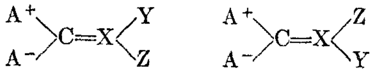
Communications TO THE EDITOR

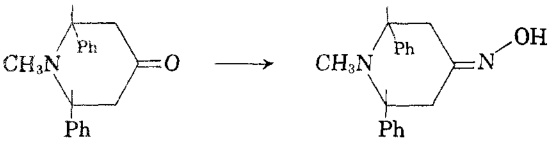
A Novel Type of Molecular Asymmetry

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

---

[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

---

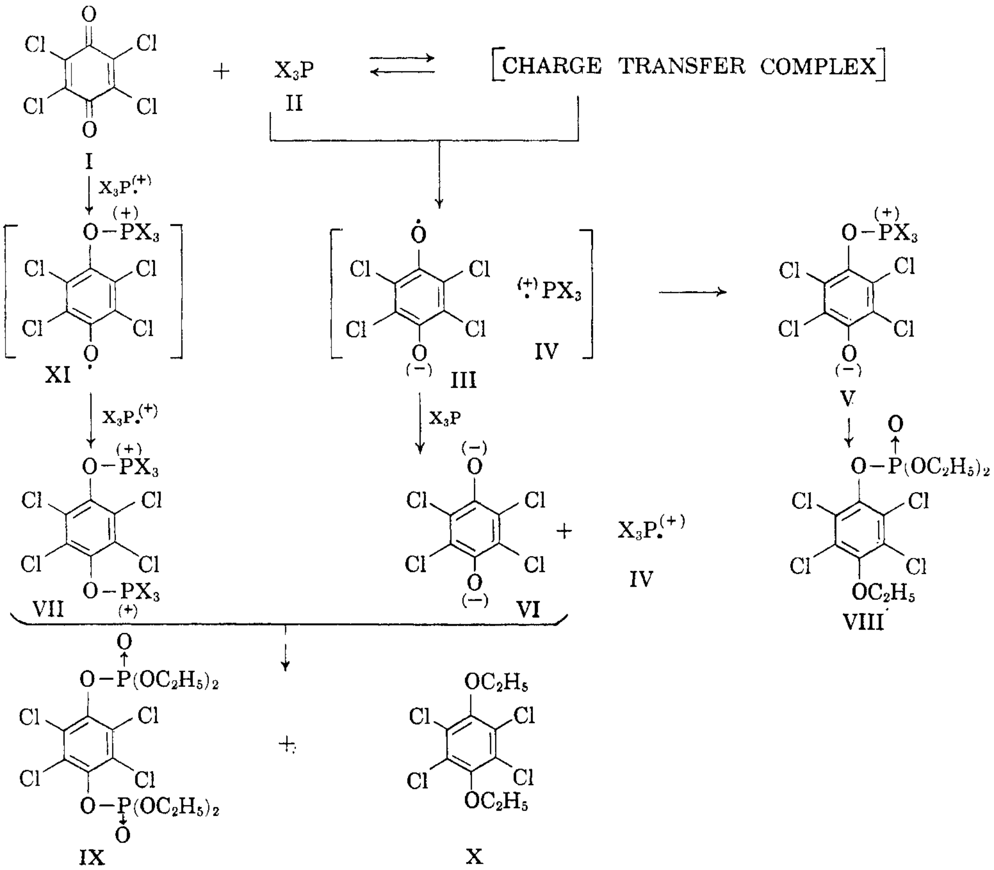
[1] The Structure of Quinone-Donor Adducts. Part II. We are grateful to the Eli Lilly Research Grants Committee for financial support.

[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.

of this phenomenon and to new types of group translocations among organophosphorus compounds. *Triethyl phosphite* (II, X = C_2H_5O) and chloranil(I) reacted at room temperature in benzene (or in dioxane) to give a deep red solution which *exhibited strong paramagnetic resonance absorption.* The color and the electronic paramagnetism slowly disappeared, but no precipitate was formed. The residue obtained upon removal of solvent at low temperature was not decomposed by water. This residue could be separated into three colorless crystalline substances: VIII [90% yield; m.p. 38–39°; calcd. for $C_{12}H_{15}Cl_4O_5P$: C, 35.0; H, 3.7; mol. wt. 412. Found: C, 34.7; H, 3.8; mol. wt. 349 (Rast); phosphate PO at 7.8μ]. IX (*ca.* 2% yield, m.p. 171–172°; calcd. for $C_{14}H_{20}Cl_4O_8P_2$: C, 32.3; H, 3.9. Found: C, 32.6; H, 3.9; phosphate PO at 7.8μ). X (*ca.* 1% yield) shown to be the diethyl ether of tetrachlorohydroquinone. Independent syntheses of VIII and IX confirmed their structures. The reaction of triethyl phosphite with chloranil in dioxane solution was reported[3] to afford ethyl chloride and diethyl trichloro-*p*-quinonephosphonate; we have been unable to substantiate this claim.

Triphenyl phosphite (II, X = C_6H_5O) did not react appreciably with chloranil at room temperature in benzene solution. However, when a suspension of chloranil in excess of triphenyl phosphite was illuminated at *ca.* 100°, a transient red color was observed resulting in a clear pale yellow solution. The residue obtained upon removal of excess phosphite was readily and quantitatively hydrolyzed to tetrachlorohydroquinone and triphenyl phosphate.

A possible interpretation of these observations is shown in Chart I. The 1:1 adduct V (or the ion pair VII-VI) undergoes no further change in the cases where X = C_6H_5 or C_6H_5O. A group translocation (presumably intermolecular) of the general type observed in the Arbuzov rearrangement, would produce the phosphate-ether VIII from the adduct V, when X = C_2H_5O. From the ion pair VII-VI, a similar group translocation would produce IX and X. If triethyl phosphite is added to a solution of chloranil in benzene containing some aqueous alcohol, a quantitative yield of tetrachlorohydroquinone and triethyl phosphate is obtained, presumably by hydrolysis of the intermediate V.



The paramagnetic resonance absorption spectrum of an equimolar solution of chloranil and triphenylphosphine in benzene consisted of two broad overlapping peaks, the spacing between the two peaks being 2.0 gauss and the *over-all* line width. 3.7 gauss; g = 2.0055. The spectrum of an equimolar solution of chloranil and triethyl phosphite in benzene was very similar, with somewhat better sepa-

---

[3] E. C. Ladd and M. R. Harvey, U. S. Patent 2,609,376, Sept. 2, 1952; *Chem. Abstr.*, 47, P7540 (1953).

ration of the two peaks (2.2 gauss) and about the same over-all width (3.7 gauss).

We should like to call attention to the similarities between these novel oxidation reactions of organophosphorus compounds and the observations of Kainer, Bijl, Rose-Innes, and coworkers[4] involving the complex of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine with chloranil. These authors[4] have described magnetic susceptibility, molar conductivity, and ultraviolet and infrared absorption measurements on this type of complex which they call "an ionic magnetically decompensated molecular compound." It would appear that all of these phenomena might be included in the category of "charge-transfer complexes." [5] On this basis, the species responsible for the color and for the electronic paramagnetism in the reaction of the organophosphorus compounds could perhaps be described in terms of the *ground state* $(\overset{-}{A}\text{–}\overset{+}{D})$ or the corresponding radical ion pair (III, IV) and of the *excited state* (A, D), where A and D stand for the electron acceptor and donor, respectively. In the more usual charge transfer complexes,[5] the situation is reversed and the color is due to the transition $(A, D) \rightarrow (\overset{-}{A}\text{–}\overset{+}{D})$. More information is being sought in a detailed spectrophotometric study now in progress.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

FAUSTO RAMIREZ
SAMUEL DERSHOWITZ

Received April 24, 1957

---

(4) H. Kainer and A. Überle, *Chem. Ber.*, **88**, 1147 (1955); H. Kainer and W. Otting, *Chem. Ber.*, **88**, 1921 (1955); H. Kainer, D. Bijl, and A. C. Rose-Innes, *Naturwissenschaften*, **41**, 303 (1954).

(5) (a) R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956) and references therein; (b) *cf.*, J. E. Wertz, *Chem. Revs.*, **55**, 922 (1955). We are grateful to Prof. Mulliken and Dr. Murrell (University of Chicago) for valuable theoretical suggestions.

The Direct *C*-Acylation of Pyridine

Sir:

We have succeeded in preparing pyridyl ketones by the reaction of pyridine and acid derivatives with amalgamated magnesium in 30–60% yields. Since the Friedel-Crafts and related reactions fail in the pyridine series, this new synthesis provides a means for obtaining directly a series of heterocyclic ketones heretofore available only through syntheses involving two or more steps.

The preparation of 2- and 4-benzoylpyridines was accomplished as follows: Magnesium, 24.3 g. (1.0 mole), was heated at 100° for 1 hr. with mercuric chloride, 46.0 g. (0.17 mole). The product (0.83 mole magnesium) was placed in a three-necked flask fitted with a stirrer, a reflux condenser, and a dropping funnel. A mixture of 25 g. each of pyridine and *N,N*-dimethylbenzamide was added and the materials heated to reflux. Within a few minutes a deep brown color appeared. The remainder of the pyridine, 250 g. (total 3.5 moles) was added slowly within 1 hr. Then the remainder of the amide, 273 g. (total 2.0 moles), was added over a period of 4 hr. maintaining the mixture at reflux throughout this period and until the magnesium disappeared (about 4 more hr.). The cooled reaction mixture was hydrolyzed with 100 g. of ammonium chloride in 500 cc. of water, filtered through Celite to remove insoluble salts, the upper layer of the filtrate extracted 5 times with 300-cc. portions of $6N$ HCl, the acid extracts made basic with $6N$ NaOH, the separated oil extracted with several 500-cc. portions of ether, the ether extracts dried and fractionally distilled, eventually under diminished pressure. The fraction b.p. 138–156° (2.8 mm.) was seeded with a crystal of 4-benzoylpyridine and was refrigerated in an ice box until no further product precipitated. Recrystallization of the solid from petroleum ether (90–100°) gave 8.2 g. (5.4% yield) of 4-benzoylpyridine, m.p. 72–73° (literature[1] 71.5–72.5°). The residual oil was redistilled and yielded 75.1 g. (50% theory) of 2-benzoylpyridine, b.p. 128–135° (1.0 mm.), literature[2] 133° (2 mm.). Total yield of benzoylpyridines based on gram atoms of magnesium reacted, 55.4%. A number of derivatives of each of the two isomers were prepared and found to correspond in properties with published values.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, IND.

G. BRYANT BACHMAN
R. M. SCHISLA

Received May 23, 1957

---

(1) K. E. Crook and S. M. McElvain, *J. Am. Chem. Soc.*, **52**, 4006 (1930).

(2) E. H. Huntress and H. C. Walter, *J. Am. Chem. Soc.*, **70**, 3704 (1948).

Reaction of *N*-Nitrosodibenzylamines with Sodium Hydrosulfite. A New Reaction

Sir:

We wish to report the discovery of a new reaction. The powerful reducing action of sodium hydrosulfite ($Na_2S_2O_4$) toward C-nitro and C-nitroso groups in basic media has previously been reported.[1,2]

An attempt to reduce *N*-nitrosodibenzylamines to the corresponding 1,1-disubstituted hydrazines using sodium hydrosulfite at 60° in basic ethanolic

---

(1) C. T. Redemann and C. E. Redemann, *Org. Syntheses*, Coll. Vol. III, 69 (1955).

(2) J. B. Conant and B. B. Corson, *Org. Syntheses*, Coll. Vol. II, 33 (1943).