

ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Monocyclopentadienyltitanium Dichloride

BY PAUL D. BARTLETT AND BERNHARD SEIDEL

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A concentrated solution of dicyclopentadienyltitanium dichloride with 1.3 equivalents of diisobutylaluminum chloride in a toluene-heptane solvent gives as precipitate the insoluble violet compound, cyclopentadienyltitanium dichloride. This material is insoluble in all hydrocarbon solvents but yields a blue solution in acetonitrile. It is extremely sensitive to oxygen, forming a yellow benzene-soluble oxidation product. Its ultraviolet, e.s.r. and n.m.r. spectra have been observed. It is not a catalyst for ethylene polymerization but shows low catalytic activity on addition of diisobutylaluminum chloride.

Introduction

The interaction of titanium tetrachloride with trialkylaluminums or alkylaluminum chlorides has yielded a variety of characterized and uncharacterized products, whose chemical properties are strikingly different from those of the separate reactants.¹⁻³ Dicyclopentadienyltitanium dichloride in a similar reaction with organoaluminum compounds has led to a series of complexes always containing at least one atom each of titanium and aluminum and, when formed under mild conditions, preserving the sandwich complexing of the titanium with two cyclopentadienyl groups.⁴⁻¹¹ In this connection it is of interest that a concentrated solution containing dicyclopentadienyltitanium dichloride and diisobutylaluminum chloride in a molar ratio of 1:1.3 deposits spontaneously an extremely air-sensitive violet crystalline compound whose composition and molecular weight show it to be monocyclopentadienyltitanium dichloride.

Experimental

Cyclopentadienyltitanium dichloride, as well as all polymerization catalysts of related structure, is extremely sensitive to minute amounts of oxygen and of moisture, a fact which probably accounts for the generally poor reproducibility of reaction rates observed in the Ziegler polymerization of ethylene. The 5 parts per million of oxygen contained in the prepurified nitrogen available commercially is far too much for the work reported in this paper. Use has been made here of a combined vacuum-line and syringe technique based upon procedures worked out for this program by Drs. E. M. Arnett and R. L. Baird.

Nitrogen (prepurified grade containing 5 p.p.m. oxygen, dew point -75° , from Air Reduction Co.) was further purified in an apparatus sealed to the vacuum line, shown schematically in Fig. 1. The nitrogen was passed through

a mercury bubbler A, then through a long tower B containing indicating Drierite, Ascarite, dry molecular sieves, magnesium perchlorate and a section of glass wool. This tower was followed by an empty safety trap C, a trap D heated to $60-80^{\circ}$, containing a 35% solution of triisobutylaluminum in purified mineral oil, a foam trap E, and finally a trap F chilled with Dry Ice-acetone and filled with glass wool. For higher flow rates of nitrogen the addition of a second cool trap (reverse) is advisable. The system was kept under a positive nitrogen pressure (about 4 cm.) at all times. In the connections from the cylinder to the purifying train rubber was replaced by polyisobutylene or copper, and all non-glass connections were made as short as possible. By the inclusion of a little of the trialkylaluminum solution in trap C, bubbles are formed in the tube from C to D and serve to indicate the flow of gas. The gas is dispersed in D into fine bubbles by a glass frit. Dilution of the triisobutylaluminum with mineral oil increases the safety of handling when the solution needs to be changed; the heating decreases the viscosity of the solution and increases its efficiency in oxygen removal. Prior to filling, the whole apparatus was evacuated and flamed out. Only by the treatment described could nitrogen be obtained under which cyclopentadienyltitanium dichloride was indefinitely stable and showed no oxidation to the yellow, benzene-soluble product.

Transfer Technique.—All solvents were thoroughly dried, degassed and stored on the vacuum line under their own vapor pressure. Where stopcock grease was necessary, only silicone grease was found satisfactory. All transfers of solvents were made by direct distillation on the vacuum line.

- (1) K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, **67**, 426 (1955).
- (2) K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *ibid.*, **67**, 541 (1955).
- (3) K. Ziegler, H. Martin and A. J. Stedefeder, *Tetrahedron Letters*, No. 20, 12 (1959).
- (4) G. Natta, P. Pino, G. Mazzanti and U. Giannini, *THIS JOURNAL*, **79**, 2975 (1957); G. Natta, P. Corradini and I. W. Bassi, *ibid.*, **80**, 755 (1958).
- (5) G. Natta, *Experientia Suppl.* **VII**, 21 (1957); G. Natta, U. Giannini, G. Mazzanti and P. Pino, *Ricerca Sci. Suppl.*, **28** (1958).
- (6) G. Natta, P. Pino, G. Mazzanti and U. Giannini, *J. Inorg. Nucl. Chem.*, **8**, 612 (1958).
- (7) G. Natta, G. Mazzanti, P. Corradini, U. Giannini and S. Cesa, *Atti. acad. naz. Lincei, Rend. Classe sci. fis. mat. Nat.*, **26**, 150 (1959).
- (8) G. Natta and G. Mazzanti, *Tetrahedron*, **8**, 86 (1960).
- (9) D. S. Breslow and N. R. Newburg, *THIS JOURNAL*, **79**, 5072 (1957); **81**, 81 (1959).
- (10) J. C. W. Chien, *ibid.*, **81**, 86 (1959).
- (11) W. P. Long, *ibid.*, **81**, 5312 (1959).

Transfers of solutions containing air-sensitive material were carried out by means of hypodermic syringes. Solids also were transferred by this technique, in the form of slurries in heptane or benzene. The syringes were manufactured by Becton and Dickinson; the needles were of gauge 17, were quite flexible and long enough to reach to the bottoms of the traps. The syringes were baked out in an oven at 130° for several hours and cooled in a stream of pure dry nitrogen. Special sheaths were used as nitrogen locks for the protection of the needle tips during the transfers. Figure 2 shows the design of such a sheath. The long vertical tube is provided to permit easy handling of the syringe and sheath together, before attachment to the trap and while they are being moved from one trap to another. The upper end of the sheath is closed by a rubber syringe-cap, and the lower end is provided with a rubber sleeve by which it is attached, first to the nitrogen line, and then, after thorough flushing, to the sidearm of the trap which has also been flushed with nitrogen on the outer side of its stopcock. During the process of attaching the sheath to the trap, the mouth of each is further flushed with pure nitrogen from a second needle which can be inserted through the rubber sleeve and withdrawn at the last moment. Finally the stopcock is opened, the sheath flushed with nitrogen from the vacuum line as an additional precaution by slightly lifting the rubber cap on its upper end, the hypodermic needle withdrawn from the vertical arm until it is free, and then lowered straight through the open stopcock into the trap. The positive nitrogen pressure in the latter forces the liquid into the syringe without any suction being generated by the plunger of the syringe. When the necessary amount has been taken up, the needle is withdrawn and

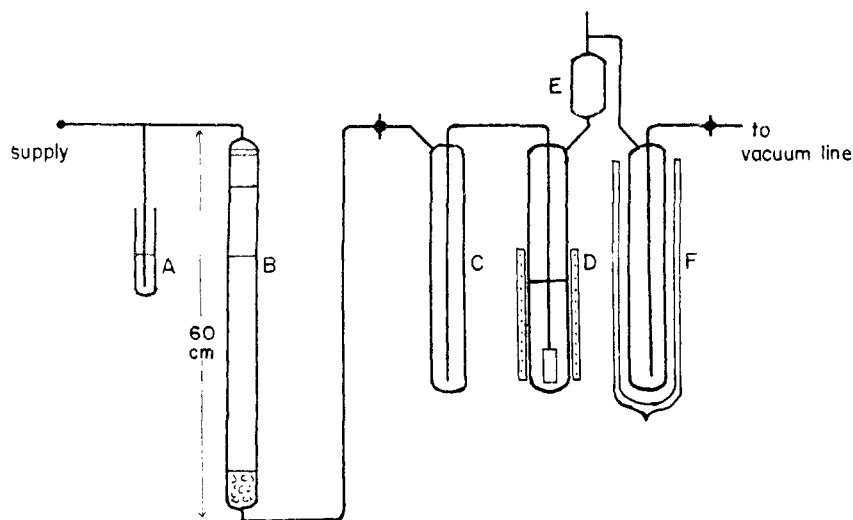


Fig. 1.

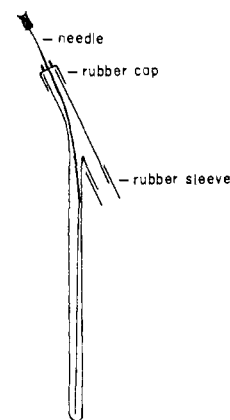


Fig. 2.

reinserted in the vertical tube of the sheath, the stopcock is closed, and sheath and syringe moved to the next trap, where the procedure is repeated. Filtrations into a trap were performed through a sidearm holding a frit and a stopcock above it in the same way. However, two needles were inserted through the rubber cap so that the space above the frit could still be kept under nitrogen after the frit was covered with liquid. After filtration the solution was frozen, and the sidearm was sealed off under vacuum.

To obtain dry solid, the solvent from slurries was distilled off slowly *in vacuo*.

Analytical samples were treated in the same way, but were transferred only within a trap to which three sidearms had been attached which carried small tared glass vessels attached by rubber sleeves. Into these the slurries were introduced with a bent needle. Drying the solids in the vessels was followed by sealing them off under vacuum or nitrogen with a micro flame after material at the sealing zone had been sublimed away *in vacuo*. Both parts of the ampoules were weighed later (and when necessary buoyancy corrections were made).

For spectroscopic measurements a quartz cell with a graded seal and sidearm with stopcocks was employed. After evacuation, solvent was distilled into the cell to fill it partially and the system filled with pure nitrogen. After removal of the apparatus from the vacuum line, some concentrated solution was introduced against a stream of purified nitrogen from the sidearm, so that the total solution reached higher than the narrow neck of the quartz cells. This prevented contamination of the solution in the cell although the upper layers were normally slightly oxidized by O_2 from the nitrogen. In the molecular weight determination the amount of substance in the Siguer apparatus was calculated from the titanium content of the solution, which was determined after the vessel was opened at the end of the experiment.

Preparation of Monocyclopentadienyltitanium Dichloride.—Five grams of dicyclopentadienyltitanium dichloride was introduced under nitrogen into a reaction vessel, the vessel attached to the vacuum line, evacuated twice and refilled with nitrogen. Then a mixed solvent consisting of 2 ml. of toluene and 8 ml. of heptane was introduced and the solution degassed three times by freezing to -78° , evacuating, warming and repeating the cycle. Finally, 5.05 ml. of diisobutylaluminum chloride was added and the mixture warmed to 50° for 3 hours to facilitate solution of the titanium compound. The originally red solution turned brown and then green over a period of 2 hours and was allowed to stand overnight at room temperature. On standing, a violet precipitate was formed and was isolated by filtering off the supernatant solution. The precipitate could be washed with heptane, in which it is quite insoluble.

Properties of the Violet Compound. A. Solubility.—First tests with benzene yielded a yellow solution, but, after introduction of the final precautions described and purification of the nitrogen, thoroughly degassed benzene could

be distilled into the vessel containing the violet compound with no coloration of the benzene observable. Prior drying and baking of the glassware was also an essential precaution in the attainment of this result. It was thus found that the compound possesses no observable solubility in heptane, benzene, chlorobenzene or diphenyl ether. It was soluble to the extent of about 5% in pure acetonitrile at room temperature and slightly above and could be recovered unchanged by evaporation of this solvent *in vacuo*. It dissolved also in methanol and other alcohols but was not recovered from these solutions.

B. Purification.—As the solubility in acetonitrile did not seem to change much with temperature, a reprecipitation process was used. The crude product in heptane was transferred into a clean vessel attached to the vacuum line, the transfer being effected by a hypodermic syringe against a stream of the purest nitrogen. After washing by adding heptane and benzene (by distillation or sublimation and thawing) and withdrawing the supernatant liquid with a hypodermic syringe, acetonitrile was distilled into the vessel *in vacuo* followed by an amount of benzene insufficient to cause precipitation. The blue-green solution was allowed to stand for several hours at room temperature during which all insoluble material settled in a small depression in the bottom of the vessel. The solution was withdrawn from the insoluble matter with a hypodermic syringe, transferred into another similar flask under nitrogen and frozen. Acetonitrile and benzene were sublimed off *in vacuo* so that the violet compound remained nearly dry. Then more benzene was introduced by sublimation so that the resultant solid contained only a small amount of acetonitrile. This produced a solvent capable of dissolving the greater part of the remaining impurities, mostly oxidation products, but dissolving only a minute amount of the violet compound. This purification procedure was repeated until the benzene remained colorless, which normally occurred after the second reprecipitation.

The compound was prepared for analysis by four reprecipitations as described above. During the last of these the solution was filtered through a fritted glass disk of medium porosity. The precipitated product was then transferred into the preweighed analysis ampoules as a slurry, benzene being removed by sublimation. The compound finally was dried under a pressure of less than 1μ , the powdered sample being heated to about 80° for 20 minutes during the evacuation. The ampoules were sealed off, both parts of them weighed, and the weights corrected for buoyancy. For all analyses and most experiments only samples treated in this way were used.

C. Sublimation and Thermochromism.—No definite melting point was found. A small sample sealed under vacuum sublimed at about 150° . At about 300° there was some decomposition to a black residue.

On cooling a dilute light blue solution (about 0.01 molar) in acetonitrile, the color changed to green close to the freezing point (-44°). Finally at Dry Ice-acetone temperature

(-78°) the color was yellow. These color changes reversed themselves on warming to room temperature and could be repeated. Thus, no oxidation was involved.

Characterization. A. Elementary Analysis.—Since the compound was originally expected to contain both titanium and aluminum, titanium was determined by the colorimetric hydrogen peroxide method, and the combined aluminum and titanium were determined by chelatometric titration with cyclohexanediaminetetraacetic acid (Hexaver). In both cases we followed procedures supplied by the B. F. Goodrich Research Center, Technical Service Research Department, with slight adaptations.¹² The methods were checked with dicyclopentadienyltitanium dichloride, which was digested beforehand with concentrated sulfuric and nitric acids.

The slightest contact with oxygen converted the violet compound into a yellow benzene-soluble product. This compound was investigated first and found to contain no aluminum. Sample results were

| Ti (peroxide method, mg./ml.) | Ti + Al (Hexaver titration, mg./ml.) |
|----------------------------------|---|
| 0.118 | 0.119 |
| 0.114 | 0.1135 |

The pure violet compound was subjected to analysis in the same way from an ampoule broken under methanol containing some sulfuric acid. The results of this titration showed: Ti, 26.32, 26.62; Ti + Al, 26.38%. Therefore, no aluminum was present, and the average value for Ti was 26.44%. This figure combined with carbon and hydrogen analyses by Dr. S. M. Nagy at the Massachusetts Institute of Technology gives the following analytical picture. The molecular weight was determined by isothermal distillation in a Signer apparatus using acetonitrile as solvent at 60° and as standards methyl 3,5-dinitrobenzoate in one experiment and the C-22 steroid lactone of Fieser and Jacobsen^{13,14} in another. We thank Dr. A. Chatterjee for supplying us with this compound.

Anal. Calcd. for $C_5H_5TiCl_2$: C, 32.65; H, 2.74; Ti, 26.05; mol. wt., 183.9. Found: C, 32.80; H, 2.84; Ti, 26.44; mol. wt., 184.6.

Ultraviolet Spectra.—The ultraviolet spectrum of cyclopentadienyltitanium dichloride in acetonitrile was obtained using a sealed cell and all the precautions described above. Figures 3 and 4 show the absorption of unoxidized and oxidized solutions of this compound at two different concentrations. Oxidation gives rise to a maximum in the neighborhood of $400\text{ m}\mu$, which is absent in the original compound, and causes the disappearance of the low flat absorption, which in cyclopentadienyltitanium dichloride is still rising at about $800\text{ m}\mu$.

Electron Spin Resonance.—A solution of cyclopentadienyltitanium dichloride approximately 0.002 M in acetonitrile, which showed a very faint blue color, was examined by Mr. Edward Waters with an electron spin resonance spectrometer built by Dr. A. H. Maki. We are grateful to both of these investigators for their assistance. The spectrum showed a g -factor of 1.975 ± 0.001 corresponding to one unpaired d -electron at a line width of 6.1 gauss, 15.3 megacycles. No hyperfine structure could be observed at room temperature. These observations are consistent with the presence of trivalent titanium.

Nuclear Magnetic Resonance.—The n.m.r. spectrum of cyclopentadienyltitanium dichloride in acetonitrile was observed at 40 megacycles with tetramethylsilane as an internal standard. Unlike dicyclopentadienyltitanium dichloride and monocyclopentadienyltitanium trichloride,^{15,16} the main absorption was broad and diffuse both in concentrated solution and at 0.02 M .

Experiments on the Polymerization of Ethylene.—Pure cyclopentadienyltitanium dichloride, 30 mg. suspended

(12) E. Wännigen and A. Ringbom, *Anal. Chim. Acta*, **12**, 308 (1955); E. B. Sandell, "Colorimetric Determinations of Traces of Metals," 3rd ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 870.

(13) L. F. Fieser and R. P. Jacobsen, *THIS JOURNAL*, **60**, 2753 (1938).

(14) R. E. Marker and A. C. Shabica, *ibid.*, **64**, 813 (1942).

(15) R. D. Gorsich, *ibid.*, **80**, 4744 (1958).

(16) C. L. Sloan and W. A. Barber, *ibid.*, **81**, 1364 (1959).

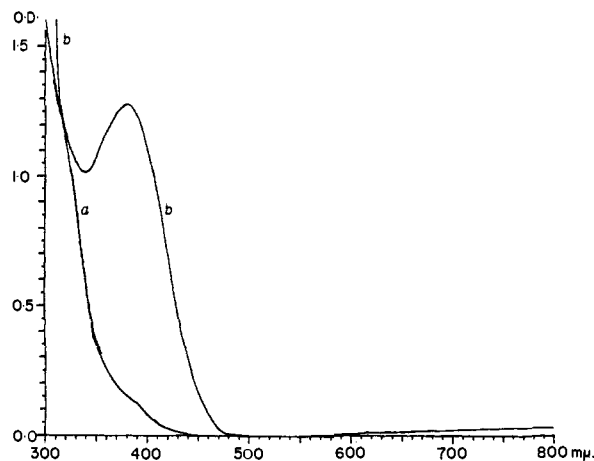


Fig. 3.—Absorption spectrum of $CpTiCl_2$ in acetonitrile, $c \sim 2.5 \times 10^{-4}\text{ M}$ (estimated), $d = 0.5\text{ cm.}$ (quartz cell): curve a, pure $CpTiCl_2$; curve b, solution oxidized with dry O_2 .

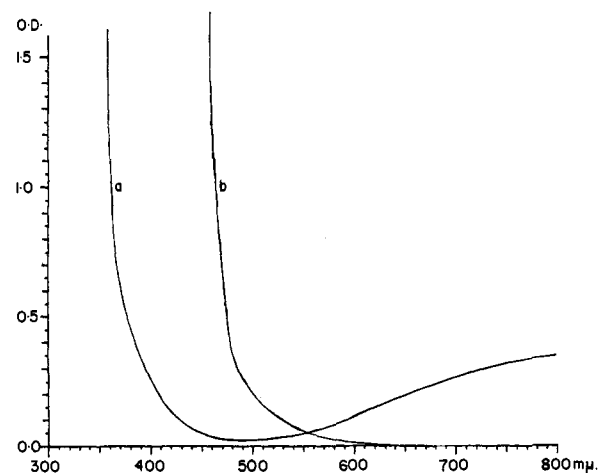


Fig. 4.—Absorption spectrum of $CpTiCl_2$ in acetonitrile, $c \sim 4 \times 10^{-3}\text{ M}$ (estimated), $d = 0.5\text{ cm.}$ (quartz cell): curve a, pure $CpTiCl_2$; curve b, solution oxidized with dry O_2 .

in 30 ml. of pure benzene, showed no uptake of ethylene during a period of 3 hours except for the initial saturation of the benzene. The same was true at room temperature and at 60° .

The addition of an excess of diisobutylaluminum chloride to this suspension at room temperature resulted in no detectable reaction but slowly produced a green solution on slight heating. The effect was the same in benzene and in heptane. The green solution polymerized ethylene although the rate was very slow in comparison to the system $(C_6H_5)_2TiCl_2-(i-C_4H_9)_2AlCl$ in benzene under normal conditions. At the end of the experiment, a few tiny crystals of cyclopentadienyltitanium dichloride were seen to be undissolved but to have polyethylene clustered around them. These centers seemed to have been rather active in the polymerization.

The absorption spectrum of the green solution from cyclopentadienyltitanium dichloride and diisobutylaluminum chloride was strikingly similar to that of the green solution from dicyclopentadienyltitanium chloride.¹⁷ Like the violet compound, this solution was oxidized readily with dry oxygen with the formation of a new maximum at $365\text{--}370\text{ m}\mu$ and disappearance of the maximum at $690\text{ m}\mu$.

When dissolved in acetonitrile, cyclopentadienyltitanium dichloride did not polymerize ethylene either alone or with

(17) R. L. Baird, unpublished work in this Laboratory.

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 bimetallic 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.

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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. Vennesland 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).