 308. Refluxing VII with hydrochloric acid led to *p*-chloroaniline (m.p. 70–71°) and acetone (semicarbazone, m.p. 185–186°).[4]



When a 1:3-mixture of nitrobenzene and cyclohexene was irradiated, azobenzene (m.p. 66°) and adipaldehyde (dioxime, m.p. 170–172°; adipic acid, m.p. 150–152°) were formed in about 10% yield.

We wish to propose the following, mainly speculative, sequence of events to rationalize the formation of the products observed: (a) light catalyzed addition of nitrobenzene to the olefin to give intermediate I (similar to the one proposed by Splitter and Calvin, ref. 6); (b) fragmentation of I (possibly by a dark reaction) into two zwitterions (II and III) and the respective carbonyl compound, followed by (i), further decomposition to the carbonyl compounds and IV, which dimerizes to azobenzene, and (ii) dimerization of the zwitterions to the previously unreported heterocyclic derivatives (VII and V). Compound VII had no activated hydrogen atoms and might therefore be stable; V, however, decomposes into two molecules of N-phenylacetamide (VI).

The photolysis of nitrobenzene in the vapor phase has been studied and the products isolated were nitrosobenzene and *p*-nitrophenol.[5] Intramolecular, light induced oxygen transfer from nitro groups to double bonds, has been observed before.[6] The above, however, seems to be the first intermolecular change of this type reported. In conclusion we would like to point out the striking similarities between the products obtained in this oxidation and in the ozonization reaction.

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(3) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

(4) The hydrolysis of O,N-substituted hydroxylamines has been investigated by J. Meisenheimer, *Chem. Ber.*, **52**, 1667 (1919), and by R. F. Kleinschmidt and A. C. Cope, This Journal, **66**, 1929 (1944).

(5) S. H. Hastings and F. A. Matsen, This Journal, **70**, 3514 (1948).

(6) *E.g.*, the light catalyzed conversion of *o*-nitrostilbenes to isatogens, J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955), and earlier literature cited therein.

Contribution from the Department of Chemistry
Massachusetts Institute of Technology G. Buchi
Cambridge, Massachusetts D. E. Ayer

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THE POLYMERIZATION OF *l*-PROPYLENE OXIDE

Sir:

l-Propylene oxide,[1] $[\alpha]^{21}\text{D}$ +14.75° (ether), has been polymerized by shaking at 25° with powdered potassium hydroxide catalysis to produce a solid crystalline polymer, 88% yield, m.p. 55.5–56.5°, η_{sp}/c = 0.141 (0.7%, benzene, 25°), $[\alpha]^{20}\text{D}$ +25° ($CHCl_3$). *Anal.* Calcd. for C_3H_6O: C, 62.04; H, 10.41. Found: C, 62.19; H, 10.34. This is in contrast to the liquid polymer of about the same molecular weight (η_{sp}/c = 0.129) produced from racemic oxide under the same conditions.[2]

The polymerization of *l*-propylene oxide in an equal volume of ether in a sealed tube at 80° for ten days, using 1–2% of a recently disclosed ferric chloride-propylene oxide complex catalyst,[3] produced a mixture of amorphous intermediate molecular weight optically inactive polymer (30%, η_{sp}/c = 2.23) and crystalline high-molecular weight polymer (20%), m.p. 70–75°, η_{sp}/c = 10.60, $[\alpha]^{20}\text{D}$ + 23° ($CHCl_3$). The crystalline material separated from a 1–2% solution of mixed polymer in acetone on cooling to −30°.

From racemic monomer with this same iron catalyst under the same conditions, a 60% yield of amorphous and 30% yield of crystalline polymer were obtained. The latter had the same melting point, reduced viscosity, and X-ray diffraction spacings as the crystalline polymer from *l*-monomer but was optically inactive. This must mean that the racemic crystalline polymer consists of a mixture of all *d*- and all *l*-polymer molecules. The racemization involved in formation of the

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(1) P. A. Levene and A. Walti, *J. Biol. Chem.*, **73**, 263; **75**, 325 (1927).

(2) C. C. Price and L. E. St. Pierre, 128th Meeting, Am. Chem. Soc., Minneapolis, Minn., Sept. 12, 1955.

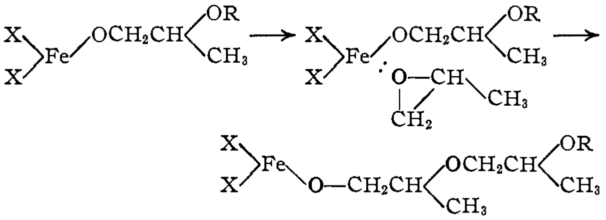
(3) M. E. Pruitt and J. M. Baggett, U. S. Patent 2,706,181, April 12, 1955.

amorphous polymer evidently occurs during polymerization since monomer recovered from a polymerization experiment after two days at 80° had lost no optical activity.

We ascribe the difference in melting point between the crystalline polymers prepared by the two catalysts to the great difference in molecular weight, since the optical rotations, infrared spectra and X-ray spacings for the two materials were identical. The principal X-ray diffraction lines at 4.25 and 5.20 Å. and the density (1.03) are consistent with a model involving a compressed *trans* zig-zag chain.

These observations further support the accumulating evidence[4] that the configuration of the asymmetric centers along a polymer chain have a remarkable influence on the physical properties and that polymerization catalysts can exert a remarkable degree of steric control on the configuration of these asymmetric centers.

The fact that amorphous polypropylene oxide of random configuration and crystalline polymer with all centers of the same configuration are formed simultaneously suggests that two different catalyst sites are present. We believe that this high degree of steric selectivity may be accounted for by a mechanism of the following type.



If the iron atom of this alcoholate were at solid surface, the steric requirements for the intermediate coördination might be rigid enough to produce oriented polymer. A soluble catalyst of similar structure might be responsible for the amorphous polymer.

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[4] C. E. Schildknecht, S. T. Gross and A. O. Zoss, *Ind. Eng. Chem.*, **41**, 1998 (1949); H. Staudinger, "Hochmolekulare organische Verbindungen," Springer, Berlin, 1932, p. 295; G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); C. W. Bunn and E. R. Howells, *ibid.*, **18**, 307 (1955).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA 4, PA.

CHARLES C. PRICE
MASEH OSGAN
ROBERT E. HUGHES
CHARLES SHAMBELAN

RECEIVED DECEMBER 21, 1955

THERMO-OSMOSIS OF RARE GASES THROUGH A RUBBER MEMBRANE[1]

Sir:

Using an apparatus similar to the "membrane assembly B" of Denbigh and Raumann[2] we have observed the thermo-osmosis through a rubber membrane of carbon dioxide and of all the rare gases except radon, and have calculated from the experimental data the heats of transfer Q^* and the permeabilities p. The calculation of p was carried out by the method of Denbigh and Raumann.[3] Table I shows our results along with the few other comparable results that we have found in the literature.

TABLE I

Gas	Run	T, mean, °C.	Q^* 10^2 cal./mole	p (Pres. exp.), 10^{-8} cm.^{2}/sec.-atm.	p (lit.) 10^{-8} cm.^{2}/sec.-atm.
CO_2	1	33.0	− 9.8 −18.6[3]		
He	2	34.0	+11.2	33.7	33 (at 35°)[5]
	3	34.0	+11.4	53.4[4]	17 (at 25°)[6]
Ne	4	34.5	+ 9.0	8.6	
A	5	34.5	− 0.6		
	6–7			22.0	
	7	34.5	+ 0.3		
Kr	8	34.5	− 1.7	48.4[4]	
Xe	9	34.5	− 3.2	73.5[4]	33 (at 25°)

The principal difference between our method and that of Denbigh and Raumann is that we read the temperatures at the two sides of the rubber membrane directly from two thermocouples whose "hot" junctions were respectively flush with the two surfaces of porous bronze adjacent to the rubber membrane, whereas the authors mentioned used thermocouple junctions imbedded in the porous bronze and found the surface temperatures by extrapolation. Either method would seem to be subject to systematic errors. From the first of our runs to the last, we left the membrane assembly undisturbed save for the degassing and admission of gas involved in changing from one gas to the next. Because of this, the systematic errors were probably the same in all of our runs, and we therefore believe that our values of Q^* and p are rather better relatively than absolutely. Our value of p for helium agrees satisfactorily with that of Van Amerongen, and the differences between our values and those of Norton, for helium and xenon, we attribute to the differences of temperature.[7]

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[1] This paper is based upon the dissertation submitted by R. J. B. to Stanford University in partial fulfillment of the requirement for the Ph.D.

[2] K. G. Denbigh and G. Raumann, *Proc. Roy. Soc.* (*London*), **A210**, 518 (1952).

[3] K. G. Denbigh and G. Raumann, *ibid.*, **A210**, 377 (1952).

[4] These permeabilities are based on fewer data than our others.

[5] G. J. van Amerongen, *J. Applied Phys.*, **17**, 972 (1946).

[6] F. T. Norton, *J. Chem. Phys.*, **22**, 1145 (1954).

[7] Details of our experimental work, together with an account of the theory, are given in the dissertation mentioned in Footnote (1), and will be published in a later paper. The dissertation itself will be available from University Microfilms, 313 N. First St., Ann Arbor, Mich.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
CALIFORNIA

RICHARD J. BEARMAN
FREDERICK O. KOENIG

RECEIVED NOVEMBER 10, 1955

REDUCED UROPORPHYRIN III IN THE BIOSYNTHESIS OF HEME[1]

Sir:

The role of uroporphyrin and coproporphyrin in heme biosynthesis, although long a matter of speculation, is now becoming clearer. Rimington[2] has recently suggested that these tetrapyrroles actually are not in the main pathway of heme biosynthesis, but rather are oxidation products of heme precursors, or porphyrinogens. In addition,

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[1] Aided by a grant from the Dazian Foundation.

[2] C. Rimington, *Endeavour*, XIV (55), 126 (1955).