α-oximinophenylacetonitrile was filtered and dried *in vacuo*, m.p. 127–129° (lit.[13] m.p. 128–129°).

Kinetic Investigation of the Base-Induced Ring Scission of Furazan and Dideuteriofurazan.—All glassware was pretreated with chromic acid in sulfuric acid, washed with distilled water, and dried at 120°. The reaction kinetics were measured in 1-cm. quartz cells and were followed on a Cary recording spectrophotometer, Model 14. The sample compartment was thermostated at 25.0 ± 0.1°.

Carbonate-free sodium hydroxide solution was used. To obtain the desired pH, aliquots of this solution were diluted with CO_2-free distilled water. Analytically pure Na_2HPO_4 was used.

Approximately 25 ml. of the base solution was thermostated at 25.0° for at least 1 hr. prior to use. A very small amount of freshly distilled furazan or furazan-d_2 was then added, and the timer was started. This solution was shaken well and the cell was filled and placed in the spectrophotometer. The kinetics were followed continuously to approximately 10 half-lives at 261 mμ (λ_{max} of product). At the end of each kinetic run the pH of the reaction solution was taken. This pH differed by no more than 0.03 pH units from the pH of the initial base solution.

It was possible to show that the product, the anion from α-oximinoacetonitrile, obeys Beer's law even though this substance could not be isolated in the pure state. Standard solutions of furazan in base were allowed to react to 10 half-lives and the optical densities of the solutions were then measured. A straight line was obtained when optical density was plotted against concentration.

The pseudo-first-order rate constants were obtained from a plot of log (O.D. at t_∞ − O.D. at t) *vs.* time. This plot gave a straight line for over 4 half-lives except in the reactions of dideuteriofurazan which shows a slightly faster initial rate as expected. The second-order rate constants were obtained from $k_1/(OH^-)$. The primary isotope effect k_H/k_D is 2.9.

The results are found in Table II.

Kinetics of the Decomposition of the Sodium Salt of α-Oximinoacetonitrile.—A solution of furazan in pH 12.08 sodium hydroxide solution was allowed to stand for 290 hr. at 25°. Ultraviolet spectra were taken about every 10 hr. The decomposition was followed at 261 mμ (substrate) and a crude calculation indicated a half life of about 35 hr., too slow to interfere with the furazan cleavage kinetics.

A Free-Radical Oxidation of a Dihydropyridine*,[1a]

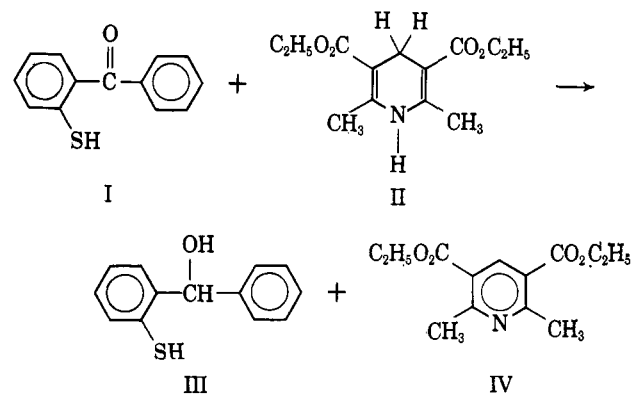
K. A. SCHELLENBERG[1b] AND F. H. WESTHEIMER

James Bryant Conant Laboratory of Harvard University, Cambridge, Massachusetts

Received October 14, 1964

2-Mercaptobenzophenone (I) oxidizes 3,5-dimethyl-2,4-dicarboethoxy-1,4-dihydropyridine (II) to the corresponding pyridine; the ketone is reduced to 2-mercaptobenzhydrol. The oxidation–reduction requires the *o*-sulfhydryl group and fails with the corresponding *para* compound or with benzophenone substituted by *ortho* hydroxy, amino, or thiomethyl groups. The reaction between I and II occurs rapidly at room temperature in neutral aqueous alcoholic solution when promoted by peroxides and ferrous ion and thus has the characteristics of a free-radical process. During the oxidation–reduction, hydrogen is introduced from the solvent into the mercaptobenzhydrol formed; the reaction therefore does not involve direct hydrogen transfer and is not a model for the biochemical oxidation–reductions of dihydropyridines.

Enzymic reactions which involve diphosphopyridine nucleotide constitute one of the most important classes of biochemical oxidation–reduction processes. These reactions (such as the reduction of acetaldehyde to alcohol, the reduction of pyruvate to lactic acid, etc.) are characterized by the direct and stereospecific transfer of hydrogen from the dihydropyridine to the substrate.[2] Chemical models for the biochemical oxidation–reduction reaction which likewise involve direct hydrogen transfer include the reduction of pyruvate,[3] benzoyl formate,[3] thiobenzophenone,[4] 1-phenyl-4,4,4-trifluorobutene-2-one-1 (reduced at the double bond),[5] hexachloroacetone,[6] malchite green,[7] dipicrylhydrazyl[7] and (photochemically) bromotrichloromethane,[8] and diphenyl disulfide.[7] Of these oxidation–reduction reactions, the last three or four are free-radical processes, whereas the others presumably proceed by polar mechanisms. Other model reactions have been developed where the question of direct hydrogen transfer has not yet been investigated.[9] We have now found an example of a free-radical oxidation–reduction process involving the reduction of a carbonyl compound by 2,6-dimethyl-3,5-dicarboethoxy-1,4-dihydropyridine (the "Hantzsch compound," I) which proceeds with hydrogen transfer from the solvent, *i.e.*, without direct transfer from the reducing agent to the substrate. The reaction follows.



I II III IV

The reaction is promoted by air or by hydrogen peroxide or other peroxides and by ferrous ion (Tables

* To Professor Louis F. Fieser.

(1) (a) This research was supported by the National Institutes of Health under Grant GM-04712. (b) National Institutes of Health Postdoctoral Fellow, 1960–1963.

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TABLE I

REDUCTIONS OF 2-MERCAPTOBENZOPHENONE BY THE HANTZSCH COMPOUND IN 70% ETHANOL[a] AT 69°

Oxidant	Concn., *M*	Hantzsch compd., *M*	"pH"[b]	Time, hr.	Reaction, %	Comment
2-Mercaptobenzophenone	0.01	0.01	5.1	12	98	25°
	0.01	0.01	5.1	11	92	
	0.01	0.01	6.1	11	27	
	0.01	0.01	7.1	11	4	
	0.005	0.005	6.1	11	68	
	0.005	0.005	6.1	11	25	Evacuated to 10^{-6} mm.
	0.001	0.001	6.1	15	64	
	0.001	0.001	6.1	15	27	0.0001 *M* EDTA
	0.01	0.01	5.0	11	92	Methoxyacetate buffer
	0.01	0.01	4.3	11	83	Citrate buffer
	0.01	0.01	5.5	11	51	Citrate buffer
4-Mercaptobenzophenone	0.01	0.01	5.1	8	Small	
2-Hydroxybenzophenone	0.01	0.01	5.1	8	Small	
Benzophenone	0.01	0.01	5.1	12	Small	
2-Aminobenzophenone	0.005	0.005	6.2	46	Small	

[a] Acetate buffer unless otherwise specified. [b] pH is corrected for 70% ethanol as solvent; see text.

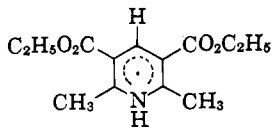
TABLE II

KINETIC STUDIES. REDUCTION OF 2-MERCAPTOBENZOPHENONE IN 70% ETHANOL AT 30°

Hantzsch compd., *M*	2-Mercapto-benzophenone, *M*	H_2O_2, *M*	"pH"[a]	Thiophenol, *M*	Other reagents	*M*	Initial rate, mole $l.^{-1}$ $sec.^{-1}$ $\times 10^6$
0.005	0.005	None	4.9, M	...	...	...	0.11
0.005	0.005	None	4.9, M	...	...	...	0.15
0.005	0.005	None	4.9, M	...	Air	...	4.56
0.005	0.005	None	4.9, M	...	Air	...	6.15
0.005	0.005	None	4.9, M	...	Air + EDTA	0.001	0.17
0.005	0.005	0.001	4.9, M	...	...	...	1.31
0.005	0.005	0.005	4.9, M	0.05	...	...	4.31
0.005	0.005	0.1	4.9, M	0.05	...	...	12.62
0.0127	0.0083	0.01	5.1, F	...	...	...	11.25
0.0075	0.005	0.01	5.1, F	...	Fe^{2+}	10^{-6}	12.05
0.0134	0.005	0.01	5.1, F	...	Fe^{2+}	2×10^{-6}	22.50
0.0075	0.005	0.01	5.1, F	...	Fe^{2+}	10^{-6}	48
0.005	0.005	0.01	5.1, F	...	...	...	3.44
0.005	0.005	0.01	5.1, F	0.01	...	...	3.04
0.005	0.005	0.01	5.1, F	0.15	...	...	4.65
...	0.005	0.01	5.1, F	...	4-Deuterated Hantzsch compd.	0.0085	4.23
0.005	0.005	0.001	5.0, M	0.01	EDTA	0.001	0.20

[a] F for formate buffer, M for methoxyacetate buffer. pH is corrected for 70% ethanol as solvent; see text.

I and II). It requires the sulfhydryl group, since it fails with the corresponding *para* compound or with *o*-hydroxybenzophenone or *o*-aminobenzophenone or *o*-thiomethylbenzophenone. It also fails with *o*-mercaptoacetophenone or with N-methyl Hantzsch compounds. When the reaction is carried out in D_2O, deuterium is introduced into the mercaptobenzhydrol formed; when the reaction is carried out with 4-deuterio Hantzsch compound, no deuterium is introduced into the mercaptobenzhydrol. These facts are consistent with a free-radical chain reaction such as is shown in Scheme I with the termination steps unspecified. Here RS· can be either VI or, in the presence of C_6H_5SH, C_6H_5S·. The radical PyH· is presumably the following.



The large increase in rate in the presence of oxygen or hydrogen peroxide shows that an oxidation initiates the reaction. The fact that the sulfhydryl group is needed again suggests free radicals, since the RS· radical is a familiar participant in radical reactions.[10] The fact that the reaction proceeds best when the sulfhydryl group is *ortho* shows that its participation is a direct one.

The need for two phenyl groups (*i.e.*, the lack of reaction with *o*-mercaptoacetophenone) is significant. Benzophenone is more sterically hindered than acetophenone. If the former reacts and the latter does not, some intermediate must be involved in the reaction for which the second phenyl is required. The free-radical V, postulated above, would be a proper intermediate.

The data in Table I show that the dihydropyridine is most rapidly consumed at a "pH" (pH in 70% ethanol as solvent) in the neighborhood of 5. Control experiments showed that the Hantzsch compound, in sharp contrast to DPNH or to N-alkyl-1,4-dihydronicotinamides, is not affected by dilute acids; presumably it is stabilized by the two carboethoxy groups. Thus the

(10) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *J. Am. Chem. Soc.*, **86**, 3060 (1964).

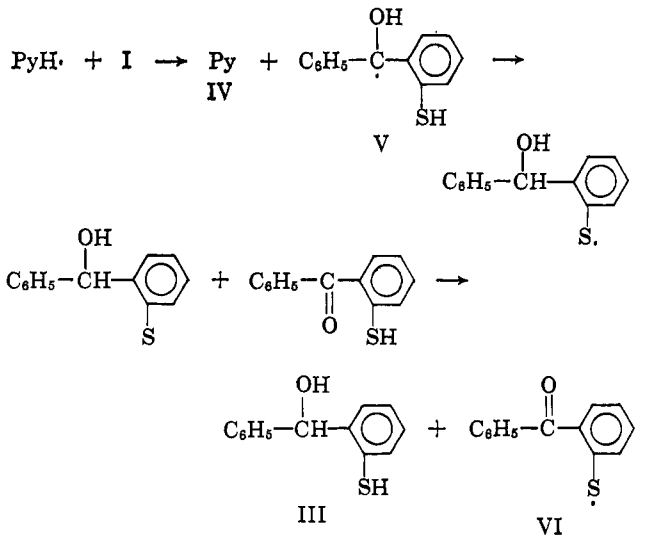
SCHEME I

Initation

$$H_2O_2 + Fe^{2+} + RSH \longrightarrow Fe^{3+} + H_2O + {}^{-}OH + RS\cdot$$

Propagation

$$RS\cdot + II \longrightarrow RSH + PyH\cdot$$



change in spectrum is not caused by decomposition of the Hantzsch compound, but by its interaction with the thio ketone. The cause of the decrease in rate at a "pH" of 7 was not investigated. However, in view of the effect of oxygen and peroxides in promoting the reaction, it seems unlikely that the optimum rate near "pH" 5 is caused by an acid-catalyzed transfer of a hydride ion. In fact, if the Hantzsch compound is protonated, this would diminish the rate of such a process.

Free-radical reactions have been postulated[11] for biochemical oxidation–reductions involving DPN, and a stable free radical has actually been prepared and isolated from a dihydropyridine substituted with a carboethoxy group *para*, rather than *meta*, to the pyridine nitrogen atom.[12] The present results suggest again that free-radical reactions of the dihydropyridines occur readily, but the lack of direct hydrogen transfer probably indicates that this mechanism is not similar to the enzymic ones.

Finally, we have considered but rejected the possibility that the enzyme–substrate complex is so tightly bound that transfer between solvent and the –SH group of the enzyme is prevented. Phosphoglucose isomerase[13] is the outstanding example where such an explanation has previously been offered, but the specificity of transfer is not so complete as for the reactions[3] of DPNH. A steroid isomerase[14] converts Δ^5-androstene-3,17-dione to its Δ^4 isomer with little or no exchange between the hydrogen atoms of the medium and those of the steroid. Although the enzyme does catalyze a slow exchange between D_2O and the product, the isomerization itself may occur by internal rearrangement, catalyzed by the enzyme, but without proton transfer between the steroid and the protein. Thus the reaction is probably not a case where the protein shields a proton so that it is sterically incapable of exchange with the medium, but rather an example where the proton is never lost by the substrate. Further pertinent evidence for this point comes from studies of yeast alcohol dehydrogenase begun in our laboratory.[15]

Experimental

Materials.—2,6-Dimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine[16] (Hantzsch compound) was prepared by Dr. J. Kurz.[8] 4,4-Dideuterio-2,6-dimethyl-3,5-dicarboethoxy-1,4-dihydropyridine was prepared from dideuterioformaldehyde according to Norcross, *et al.*[5] 2-Mercaptobenzophenone was prepared by the general method of Leuckart.[17] 2-Aminobenzophenone (Aldrich Chemical Co.), 19.7 g., 22 ml. of concentrated hydrochloric acid, and 200 ml. of water were stirred at −2°, while a solution of 7.2 g. of sodium nitrite in 20 ml. of water was added over 15 min.; the mixture was stirred for an additional 20 min. The excess nitrite was destroyed with 0.5 g. of urea in 10 ml. of water. The suspension of yellow diazonium salt was added over 0.5 hr. to a stirred solution at room temperature of 80 g. of potassium ethyl xanthate (technical grade) in 100 ml. of water. The temperature of the mixture rose to 40° during mixing; it was heated to 80° for 0.5 hr., cooled to 0°, and extracted with ether. After the ether solution had been washed and the ether removed by rotary evaporation, the aryl ethyl xanthate was saponified by refluxing with 200 ml. of ethanol and 20 g. of potassium hydroxide under nitrogen for 16 hr. The mixture was acidified and the mercaptan was extracted with ether, washed with acid and water, and extracted into 1 *N* sodium hydroxide. The alkaline extract was acidified and re-extracted with ether, which was washed and then dried with magnesium sulfate; the ether was removed. The oil prepared from 19.7 g. of 2-aminobenzophenone was dissolved in benzene and purified by chromatography on an 8 × 1.8 cm. column of Woelm neutral grade III alumina. Following the addition of the sample, the column was eluted with petroleum ether (b.p. 38–54°)–benzene, benzene, and ether–benzene. The material (identified by infrared) was crystallized from ethanol and from ethyl acetate–heptane; the melting point in an evacuated capillary was 42.6–44.6° cor. The yields in six preparations ranged from 20 to 25%; principal infrared bands were at 3.92 and 6.08 μ; ultraviolet bands showed (97% ethanol) λ_{max} 332 mμ (ϵ 3000) and 242 mμ (ϵ 14,500); n.m.r. (CCl_4) gave $-\delta$ 4.45 and 7.3, with ratio 1:9.

Anal. Calcd. for $C_{13}H_{10}OS$: C, 72.87; H, 4.70; S, 14.96. Found: C, 72.83; H, 4.81; S, 14.88.

4-Mercaptobenzophenone was prepared in an analogous fashion in 30% yield from 4-aminobenzophenone; principal infrared bands were at 3.96 and 6.12 μ; ultraviolet bands showed (95% ethanol) λ_{max} 380 mμ (ϵ 10,300), 300 (7500), and 240 (11,500); n.m.r. gave $-\delta$ 3.5 and 7.4 with ratio about 1:9.

Anal. Calcd. for $C_{13}H_{10}OS$: C, 72.87; H, 4.70; S, 14.96. Found: C, 73.08; H, 4.73; S, 14.67.

Methyl (2-benzoylphenyl) sulfide was prepared as an oil from 70 mg. of the corresponding thiol by methylation with dimethyl sulfate in methanolic sodium hydroxide; the principal infrared band was at 6.03 μ; ultraviolet bands (absolute ethanol) showed λ_{max} 340 mμ (ϵ 1200) and 245 mμ (ϵ 13,000); n.m.r. gave $-\delta$ 2.30 and 7.3, with a ratio of areas of 2.5:9 (theoretical 3:9).

Anal. Calcd. for $C_{14}H_{12}OS$: C, 73.65; H, 5.30. Found: C, 73.42; H, 5.28.

2-Hydroxybenzophenone was prepared according to Hey and Mulley[18] and purified by chromatography over alumina. Principal infrared bands were at 3.60 and 6.16 μ.

2-Mercaptoacetophenone[19] was prepared from 2-aminoacetophenone by a process analogous to that described for the prepara-

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(17) "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 305.
(18) H. Hey and R. D. Mulley, *J. Chem. Soc.*, 2276 (1952).
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tion of 2-mercaptobenzophenone; principal infrared bands were at 3.97 and 6.00 μ. The disulfide melted at 167–168.5° (lit.[19] 167–168°).

2-Mercaptobenzhydrol was prepared by the lithium borohydride reduction of 2-mercaptobenzophenone in 1,2-dimethoxyethane, followed by chromatography over alumina. The product was an oil; principal infrared bands were at 2.99, 3.30, 3.50, and 3.93 μ; n.m.r. showed (CCl_4) $-\delta$ 3.2, 5.8, and 7.1 in approximate ratio 2:1:9.

Anal. Calcd. for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; S, 14.82. Found: C, 72.46; H, 5.63; S, 14.85.

α-Deuterio-2-mercaptobenzhydrol was prepared by the lithium aluminum deuteride reduction of mercaptobenzophenone in ether, and purified by chromatography over alumina; principal infrared bands were at 2.94, 3.25, 3.90, and 4.65 μ.

Anal. Calcd. for $C_{13}H_{11}DOS$: D, 8.33 atom % excess. Found: 5.15 atom % excess.

Isolation of Products.—Reaction of 0.01 *M* Hantzsch compound with 0.01 *M* 2-mercaptobenzophenone for 4 hr. at 69° in 70% aqueous ethanol in a sealed tube, evacuated to a pressure of 0.7 mm. gave a 90% yield of 2,6-dimethyl-3,5-dicarboethoxypyridine and a 79% yield of 2-mercaptobenzhydrol. The corresponding reaction, run for 16 hr. in a mixture of 70% CH_3OD and 30% D_2O, yielded IV together with α-deuterio-2-mercaptobenzhydrol which was identical (infrared and n.m.r.) with authentic material. Reduction using 4-deuterio Hantzsch compound yielded 2-mercaptobenzhydrol, which was purified by chromatography on Florisil. It showed no deuterium in infrared, and analysis for deuterium showed 0.00 atom % excess deuterium. (Deuterium analyses were by J. Nemeth, Urbana, Ill.)

Methods.—Reductions were followed by measuring the disappearance of the ultraviolet absorbance of the dihydropyridines, which show a broad absorption band between 340 and 370 mμ. This band is absent in the corresponding pyridine, and usually absent in the other reactants or products. For more concentrated solutions, the shoulder of the band (up to 430 mμ) was used, or a sample was withdrawn and diluted for ultraviolet measurement. Anaerobiasis was established either by multiple degassing on the vacuum line or more conveniently by scrubbing the solution with prepurified nitrogen in a special cuvette[20] equipped with gas-bubbling tube and a ground joint designed to hold a slight pressure of nitrogen.

The "pH" values reported for 70% ethanol are those measured for the various buffers in water, increased by 1.5 pH units. This procedure approximately compensates for the change in meter reading for 0.001 *M* HCl between water and 70% ethanol.

(20) Designed by I. Fridovich.

Studies on the Mechanism of the Reaction of Peroxides and Alkenes with Copper Salts*,[1]

JAY K. KOCHI AND HAROLD E. MAINS

Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106

Received November 10, 1964

Pertinent new information regarding the mechanism of the reactions of peroxides, particularly *t*-butyl peresters, with alkenes catalyzed by copper salts has accumulated in the last several years. The various mechanisms which have been proposed for these reactions since their discovery by Kharasch and his co-workers are reviewed critically. The original assertion that the substitution occurs without migration of the double bond is no longer tenable and mechanisms which have been invoked on this basis must be modified. The mechanism which involves free alkyl and alkenyl radicals as intermediates and copper salts in an oxidation–reduction capacity is elaborated. The essential unity between these perester types of substitution reactions and the catalyzed decomposition of peroxides is stressed. For example, octenyl acetates can be generated from octene-1 and *t*-butyl perester and they consist of the same isomeric mixture as that produced from valeryl peroxide and butadiene. The oxidation of allylic radicals by cupric salts is examined further. The conclusion that the high specificity in the oxidation of octenyl and related radicals by cupric salts arises from an interaction between the incipient carbonium ion and the copper(I) species is further delineated.

Since the discovery of the metal salt promoted reactions of peroxides with organic substrates,[2] there have been a number of additional examples of its synthetic utility.[3,4] Of the variety of hydrogen donors which have been treated with peroxides under these conditions, alkenes probably represent the one class about which the most serious investigations have revolved. No doubt information regarding the mode of substitution in alkenes would also aid in the understanding of the reactions of other substrates. Since the original review of the reaction was written,[5] other mechanisms have been proposed and recent reviews[6,7] have failed to clarify the vital steps in the reaction. We have felt that a common mechanism is applicable to *all* reactions of peroxides with copper salts, and the plethora of mechanisms serve only to obscure the basic aspects of these reactions. In this report we wish to review the pertinent available information regarding the mechanism of this interesting reaction and to present further studies concerning the common features of the perester reaction with reactions of peroxides generally with metal salts.

As described originally the perester reaction, applicable mainly to *t*-butyl peracetate or benzoate, with alkenes is given by reaction 1. Of the three necessary

$$(CH_3)_3CO_2CCH_3 + RH \xrightarrow{CuX_n} (CH_3)_3COH + RO_2CCH_3 \qquad (1)$$

components of the reaction, copper salt, perester, and alkene, only the copper salt and peroxide are required for the more general reaction involving the catalytic decomposition of peroxides.[5,8] Common intermediates are involved in both reactions (*vide infra*), and

* Submitted in honor of Professor Louis F. Fieser by J. K. K.

(1) Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

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