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

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*.

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.

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 possi-

$$\text{square ground state} \xrightarrow{h\nu} \text{excited square singlet} \longrightarrow \text{excited square triplet} \longrightarrow \text{tetrahedral triplet} \longrightarrow \text{square ground state} \quad (1)$$

bility 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]

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

(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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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 $[\alpha]^{25}D$ +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-

(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).

TABLE I

BASE-CATALYZED CONVERSION OF D-GLYCERALDEHYDE TO D-FRUCTOSE AND D-SORBOSE

Base	Concn. %	pH	Temp., °C.	Time, hr.	Buffer	Product composition, % Glyceraldehyde	Fructose	Sorbose
OH^-		12.7	25	2	None	17	41	40
H_2O		6.8–7.0	35	40	None[a,b]	90	7	6
H_2O		7.0	35	40	$HPO_4^=$–$H_2PO_4^-$[a]	75	15	12
Pyridine	4	7.0	35	40	B–B·HCl[a]	25	36	35
Imidazole	4	7.0	35	40	B–B·HCl[a]	20	37	36
Pyridine	4	6.0	35	40	B–B·HCl[a]	25	36	35
Pyridine	4	5.0	35	72	B–B·HCl	75	9	7
Pyridine	2	7.4[c]	30	48	None	62	18	19
2-Methylpyridine	2	7.8[c]	30	48	None	56	20	22
4-Methylpyridine	2	7.8[c]	30	48	None	36	30	30
2,4-Dimethylpyridine	2	8.4[c]	30	48	None	32	32	30
2,6-Dimethylpyridine	2	8.5[c]	30	48	None	78	8	10
2,4,6-Trimethylpyridine	2	8.8[c]	30	48	None	57	18	25
N-Methylimidazole	2	8.4[c]	30	48	None	32	31	30

[a] Total ionic strength of system = 0.150. [b] Reaction carried out in a closed apparatus equipped with calomel and glass electrodes and a serum cap to allow periodic check and adjustment of pH. [c] Initial pH of the reaction mixture.

densation catalysts. Table I shows that (a) catalysis by hydroxide ion is almost negligible at pH 7, (b) catalysis by the buffer ions $HPO_4^=$–$H_2PO_4^-$ at pH 7 is small but possibly real, (c) catalysis by pyridine at pH 7 and pH 6 is striking and even at pH 5 is demonstrable, (d) catalysis by pyridine bases is sensitive to the steric environment around the nitrogen, and (e) imidazole appears to be an even more effective catalyst than pyridine. From these observations one must conclude that the aldol condensation of glyceraldehyde with dihydroxyacetone is general base-catalyzed.

Although aldol-type condensations such as the Perkin reaction are known to be catalyzed by tertiary amines,[7] no example of a simple aldol condensation catalyzed by this species has been reported. Westheimer and Cohen,[8] in checking earlier claims regarding the general base-catalysis of the aldol condensation[9] discovered, in fact, that the dealdolization of diacetone alcohol is catalyzed by methylamine and dimethylamine but *not* by trimethylamine. They ascribed the effectiveness of the primary and secondary amines not to a general base catalysis (*i.e.* facilitation of removal of the α-proton by direct participation at the C–H bond) but to a specific amine effect in which the interaction involves the carbonyl group to form intermediates of the ketimine type. Their conclusion that the aldol condensation of acetone is not an example of general base catalysis but rather an example of specific solvent anion catalysis is in accord with other data concerning the reaction,[10] *viz.*, that the condensation step is much slower than the proton removal step. In aldol condensations where the proton removal step is slower than the condensation step, however, the possibility for general base catalysis exists.[11] Recent work by Bell and McTigue[12] has established that in borate and carbonate buffers the aldol condensation of acetaldehyde exhibits general base catalysis, and additional evidence for this phenomenon is now also provided by the demonstration of tertiary amine catalysis of the glyceraldehyde–dihydroxyacetone condensation.

The aqueous pyridine-catalyzed conversion of glyceraldehyde → dihydroxyacetone → hexoses was unanticipated because of the known efficacy of anhydrous pyridine as a Lobry de Bruyn–Alberda van Ekenstein catalyst[13]; *e.g.*, glyceraldehyde is converted only to dihydroxyacetone by refluxing anhydrous pyridine. That a real difference between aqueous and anhydrous pyridine does exist for this system has been demonstrated by the fact that the extent of hexose formation remains essentially constant over the range of pyridine concentration of 10–60% but falls almost to zero at 85% pyridine concentration. Thus, in a crude sense, anhydrous pyridine acts as a triose isomerase model while aqueous pyridine acts as an aldolase model. A decision as to whether this is anything but a formal analogy must await more detailed information concerning the enzyme-catalyzed reactions. Amines have, indeed, been implicated in aldolase action[14] but in the sense of forming an intermediate of the ketimine type (with dihydroxyacetone phosphate) rather than in the sense of providing a basic center for receipt of the proton from the α-carbon atom. The present work indicates the possibility of the latter.

A more detailed study of the kinetics and the effects (or lack thereof) of cations in this condensation will be reported at a later time.

Acknowledgment.—We are indebted to the Research Corporation for financial aid in the initial

(7) P. Kalnin, *Helv. chim. acta*, **11**, 977 (1928); R. Kuhn and S. Ishikawa, *Ber.*, **64**, 2347 (1931).

(8) F. H. Westheimer and H. Cohen, *J. Am. Chem. Soc.*, **60**, 90 (1938).

(9) C. C. French, *ibid.*, **51**, 3215 (1929); J. Miller and M. Kilpatrick, *ibid.*, **53**, 3217 (1931).

(10) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed. John Wiley and Sons, New York, N. Y., 1961, p. 335, for a good discussion.

(11) K. F. Bonhoeffer and W. D. Walters, *Z. physik. Chem.*, **A181**, 441 (1938).

(12) R. P. Bell and P. T. McTigue, *J. Chem. Soc.*, 2983 (1960).

(13) See J. C. Speck, Jr., "Advances in Carbohydrate Chemistry," Academic Press, Inc., New York, N. Y., Vol. 13, 1958, p. 63, for a review and references.

(14) E. Grazi, T. Cheng and B. Horecker, *Biochem. and Biophys. Res. Communications*, **7**, 250 (1962).

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TRANSFER REACTIONS INVOLVING BORON. I. ALKYL TRANSFER FROM OXYGEN TO SULFUR[1]

Sir:

It has been observed that on generation of diborane in the presence of a mercaptan in an ether solvent, an alkyl transfer occurs from the solvent molecule to sulfur giving sulfides often in good yields.[2] Table I lists experiments in which 0.05 mole of mercaptan and 0.0313 mole of sodium borohydride were dissolved in 40 ml. of the ether, with in *situ* generation of diborane by the addition of 0.025 mole of boron trifluoride etherate. The reaction mixtures were allowed to stand at room temperature for 20 hours, then hydrolyzed with aqueous sodium hydroxide and extracted with diethyl ether to recover the sulfide. Although the experiments were carried out by the *in situ* generation of diborane, it was shown that the reaction was not dependent on the presence of a strong Lewis acid (boron trifluoride). Diborane generated externally and bubbled into a solution of thiophenol in diethylene glycol dimethyl ether also led to alkyl transfer.

In cases of otherwise similar ethers, entries 1 and 2, and the cyclic ether, entry 5, it is apparent that methyl reacts more rapidly than methylene which in turn reacts more rapidly than methine. The over-all structure of the ether greatly affects the rates of transfer as is illustrated in entries 8, 9 and 10 in which the transfer of ethyl competes with the transfer of methyl. The reaction rate appears to be greatly dependent on the steric bulk of the radicals attached to oxygen and on the basicity of the ether oxygen. At the present time the synthetic utility of this reaction lies mostly in preparation of various sulfides. The usefulness of the reaction as a means to carry out O-demethylations is severely hindered by competing reactions with the solvent. Further work is being carried out in this respect.

Chemical evidence in the case of thiophenol indicates that monothiophenoxyborane ($C_6H_5SBH_2$) is the reactive species which takes part in the alkyl transfer. The graph illustrates the effect on the extent of reaction over a given period of time when the ratio of diborane to trithiophenoxyborane is progressively increased. Attempted alkyl exchange in the presence of thiophenoxide ion and diborane failed, indicating that a species corresponding to $[C_6H_5SBH_3]^-$ is not operative in this reaction. Alkyl exchange did not occur in the presence of trithiophenoxyborane $[(C_6H_5S)_3B]$ generated by treating thiophenol with an equivalent of sodium borohydride.

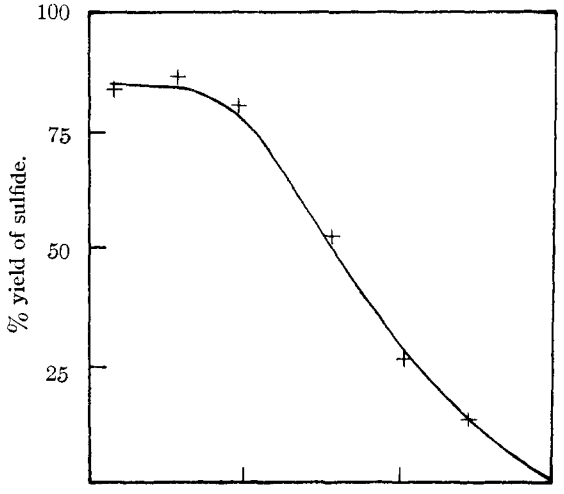

Fig. 1.—Exchange with thiophenol in diglyme after 20 hours.

The above experimental results would suggest that the alkyl transfer occurs *via* a four-centered transition state involving the ether and monothiophenoxyborane. A nucleophilic attack by sulfur on the alkyl carbon adjacent to a complexed oxygen does not seem reasonable in that the nucleophilicity of the sulfur will be reduced by interaction of its electron pairs with the vacant orbital of boron. Likewise, partial carbon–oxygen bond cleavage leading to the partial formation of a carbonium ion, which then is attacked by sulfur, is not a reasonable mechanism if one considers entry 5 of Table I. Had the mechanism proceeded by partial carbonium ion formation, the expected product would have been 4-thiophenoxypentanol-1 instead of the observed 5-thiophenoxypentanol-2.

The reaction mechanism may thus be illustrated as

$$RSBH_2 + R'\text{—}O\text{—}R'' \longrightarrow \left[\begin{array}{c} H \\ | \\ R\text{—}S\cdots B\text{—}H \\ \vdots \quad \vdots \\ R'\cdots O\text{—}R'' \end{array}\right] \longrightarrow R\text{—}S\text{—}R' + H\text{—}B\text{—}OR'' \quad (H)$$

The greater reactivity of $C_6H_5SBH_2$ over that of $(C_6H_5S)_2BH$ and $(C_6H_5S)_3B$ may be explained in part by the steric restrictions in forming the four-centered transition state and in part by the reduced Lewis acid character of the boron atom, due to interaction with a greater number of thiophenoxy groups, leading to a weaker complex with the ether oxygen.

Four-centered transition states and reactions are quite common in boron chemistry: *i.e.*, the addition of B–H to unsaturated linkages[4], base-catalyzed reductive cleavage of carbon-boron bonds to produce hydrocarbons,[5] disproportiona-

(1) Presented at the 1962 Fall American Chemical Society Meeting at Atlantic City, New Jersey.

(2) All product sulfides were converted to known derivatives for identification or were satisfactorily analyzed if not previously reported. In cases of mixtures, analyses were carried by vapor phase chromatography or nuclear magnetic resonance spectroscopy.

(4) H. C. Brown, "Organo Metallic Chemistry," H. Zeiss, ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 163.

(5) A. J. Weinheimer and W. E. Marsico, *J. Org. Chem.*, **27**, 1926 (1962), and references cited therein.