

diisobutylaluminum chloride, although addition of the latter compound intensified the blue color of the solution.

Discussion

Titanium compounds with a single cyclopentadienyl group are rather rare. The compound of quadrivalent titanium, cyclopentadienyltitanium trichloride,¹⁵ is produced under comparatively vigorous conditions requiring long heating of di-cyclopentadienyltitanium dichloride with excess titanium tetrachloride at 115–120°. The mild conditions under which cyclopentadienyltitanium dichloride is produced emphasize how much more easily the organic anion is displaced from trivalent than from quadrivalent titanium. In none of our experiments was it possible to determine the fate of the cyclopentadienyl residue which is removed.

Since the reduction of the titanium from valence 4 to valence 3 is effected by the organoaluminum compound, it seems likely that it occurs in a bi-metallic complex similar to those which have been so carefully investigated relative to ethylene polymerization. The formation of monocyclopentadienyltitanium dichloride probably results from the displacement of an easily established equilibrium toward the insoluble product. If indeed the kind of compound isolated from such a solution, whether a complex or a single salt, is determined by solubility considerations, the complexes so often isolated are not held together by very strong forces.

It is of course possible that the initial violet precipitate contains aluminum which is lost during the acetonitrile treatment. The visual appearance of the powder, however, undergoes no change.

The general insolubility of cyclopentadienyltitanium dichloride suggests that it may exist as a chlorine-bridged dimer or in higher association in the crystal. A related compound of trivalent titanium complexed with two acetylacetone molecules has been reported by Pflugmacher, *et al.*,¹⁸

(18) A. Pflugmacher, H. J. Carduck and M. Zucketto, *Naturwiss.*, **45**, 490 (1958).

and shown to have the dimeric formula $[\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}]_2$ in chloroform. This compound was found to be diamagnetic,¹⁹ indicating an interaction between the titanium atoms which must provide a stabilizing force for the dimer. The unique solubility of our compound in acetonitrile may reflect a unique ability of this solvent to split the dimeric molecule by its complexing with the trivalent titanium. Although the very diffuse nuclear magnetic resonance absorption might be the result of a rapid interchange of some sort, such as that between monomer and dimer, the n.m.r. absorption would be broadened in any case by the paramagnetic character of the trivalent titanium, and hence its diffuseness affords no evidence of any exchange.

Our observations on the rate of polymerization of ethylene provide no test as to whether a suitably surrounded simple aliphatic titanium compound would promote polymerization or not. However, the results are entirely consistent with the conclusion reached by others that the special properties of a Ziegler catalyst reside in a complex involving both titanium and aluminum atoms. These results also re-emphasize the much greater efficiency in ethylene polymerization of a complex of quadrivalent titanium compared to one of trivalent titanium.

The reversible change of color on cooling an acetonitrile solution would be consistent with the view that there is a small amount of dimer in equilibrium with the monomer at room temperature. If, like most dissociations, the equilibrium is shifted toward the dimer on cooling, this would account for the approach to a yellow color at -78° .

Acknowledgment.—We thank the B. F. Goodrich Company for support of this work, and the Fulbright Commission, Washington, D.C., for a travel grant to B.S.

(19) A. H. Maki, Harvard University, personal communication.

[CONTRIBUTION FROM THE JAMES BRYANT CONANT AND MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

The Photochemical Reduction of Bromotrichloromethane by Derivatives of 1,4-Dihydropyridine

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1,2,6-Trimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine and 2,6-dimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine reduce bromotrichloromethane to chloroform. The reaction has been shown to proceed by a free-radical chain mechanism, and may be initiated either photochemically or thermally. The hydrogen atom of the chloroform molecule originates in the 4-position of the dihydropyridine ring. The implications of these findings for the reaction mechanism are discussed.

Diphosphopyridine nucleotide (DPN⁺) is one of the principal coenzymes for biochemical oxidation-reduction reactions. Although it has been established that the reactions in which it takes part proceed with direct transfer of hydrogen from substrate to coenzyme,¹ their detailed mechanisms

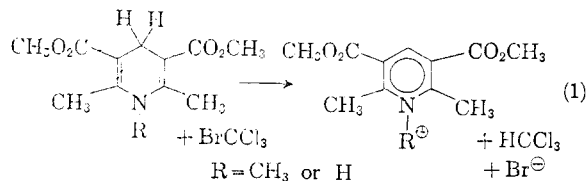
(1) B. Venesland and F. H. Westheimer, in "The Mechanism of Enzyme Action" (McElroy and Glass, Eds.), The Johns Hopkins Press, Baltimore, Md., 1954, p. 357.

are still not known. Several chemical (as contrasted to enzymatic) reactions of the coenzyme and of related pyridine derivatives have been examined, in an attempt to elucidate the chemistry of these oxidation-reduction systems. Reduced diphosphopyridine nucleotide (DPNH) and related compounds convert thiobenzophenone to benzyhydriol thiol,² and the

(2) R. Abeles, R. Hutton and F. H. Westheimer, *J. Am. Chem. Soc.* **79**, 712 (1957).

kinetics of the reaction have been investigated²; the reaction appears to be a polar one. The oxidation of DPNH by inorganic reagents suggests that several such reactions are of a free-radical nature.³ A similar conclusion arises from the electron spin resonance spectrum⁴ of an enzymatic oxidation-reduction reaction involving DPN⁺, although the signal detected was near the limit of applicability of the method. Wallenfels and Gellrich⁵ prepared dimeric products on the reduction of some N-alkyl salts of nicotinamide, and postulated a one-electron reduction product as an intermediate. Several other model reactions have been observed, but in no case has sufficient evidence been gathered to allow a definite statement of mechanism.⁶⁻⁸

In the course of the investigations of the u.m.r. spectrum of derivatives of dihydropyridine,⁹ it was observed that a slow reaction occurs between 1,2,6-trimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine and carbon tetrachloride. Further investigation identified the products of the reaction and showed that the parallel reaction (eq. 1) is much more rapid with bromotrichloromethane, that the rapid reaction may be photochemically initiated, that it proceeds with direct hydrogen transfer from reducing agent to oxidant, that it is retarded by radical scavengers, and finally that the chain length of the process is of the order of ten to one hundred.¹⁰ These data show that a radical formed in the oxidation of a 1,4-dihydropyridine is sufficiently stable to participate in chemical reactions, but of course leaves open the question of the mechanism of the enzymatic oxidation-reduction processes.



Experimental

Materials.—2,6-Dimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine (DH) was prepared by the method previously¹¹ used for the synthesis of the corresponding ethyl ester. After it had been recrystallized from methanol, it melted at 231–233° (evac. cap.).

Anal. Calcd. for C₁₁H₁₅NO₄: C, 58.65; H, 6.71; N, 6.22. Found: C, 58.71; H, 6.68; N, 5.76.

This Hantzsch compound was oxidized to 2,6-dimethyl-3,5-dicarbomethoxypyridine with nitric acid, again following the procedure¹¹ for the ethyl ester. After recrystallization from ethanol-water, the pyridine derivative melted at 101–102°.

(3) K. A. Schellenberg and L. Hellerman, *J. Biol. Chem.*, **231**, 547 (1958).

(4) B. Commoner, J. J. Heise, B. B. Lippincott, R. E. Norberg, J. V. Passonneau and J. Townsend, *Science*, **126**, 57 (1957).

(5) K. Wallenfels and M. Gellrich, *Ber.*, **92**, 1406 (1959).

(6) R. Abeles and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 5459 (1958).

(7) K. Wallenfels and D. Hofmann, *Tetrahedron Letters*, **15**, 10 (1959).

(8) B. Kadis, Abstracts of the 135th Meeting of the American Chemical Society, Boston, Mass., 1959, p. 24-O.

(9) R. Hutton and F. H. Westheimer, *Tetrahedron*, **3**, 73 (1958).

(10) See F. H. Westheimer in "The Steric Course of Microbiological Reactions," Ciba Foundation Study Group No. 2, J. A. Churchill Ltd., London, 1959, p. 3, for a preliminary communication related to this work.

(11) H. Meyer and H. Tropsh, *Monatsh.*, **35**, 207 (1914).

Anal. Calcd. for C₁₁H₁₅NO₄: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.04; H, 5.86; N, 6.24.

This compound was methylated with dimethyl sulfate according to the general method of Mumm,¹² and the product isolated as the perchlorate salt. A concentrated, filtered solution of the crude methosulfate was mixed with a twofold excess of aqueous 1 F sodium perchlorate solution, warmed to dissolve any precipitate which formed, and slowly cooled. The large needles so obtained were recrystallized from water, and melted at 143–144° (e.c.).

Anal. Calcd. for C₁₂H₁₆NO₆Cl: C, 42.70; H, 4.78; N, 4.15. Found: C, 42.97; H, 4.82; N, 4.36.

This perchlorate salt was reduced to 1,2,6-trimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine (MDH) with sodium dithionite, following the known procedure¹³ for the ethyl ester. The compound was recrystallized from methanol-water, and melted (e.c.) at 105–106°.

Anal. Calcd. for C₁₂H₁₇NO₄: C, 60.23; H, 7.16; N, 5.85. Found: C, 60.21; H, 7.27; N, 6.08.

Some difficulty was found in analyzing this compound; the analysis reported is that of the Elek Microanalytical Laboratories. 1-Benzyl-1,4-dihydronicotinamide¹⁴ melted at 123–125° (e.c.), and 9,10-dihydroanthracene¹⁵ melted at 104–106°.

Bromotrichloromethane (Matheson, Coleman and Bell) was fractionated in the dark under nitrogen through a 400-mm. column packed with glass helices; the fraction boiling at 104.8–105.2° was collected and frozen. Portions sufficient for several experiments were distilled on the vacuum line into a bulb, which was shielded from light, and stored in vacuum prior to use. Reagent grade methanol was purified by dissolving 15 g. of magnesium in 500 ml. of the solvent, and heating the system under reflux under nitrogen with 30 g. of hydroquinone. The solvent was degassed, and distilled into a storage bulb in the vacuum line. The storage bulb contained ca. 50 ml. of solvent, 1 g. of magnesium and 2 g. of hydroquinone.

Methanol purified by simple warming with MDH, when used as solvent, yielded the same kinetic behavior as did that purified and stored over alkaline hydroquinone. However, when "Reagent Grade" methanol was used without purification, rapid but irreproducible rates were obtained. An important criterion of purity for the methanol used in these experiments was that MDH was stable in it for long periods of time. For example, a solution of MDH in the solvent showed no detectable decrease in optical density after illumination at 365 mμ for 21 minutes or after 1000 minutes in the dark. The absorption spectra of solutions of MDH, bromotrichloromethane and methanol were not scanned to find whether evidence for complex formation could be obtained; the relatively rapid dark reaction makes such experiments difficult to perform. No obvious color change, however, occurred on mixing the reagents.

Deuterated Compounds.—1-Deuterio-2,6-dimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine was prepared by refluxing 5 g. of DH dissolved in 10 ml. of D₂O and 100 ml. of purified dimethoxyethane for 20 minutes. The process was repeated three times; no N-H band could then be observed in the infrared spectrum of the deuterio compound.

4,4-Dideuterio-2,6-dimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine was prepared by Dr. Robert Graves (whose assistance we gratefully acknowledge) by the standard method for the Hantzsch synthesis,¹¹ but using dideuterioformaldehyde purchased from Merck and Co.

Products.—The solution from the reaction of bromotrichloromethane with either DH or MDH was evaporated to dryness under nitrogen and the last traces of the solvent removed in vacuum. The residue was taken up in methanol, and the identity of the product established by determining its ultraviolet spectrum with a Cary recording spectrophotometer. The yields of the salt from MDH were determined on the assumption that the bromide and perchlorate have the same extinction coefficient. The salt from the oxidation of 0.4 mmole of MDH was isolated by evaporating the methanol and dissolving the residue in 1.5 ml. of a hot 1 F

(12) O. Mumm and collaborators, *Ann.*, **443**, 272 (1925).

(13) O. Mumm and J. Diederickson, *ibid.*, **538**, 195 (1939).

(14) D. Mauzerall and F. H. Westheimer, *J. Am. Chem. Soc.*, **77**, 2261 (1955).

(15) E. Clemmensen, *Ber.*, **47**, 681 (1914).

aqueous solution of sodium perchlorate. On cooling the solution perchlorate deposited, which was washed at 0°, first with sodium perchlorate solution and then with water, and dried in vacuum over silica gel. The substituted pyridine, obtained by the oxidation of DH, was isolated by precipitating it from 10 ml. of aqueous solution with ammonia.

The yield of pyridinium salt from MDH and bromotrichloromethane in the dark, as determined by ultraviolet spectroscopy, exceeded 95%. The yield of pyridinium salt from MDH, isolated as the perchlorate, from the reaction in the dark, or under room light, or promoted by the 366 m μ band from the mercury arc ranged from 67 to 79% of material of good melting point. The yield of the pyridine from DH and bromotrichloromethane under room light was about 82% of material of good melting point. In each case, the identity of the product was confirmed by comparison of the infrared spectrum of the product with that of an authentic sample.

The chloroform or deuteriochloroform was obtained in the following experiment. About 0.8 millimole of DH (or of the analogous ester labeled in the 4-position or the 1-position with deuterium) was placed in a break-seal tube on the vacuum line, and 0.8 ml. of bromotrichloromethane introduced by distillation. The tube was sealed, and the reaction carried to completion with ultraviolet light. The tube was returned to the vacuum line, the seal broken, and the volatile products removed by distillation. The yield of chloroform, determined by infrared spectroscopy, was 73%. The reaction of either DH or of the 1-deuterio derivative of DH gave ordinary chloroform, but the reaction of 4,4-dideuterio-DH with bromotrichloromethane gave deuteriochloroform, contaminated with a small amount (4%) of chloroform. The amount of the latter was consistent with that anticipated on the basis of the isotopic purity (97%) of the starting material.

Kinetic Method.—Both the dark reaction and the photochemical experiments were carried out in Pyrex cells transparent to the (relatively long wave length) ultraviolet light used in these experiments. The cells fitted directly into a Beckman model DU quartz spectrophotometer, thermostated at 30.1°, where the concentration of DH or MDH was determined. A sample of the dihydropyridine derivative was introduced into the cell, degassed on the vacuum line, and about 6 cc. of methanol distilled into the cell from the storage container on the vacuum line. The bromotrichloromethane was distilled into a graduated tube (where its volume was measured) and then into the cell. The latter was sealed off, rapidly warmed to the desired temperature, shaken to dissolve the solid, and the concentration of dihydropyridine followed spectrophotometrically. All these (and subsequent) operations were carried out using the minimum sufficient illumination of red light. The final volume of the solution was determined after completion of the reaction. Control experiments showed that the dim light (350–425 m μ) from the spectrophotometer was insufficient to effect reaction. Any additional solids or liquids were introduced as described for the dihydropyridines or bromotrichloromethane, respectively.

Quantum Yields.—The cell was cooled with a jet of air at 27–30° and irradiated for 0.25-minute intervals with a General Electric UA2 medium pressure mercury arc. Measurements of the temperature of methanol in open cells subjected to these conditions showed that the temperature was maintained close to 30°. The decrease in optical density due to the dark reaction was followed in the thermostated spectrophotometer cell between irradiations. The amount of photochemical reaction during each exposure to light was estimated by subtracting the decrease anticipated for the dark reaction from that observed. This correction usually amounted to about 10–15% of the total. The quantum yield at the initial dihydropyridine concentration was estimated by extrapolating the quantum yields calculated from the several irradiations during the course of the run. The 366 and 405 m μ lines were isolated with Corning CS7-83 and CS5-62 filters, respectively; the 313 m μ lines were isolated by filters of 2 mm. of Pyrex glass, plus 2.5 cm. of an aqueous solution containing 46 g. of nickelous sulfate hexahydrate and 14 g. of cobaltous sulfate heptahydrate per 100 ml. Additional thin Pyrex plates were used to adjust further the intensity of the 313 m μ lines.

The quantum flux entering the cell was determined by uranyl oxalate actinometry.¹⁶ The light beam was collimated by two slits, and its area, where it entered the reac-

tion cell, was 6 × 26 mm. (The reaction cells were 10 × 10 × 60 mm. i.d.) The reaction solutions were always sufficiently concentrated to absorb 96% or more of the incident light.

Experiments with mechanical stirring were carried out at 366 m μ to determine whether incomplete mixing was affecting the quantum yield. A 35-mm. length of no. 12 nickel wire was placed in the cell, and the cell shaken with a Vibro-Mixer during illumination; agitation was violent. Then the wire was held out of the light path by a magnet during measurements of optical density. Quantum yields of 10.5 and 10.7 were observed under experimental conditions which gave an average quantum yield of 7.1 in the absence of stirring. Almost all other runs had a lower optical density–initial light intensity product than these, and therefore presumably were less affected by inhomogeneities arising from incomplete mixing during the illumination.

Formation of Halide Ion.—Tubes prepared as for kinetic runs were opened after suitable time intervals, and the contents rinsed out with methanol plus 1 cc. of acetic acid. The solutions were titrated potentiometrically, using as electrodes a bare silver wire and a saturated calomel or buffered quinhydrone reference half-cell, connected by an ammonium nitrate–agar bridge. Two separate inflection points allowed the determination of both chloride and bromide in the same solution, provided that at least 2% of the total halide was present as Cl⁻.

The reaction of bromotrichloromethane with a dihydropyridine in the absence of oxygen and under illumination by fluorescent light yields an almost quantitative amount of bromide ion, accompanied by little chloride. On the other hand, in the presence of oxygen, the reaction leads to decomposition of bromotrichloromethane which produces chloride and bromide in the ratio of three to one; the process may be a modification of the gas phase oxidation of bromotrichloromethane.¹⁷ When illuminated with ultraviolet light, bromotrichloromethane reacts with methanol, even in the absence of dihydropyridine, to give bromide and chloride ion. However, in vacuum, and under the experimental conditions for the oxidation–reduction reactions carried out in these studies, the yield of bromide ion was nearly quantitative, and the yield of chloride ion low.

Results

Kinetics.—In the dark, a thermal reaction occurs between various dihydropyridines and bromotrichloromethane in methanol solution. (In pure bromotrichloromethane reaction occurs readily, but the precipitation of the reaction product, a substituted pyridinium bromide, made the determination of rates difficult.) The rates were determined in the presence of a large excess of bromotrichloromethane, and for each experiment were slightly more than first order in the dihydropyridine derivative. However, the rates are not highly reproducible, and duplicate experiments showed rates differing by as much as a factor of two. Within this range of error, the first-order rate constant is unchanged when the initial concentration of MDH is increased by a factor of 300 from 0.2×10^{-3} to 60×10^{-3} M, or when the concentration of bromotrichloromethane is increased by a factor of 30 from 0.16 M to 4.9 M. Dihydroanthracene, when present in concentrations comparable to that of the dihydropyridine, reduces the rate of reaction of the latter by factors of 20 to 100. The data are presented in Table I.

1-Benzyl-1,4-dihydropyridine disappears much more rapidly in a dark reaction with bromotrichloromethane than either DH or MDH, but the chemistry of the reaction is complex, and has not yet been elucidated.

berger's "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Vol. 11, p. 294.

(17) W. Frank and H. J. Schumacher, *Z. Physik. Chem.*, **B42**, 300 (1939).

(16) C. R. Masson, V. Boekelheide and W. A. Noyes, in Weiss-

TABLE I
KINETICS OF THE REACTIONS BETWEEN 1,4-DIHYDROPYRIDINES AND BROMOTRICHLOROMETHANE IN METHANOL AT 30°
IN THE DARK

Dihydropyridine	$10^3 \times$ initial dihydropyridine concentration	(Br-CCl ₃) ₀ , <i>M</i>	Range followed, %	<i>n</i> ^b	$10^4 k_1$, ^a sec. ⁻¹
MDH	0.2	0.27	62		1.0
MDH	0.2	0.69	75	1.3	1.1
MDH	0.2	0.84	88	1.2	1.1
MDH	0.4	0.15	90	1.2	3.1
MDH	0.4	0.12	80	1.3	2.0
MDH	0.6	0.16	66		1.8
MDH	3.4	1.7	82	1.3	2.5
MDH	3.5	1.8	80	1.4	2.6
MDH	3.4	1.7	77	1.4	3.5
MDH	4.0	1.8	66		3.5
MDH	3.7	1.8	75	1.3	4.3
MDH	3.3	1.6	80	1.4	5.0
MDH	3.4	1.6	72		3.8
MDH	3.7	1.8	85	1.4	5.7
MDH	3.5	1.7	82	1.4	4.8
MDH	3.6	1.7	80	1.4	5.3
MDH	3.5	0.16	50		1.7
MDH	3.7	0.18	68		3.3
MDH	3.8	0.18	70		1.7
MDH	3.3	4.3	70		3.1
MDH	3.5	4.6	67		1.7
MDH	3.4	4.9	68		2.5
MDH	59	1.6			2.0
MDH	66	1.7			2.3
DH	3.5	1.7	88	1.3	4.2
DH	3.4	1.7	90	1.4	6.2

^a First-order rate constant, evaluated at the end of the first half-time for 30.1°. ^b Reaction order with respect to dihydropyridine, evaluated from a plot of $\log d(\text{O.D.})/dt$ versus $\log (\text{O.D.} - \text{O.D.}_\infty)$ for those runs followed to more than two half-times.

Quantum Yields.—The quantum yields obtained in the photochemical experiments are presented in Table II. The individual experiments were reproducible to about $\pm 10\%$, which is far better than the reproducibility of the dark reaction. The quantum yield for 366 m μ radiation increases approximately with the 0.5 power of the concentration of MDH over the range from 3.5×10^{-3} to 60×10^{-3} *M*. At all three wave lengths studied, the quantum yield is independent of the concentration of bromotrichloromethane when this concentration exceeds 1.7 *M*, but decreases by a factor of about two at 0.17 *M*. As a rough first approximation, the photochemical rate varies as the half-power of the light intensity. More precisely, plots of $\log (\Phi - 1)$ against the logarithm of the product of the quantum flux and the optical density at the wave length being used, at two concentrations of bromotrichloromethane, but at all three wave lengths, give slopes between 0.5 and 0.6.

Dihydroanthracene retards the photochemical reaction as it does the dark reaction; the data are presented in Table III. Neither hydroquinone nor pyrogallol at concentrations exceeding that of the MDH appears to affect either the quantum yield or the dark rate.

When carbon tetrachloride was substituted for bromotrichloromethane, the quantum yields fell to about 0.2; with ethyl bromide they were negligible.

TABLE II
QUANTUM YIELDS FOR THE REACTION OF 1,4-DIHYDROPYRIDINES WITH BROMOTRICHLOROMETHANE IN METHANOL

λ , m μ	Dihydropyridine	$10^3 \times$ initial dihydropyridine concentration	(BrCCl ₃) ₀ , <i>M</i>	$10^3 \Phi_0$, einstein sec. ⁻¹ cm. ⁻²	Φ_0^a
366	MDH	3.4	1.7	4.7 ± 0.2	6.9
366	MDH	3.5	1.8	$4.7 \pm .2$	7.7
366	MDH	3.4	1.7	$4.7 \pm .2$	6.6
366	MDH	3.5	0.16	$4.7 \pm .2$	3.5
366	MDH	3.3	4.3	$4.7 \pm .2$	7.1
366	MDH	59	1.6	$4.7 \pm .2$	37
366	MDH	66	1.7	$4.7 \pm .2$	34
366	DH	3.5	1.7	$4.7 \pm .2$	11.5
366	DH	3.4	1.7	$4.7 \pm .2$	11.0
405	MDH	4.0	1.8	0.58 ± 0.02	36
405	MDH	3.7	1.8	$.58 \pm .02$	38
405	MDH	3.5	4.6	$.58 \pm .02$	38
405	MDH	3.7	0.18	$.58 \pm .02$	15.8
313	MDH	3.4	1.6	$.93 \pm .06$	16.0
313	MDH	3.7	1.8	$.93 \pm .06$	16.4
313	MDH	3.4	4.9	$.93 \pm .06$	16.1
313	MDH	3.8	0.18	$.93 \pm .06$	8.0
313	MDH	3.5	1.7	$.35 \pm .02$	35
313	MDH	3.6	1.7	$.10 \pm .005$	79

^a Quantum yield (moles of dihydropyridine destroyed per einstein), extrapolated to zero time.

TABLE III
EFFECT OF DIHYDROANTHRACENE

10^4 (MDH) ₀ , <i>M</i>	10^3 (DHA) ₀ , ^a <i>M</i>	(Br-CCl ₃) ₀ , <i>M</i>	$10^4 k_1$, ^b sec. ⁻¹	k_1 (no DHA) / k_1 c/	Φ_0 ^d	Φ_0 (no DHA) c/ Φ
3.6	1.7	1.7	0.17	24	2.0	3
3.6	3.5	1.8	.13	30	1.5	5
3.6	47	1.7	.03	120	0.6	12
0.6	0.6	0.16	.03	55		
0.6	18	0.16	.017	110		
62	63	1.6			1.0	35

^a DHA = 9,10-dihydroanthracene. ^b First-order rate constant, evaluated at $(\text{MDH}) = \frac{1}{2} (\text{MDH})_0$ for 30.1°. ^c k_1 (no DHA) and Φ_0 (no DHA) are average values of k_1 and Φ_0 from Tables I and II for comparable conditions. ^d Quantum yield (moles of MDH destroyed per einstein), extrapolated to zero time. Measured for 366 m μ radiation with $\Phi_0 = 0.28 \times 10^{-6}$ einstein min.⁻¹ cm.⁻².

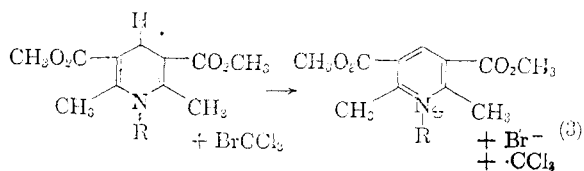
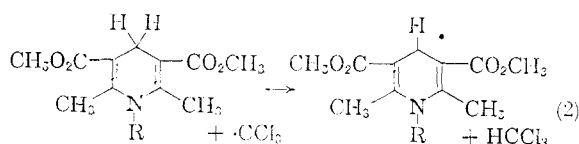
Discussion

Neither the reaction in the absence of light nor that in the presence of light is simple. However, some qualitative conclusions seem warranted.

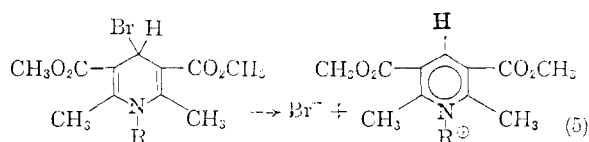
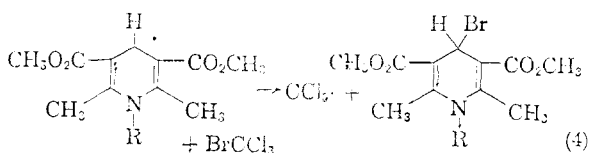
The difficulty in obtaining reproducible rates for the dark reaction, even in highly purified methanol, together with the effect of dihydroanthracene as inhibitor, suggests that the reaction is free radical in nature. Dihydroanthracene is known¹⁸ as an especially efficient scavenger for the trichloromethyl radical, and the diminution of the rate by a factor of 20–120 in the presence of this inhibitor argues strongly that the dark reaction is a radical process, with a chain length of the order of 10^2 .

The photochemical reaction has a quantum yield of about 7 to 80, depending on experimental conditions; although reaction is initiated photochemically, it continues by a non-photochemical chain process. By the addition of dihydroanthracene,

the quantum yield could be reduced to the neighborhood of unity. Presumably the chain propagation for both the light and dark reactions proceeds by the mechanism indicated in equations 2 and 3.



An alternate possibility for reaction 3, which involves the formation of a covalent intermediate, is shown in eqs. 4 and 5.



A further refinement in mechanism would envision the formation of charge transfer complexes as intermediates in the reaction.¹⁹ However, no evidence presently available distinguishes among these possibilities, and the formulation of equations 3 and 4 has the virtue of simplicity.

These experiments give little direct evidence concerning the detailed process of chain initiation. The large energy requirement for the homolytic dissociation of bromotrichloromethane²⁰ makes this reaction an unlikely one for the initiation of the dark reaction. In the photochemical process, the photoexcited molecules of dihydropyridine are presumed to initiate the reaction. This conclusion rests on the data of Table II, where the quantum yield is shown to be almost independent of wave length. The extinction coefficients for the dihydro compound, MDH, and for bromotrichloromethane are²¹

	313 m μ	366 m μ	405 m μ
Dihydropyridine, MDH	2.2×10^3	5.6×10^3	1.4×10^3
Bromotrichloromethane	1.14	5.0×10^{-4}	8×10^{-3}
			(extrap.)

(19) E. M. Kosower, *J. Am. Chem. Soc.*, **77**, 3883 (1955); **78**, 3497 (1956).

(20) J. B. Farmer, H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

(21) The extinction coefficient for bromotrichloromethane at 366 m μ was taken from the data of H. W. Melville, J. C. Robb and R. C. Tutton, *Disc. Faraday Soc.*, **10**, 154 (1951); the value at 405 m μ was extrapolated from their data.

Therefore, at the shortest wave length, when the concentration of the dihydro compound was $3.5 \times 10^{-3} M$, and that of bromotrichloromethane was 4.9 M, the latter absorbed 42% of the light. By contrast, at the longest wave length and a concentration of bromotrichloromethane of 0.17 M, it absorbed only 0.0003% of the light. Yet the quantum yield is not substantially affected by these changes. Presumably if the dihydropyridine were an inert filter, the quantum yield would fall sharply as the percentage of light absorbed by the bromotrichloromethane decreased. Further, since the bromotrichloromethane absorbs at shorter wave lengths than the photoactive band of the dihydropyridine, simple energy transfer to dissociate the halide cannot occur. The reaction is therefore almost certainly initiated by absorption of light by the dihydropyridine, but the data are insufficiently precise to decide whether initiation by photoactivation of bromotrichloromethane (especially at short wave lengths) also can occur. The details of the initiation step have not been elucidated and, in particular, the question of whether a singlet or triplet state is involved in the chemical initiation has not been determined.

No satisfactory rate law has been derived from these data, although the (approximately) half-power dependence on light intensity suggests a second-order termination step. The most important conclusion which can be drawn from this investigation is that the uncharged dihydropyridine radical, shown in eqs. 3 and 4, is sufficiently stable to sustain a chain reaction.

Two other photochemical reactions of dihydropyridines are known. Berson and Brown showed that 4-(2'-nitrophenyl)-1,4-dihydropyridines are isomerized by light of wave length 366 m μ to yield the corresponding 4-(2'-nitrosophenyl)-pyridines.²² More recently, Frisnell and Mackenzie reported the photochemical oxidation of DPNH by pyruvate.²³ This reaction was carried out with a hundred-fold excess of pyruvate in an aqueous phosphate buffer at pH 7.8 in the presence of magnesium ions. No quantum yields are given, but the authors state that they illuminated their sample with a "36-in. General Electric 'black light' fluorescent lamp" which was 2 cm. from their sample. A calculation based upon the description of their experiment and the published characteristics of the lamp suggests that the quantum yield was low, and perhaps only of the order of 10^{-4} ; this roughly corresponds with the results of similar experiments carried out with our apparatus. The present experiments, which demonstrate that a free radical related to a dihydropyridine can carry on a chain process, significantly expands the photochemistry of dihydropyridines.

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(22) J. A. Berson and E. Brown, *J. Am. Chem. Soc.*, **77**, 447 (1955).

(23) W. R. Frisnell and C. G. Mackenzie, *Proc. Nat. Acad. Sci.*, **45**, 1568 (1959).