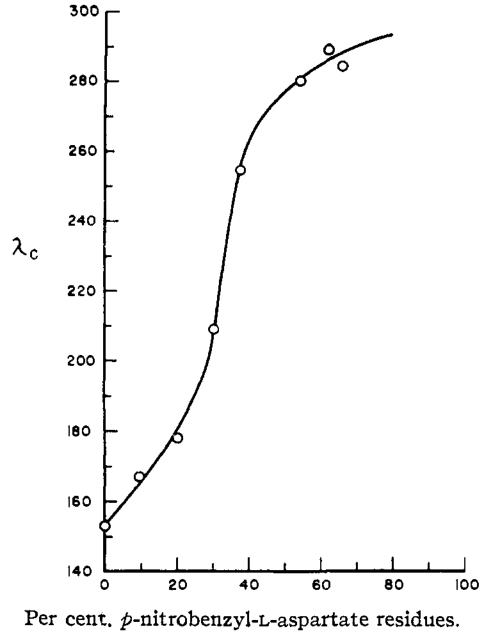


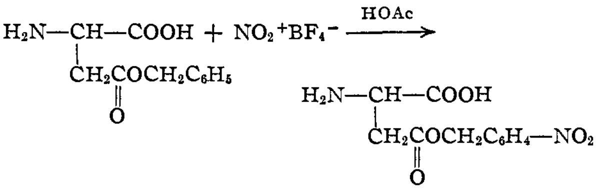
Fig. 3.—The values of λ_c from the Drude equation for copolymers of β-p-nitrobenzyl-L-aspartate: β-benzyl-L-aspartate as a function of mole % of p-nitrobenzyl-L-aspartate residues in chloroform at 25.0°.

nitrobenzyl-L-aspartate and poly-β-benzyl-L-aspartate are of opposite helical sense.

Thus, we conclude that the introduction of a p-nitro group into the β-benzyl-L-aspartate molecule does indeed reverse the sense of the helix.

The unusually large negative b_0 values (*e.g.*, -1338 at 66.0%, -1268 at 62.0% and -1016 at 54.0% nitro residue contents) may be attributed to the presence of groups in the side chain which produce Cotton effects in the near ultraviolet spectral region. Alternatively, the nitro side chain groups which can be assumed to form a rigid helix of their own may have an additive effect on the b_0 values.

β-p-Nitrobenzyl-L-aspartate was prepared[7] by nitration of β-benzyl-L-aspartate using nitronium fluoroborate[8] in glacial acetic acid, then neutralization with sodium bicarbonate.



$$\underset{\substack{|\\ CH_2\underset{\substack{\|\\ O}}{C}OCH_2C_6H_5}}{H_2N\text{—}CH\text{—}COOH} + NO_2^+BF_4^- \xrightarrow{HOAc} \underset{\substack{|\\ CH_2\underset{\substack{\|\\ O}}{C}OCH_2C_6H_4\text{—}NO_2}}{H_2N\text{—}CH\text{—}COOH}$$

The N-carboxyanhydride[9] of β-p-nitrobenzyl-L-aspartate was prepared by phosgenation of the amino acid in dioxane. It was then polymerized using diethylamine initiator in dimethylformamide and isolated by precipitation with ethyl ether.

Exclusive *para*-nitration was proved by hydrolysis of β-p-nitrobenzyl-L-aspartate with 10% hydrochloric acid. p-Nitrobenzyl alcohol was isolated and characterized unambiguously.

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[7] Details of the synthesis will be published elsewhere.

[8] S. Kuhn and G. Olah, *J. Am. Chem. Soc.*, **83**, 4570 (1961).

[9] A. Berger and E. Katchalski, *ibid.*, **73**, 4084 (1951).

[10] Undergraduate research participant for 1961 under NSF Grant G15814.

[11] Supported by grant RG 8974 from the National Institutes of Health.

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RECEIVED JULY 2, 1962

PHOTOCHEMICAL ISOMERIZATION OF SQUARE COMPLEXES

Sir:

We wish to report photochemically effected isomerizations of platinum(II) complexes. Both sunlight and a General Electric 275 watt sunlamp cause rapid isomerization of solutions of *cis*- and *trans*-bis-(triethylphosphine)-dichloroplatinum(II), $[(Et_3P)_2PtCl_2]$.[1] Mixtures of isomers were analyzed spectrophotometrically utilizing differences in the electronic absorption spectra; with known mixtures each isomer could be analyzed to ±1%. No filter was used in the experiments with sunlight; a solution of potassium hydrogen phthalate (5 g./l.) was used as a filter[2] (sharp cut-off at 304 mμ) with the sunlamp. The electronic absorption spectra are shown in Fig 1; they indicate that it is the low intensity, d→d transition at long wave length that is active in the isomerization. When the isomers were irradiated with unfiltered light from the sunlamp, a dark precipitate formed indicating decomposition.

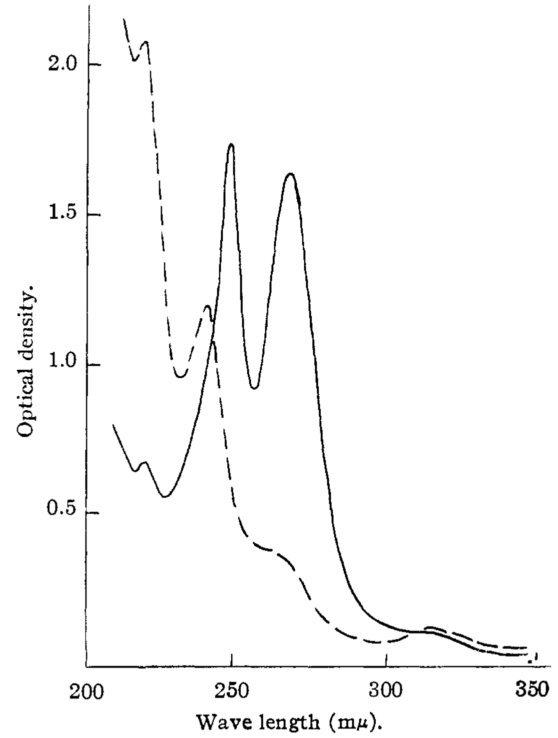

Fig. 1.—Spectra of $(Et_3P)_2PtCl_2$ isomers in methanol: *trans*, $1.592 \times 10^{-4}M$, ——; *cis*, $1.863 \times 10^{-4}M$, — —.

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[1] Prepared by the procedure of K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 238 (1936).

[2] M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

TABLE I

PHOTOCHEMICAL ISOMERIZATIONS[a]

Solvent	Starting isomer	Concn., *M*	Time, hr.	% *trans*
Benzene	*cis*	2.08×10^{-3}	6	66.4
Benzene	*trans*	2.05×10^{-3}	6	65.9
Methanol[b]	*cis*	1.96×10^{-4}	2	33.7
Methanol[b]	*trans*	1.96×10^{-4}	2	34.1

[a] Irradiated at room temperature with a 275 watt sunlamp equipped with a potassium hydrogen phthalate filter. [b] Containing 0.01 *M* HCl.

It took 2–6 hours to reach a photochemical steady state in benzene or methanol as shown in Table I. After 10 weeks there was less than 10% isomerization in methanol in the dark at room temperature, and there was no apparent isomerization in benzene after three weeks under the same conditions. The photochemical steady-state is clearly not the position of thermodynamic equilibrium since this has been shown[3] to consist of 92.5% *trans* complex in benzene at 25°. The large dipole moment[3] (10.7 *D*) of the *cis* complex and the negligible dipole moment of the *trans* complex are reflected in the solvent dependence of the steady state (Table II); a plot of log K against dielectric constant is nearly linear. The quantum yield has been measured using uranyl oxalate as a chemical actinometer and a filter which gave a band of transmittance from 300 to 350 mμ with maximum transmittance at 315 mμ. Quantum yields of 0.01 and 0.02 were obtained at low percentage isomerizations.

TABLE II

SOLVENT DEPENDENCE OF THE PHOTOCHEMICAL STEADY STATE

Solvent	Starting isomer	% *trans*[a]	Average K^b
Dimethylsulfoxide	*cis*	25.2	2.82
	trans	27.1	
Methanol–0.01 *M* HCl	*cis*	33.7	1.95
	trans	34.1	
Methanol	*cis*	36.7	1.69
	trans	37.6	
Ethanol	*cis*	43.8	1.15
	trans	49.1	
Chloroform	*cis*	60.6	0.63
	trans	61.7	
1,2-Dimethoxyethane	*cis*	71.2	0.42
	trans	70.1	
Benzene	*cis*	66.4	0.51
	trans	65.9	

[a] After three hours in sunlight except for methanol–0.01 *M* HCl and benzene where the results are taken from Table I. [b] K = % *cis*/% *trans*.

It seems most likely considering the quantum yield that these isomerizations are proceeding through a triplet state. On the basis of ligand field theory and analogy[4] to the Ni(II) complexes, one would expect the most stable electronic configuration of a tetrahedral platinum(II) complex to be a triplet. Therefore, a reasonable hypothesis for the mechanism of these isomerizations is that an initial excited singlet decays to a triplet which still has the square configuration but which can rearrange to a tetrahedral configuration. The tetrahedral triplet then can decay to either the *cis* or *trans* ground state (equation 1). Another possibility is that solvated ground state undergoes excitation and the isomerization proceeds through a trigonal bipyramid containing one solvent molecule; such a mechanism would be analogous to one proposed[5] for the thermal isomerization.[3]

$$\begin{tikzcd} \text{square ground state} \arrow[r, shift left, "h\nu"] & \text{excited square singlet} \arrow[l, shift left] \arrow[r] & \text{excited square triplet} \arrow[r] & \text{tetrahedral triplet} \arrow[r] & \text{square ground state} \end{tikzcd} \qquad (1)$$

Acknowledgment.—We are indebted to the United States Public Health Service for a grant, RG-9294, in support of this research.

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(3) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 273 (1952).

(4) F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 253.

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RECEIVED JULY 27, 1962

TERTIARY AMINE CATALYSIS OF THE ALDOL CONDENSATION[1]

Sir:

The aldol condensation provides the organic chemist with a synthetic method of great *in vitro* utility and the living cell with a method of great *in vivo* utility. In studying systems in which these applications might be brought into closer correspondence, the base-catalyzed conversion of glyceraldehyde to hexoses has been investigated. The result has been to shed some new light on this particular reaction and, presumably, on the aldol condensation in general.

The reaction of glyceraldehyde with inorganic bases in aqueous solution to yield fructose and sorbose has been quite well-studied both from the standpoint of the chemistry involved[2] and the kinetics of the process,[3] and it is established that the reaction sequence involves a rearrangement of glyceraldehyde to dihydroxyacetone (slow step) which then undergoes an aldol condensation with unchanged glyceraldehyde (fast step) to yield the hexoses. Employing optically pure D-glyceraldehyde with $[\alpha]^{25}\text{D}$ +13.5° as starting material and using the Willstätter–Schudel method[4] to measure the amount of unreacted glyceraldehyde, an enzymatic method[5] to measure the amount of D-fructose formed, and the resorcinol method[6] to measure the amount of sorbose (or total hexose) formed we have demonstrated that, in addition to hydroxide ion, tertiary amines are effective con-

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(1) Presented, in part, at the Vth International Congress of Biochemistry, Moscow, USSR, August 10–16, 1961.

(2) H. O. L. Fischer and E. Baer, *Helv. chim. acta*, **19**, 519 (1936).

(3) W. G. Berl and C. E. Faezel, *J. Am. Chem. Soc.*, **73**, 2054 (1951).

(4) R. Willstätter and G. Schudel, *Ber.*, **51**, 780 (1918).

(5) We are indebted to Dr. R. K. Crane for the details of this method which involves the three step conversion of fructose to 6-phosphogluconate with the concomitant formation of TPNH, measured by its absorption at 340 mμ.

(6) J. H. Roe, J. H. Epstein and N. P. Goldstein, *J. Biol. Chem.*, **178**, 839 (1949).