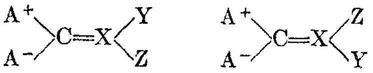
Communications TO THE EDITOR

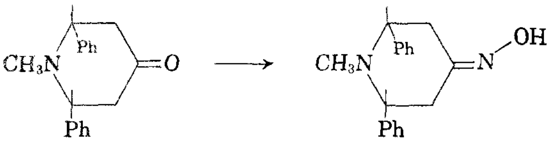
A Novel Type of Molecular Asymmetry

Sir:

Since the proposal by Van't Hoff and Le Bel in 1874 that the bonds of the quadricovalent carbon atoms form a perfect tetrahedron, the existence or absence of optical isomerism has been predicted for many unusual types of organic compounds.[1] Many of these predictions have been confirmed by the synthesis of and success or failure to resolve model compounds.[2] This communication describes the synthesis and resolution of enantiomorphs of an unsymmetrical molecule whose asymmetry is due to the *cis-trans* relationship of a substituent with respect to two similar asymmetrical carbon atoms having opposite configuration.[3]



Compounds which show geometrical enantiomorphic isomerism can be prepared by creating an unsymmetrically substituted double bond in a central location in a *meso* isomer. This was achieved by forming the oxime of the *meso* form of 2,6-diphenyl-1-methyl-4-piperidone (I).



I (meso) II (d or l)

2,6-Diphenyl-1-methyl-4-piperidone (I) was prepared by the condensation of dibenzylacetone with methylamine[4] and was obtained as a single modification. An attempt to resolve the ketone failed, and reduction of I with lithium aluminum hydride and catalytic hydrogenation led to two isomeric *meso* alcohols indicating that the ketone was the *meso* form. Catalytic hydrogenation of I produced α-2,6-diphenyl-1-methyl-4-piperidinol, m.p. 155–156.5° (calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 80.86; H, 7.71). Reduction of I with lithium aluminum hydride led to β-2,6-diphenyl-1-methyl-4-piperidinol, m.p. 170–172.5° (calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found C, 81.03; H, 8.02). A mixture of the two isomers melted 151–154°. Equilibration of the α-alcohol with sodium amyloxide gave a mixture containing both the α- and β-alcohols. Reduction of I with sodium in a solution of amyl and ethyl alcohols led to decomposition of the ketone by reversal of the aldol condensation.

The oxime (II)[5] of 2,6-diphenyl-1-methyl-4-piperidone, m.p. 194–196°, was converted to the *d*-10-camphor sulfonic acid salt (oxime salt: calcd. for $C_{28}H_{36}N_2O_5S$: C, 65.60; H, 7.08. Found: C, 65.67; H, 7.43). After three recrystallizations from methanol-ether, the more dextrorotatory isomer of the salt was obtained in pure form, m.p. 172–174° (dec.), $[\alpha]_D^{25}$ + 30.1° (calcd. for $C_{28}H_{36}N_2O_5S$: C, 65.60; H, 7.08. Found: C, 65.40; H, 7.33). The salt was converted to the oxime, m.p. 196–198°, $[\alpha]_D^{25}$ + 15.3°. Hydrolysis of the oxime with pyruvic acid in hydrochloric acid solution yielded the ketone, m.p. 148–151°, which showed no depression in melting point on mixture with an authentic sample and gave no rotation of plane polarized light.

Department of Chemistry
University of New Hampshire
Durham, N. H.

Robert E. Lyle
Gloria G. Lyle[6]

Received May 9, 1957

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(1) R. Shriner, R. Adams, and C. Marvel, *Organic Chemistry*, 2nd Ed., John Wiley and Sons, New York, 1943, Vol. I, p. 214.

(2) G. E. McCasland and S. Proskow, *J. Am. Chem. Soc.*, **78**, 5646 (1956); D. C. Iffland and H. Siegel, *J. Org. Chem.*, **21**, 1059 (1956).

(3) The authors suggest the name "geometrical enantiomorphic isomerism" to describe this type of isomerism.

(4) J. D. Riedel, German Patent *269,429*, July 18, 1913; *Beilstein's Handbuch der Organischen Chemie*, 4th Ed., Verlag von Julius Springer, Berlin, 1935, Vol. 21 I, p. 314.

(5) P. W. Neber, A. Burgard and W. Thier, *Ann.*, **526**, 277 (1936).

(6) Abstracted from the thesis to be submitted by G. G. L. to the Graduate School of the University of New Hampshire in partial fulfillment of the requirements for the Ph.D. degree.

Paramagnetic Resonance Absorption and New Types of Group Translocations in the Reaction of Trialkyl Phosphites with Chloranil[1]

Sir:

We have observed[2] that the red solution obtained when chloranil (I) and *triphenylphosphine* (II, X = C_6H_5) are mixed in benzene exhibits strong paramagnetic resonance absorption.[2] The pale yellow 1:1 adduct which precipitates quantitatively from the solution was formulated[2] as V or as the ion pair (VII-VI). Water converted this adduct into tetrachlorohydroquinone and triphenylphosphine oxide.

We wish now to call attention to the generality

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(1) The Structure of Quinone-Donor Adducts. Part II. We are grateful to the Eli Lilly Research Grants Committee for financial support.

(2) F. Ramirez and S. Dershowitz, *Chemistry & Industry*, 665 (1956); *J. Am. Chem. Soc.*, **78**, 5614 (1956). We thank Drs. G. Fraenkel, B. Venkataraman, and B. Segal for the paramagnetic resonance absorption measurements.