structure and other features in a biomolecule may be obtained. Because nonprotonated carbon lines tend to remain narrow even in molecules of considerable size, selective ^{13}C enrichment of these sites holds the promise of revealing many more subtle features of the secondary and tertiary interactions in biomolecules. In addition to the superior resolution, ^{13}C-labeling techniques also can claim the advantage of using atomic labels which are normally found in living systems.

References and Notes

(1) This work was supported in part by the National Institutes of Health of the U.S. Public Health Service Awards RR07092 and GM 08521. The synthesis of the carbon-13-labeled uracil was supported by ERDA Award E(11-1)-2451. One of the authors (W.D.H.) is indebted to the National Science Foundation for support in the form of a predoctoral fellowship. We wish to thank Dr. W. James Horton for synthesizing the carbon-13 uracil, Dr. James McClosky for the mass spectroscopic analysis, and Dr. John Ingraham for supplying the *Salmonella typhimurium* JL-1055 culture.
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Synthesis and Characterization of $[(\eta^5\text{-}C_5H_5)V(CO)_3H]^-$, a New Anionic Vanadium Carbonyl Hydride, and a Study of Its Reduction Reaction with Organic Halides. Observation of a Free-Radical Chain Process Having an Extremely Rapid Metal-to-Carbon Hydrogen Transfer Step

Sir:

We wish to report the preparation and certain reactions of a new anionic vanadium carbonyl hydride,[1,2] $[(\eta^5\text{-}C_5H_5)V(CO)_3H]^-$ (**1**), which may be prepared from commercially available[3] $(\eta^5\text{-}C_5H_5)V(CO)_4$. We have found that **1**, in THF or acetonitrile at room temperature, replaces halogen by hydrogen in a wide range of alkyl, vinyl, and acyl halides (Chart I). These reactions appear to proceed by a radical chain mechanism which involves an exceedingly high vanadium-to-carbon hydrogen transfer rate constant.

Treatment of a THF solution of $(\eta^5\text{-}C_5H_5)V(CO)_4$ with 0.7% Na/Hg yields the yellow salt $Na_2^+[(\eta^5\text{-}C_5H_5)V(CO)_3]^{2-}$, as has been reported,[4] but we have found it more convenient to titrate THF suspensions of sodium dispersion with $(\eta^5\text{-}C_5H_5)V(CO)_4$ to generate the dianion. Reaction with aqueous HCl gives the vanadium dimer[4] $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$, but addition of 1 equiv of water to a slurry of the dianion in THF yields a solution of $Na^+[(\eta^5\text{-}C_5H_5)V(CO)_3H]^-$ (Na-**1**). Addition of $(Ph_3P)_2N^+Cl^-[PPN^+Cl^-]$ precipitates NaCl, leaving a basic solution of PPN^+-**1**. Solid PPN^+-**1** is obtained by precipitation with petroleum ether (30–60 °C) and is purified by reprecipitation from THF upon very slow addition of petroleum ether. The overall yield based on $(\eta^5\text{-}C_5H_5)V(CO)_4$ is ~70%.

Chart I

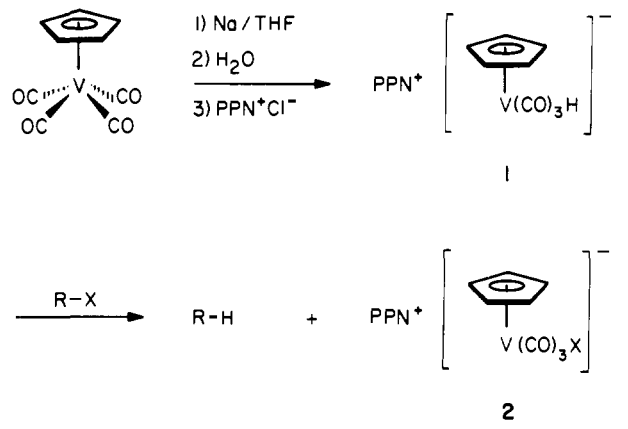
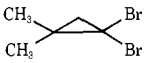
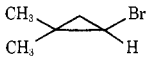
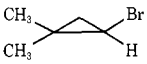
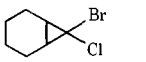
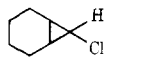


Table I. Interaction of Organic Substrates with $PPN^+[(\eta^5\text{-}C_5H_5)V(CO)_3H]^-$ at 25 °C in THF

Substrate	Reaction time, h	Product	Yield,[a] %
$n\text{-}C_8H_{17}Br$	4	$n\text{-}C_8H_{18}$	75
$n\text{-}C_6H_{13}Br$	7	$n\text{-}C_6H_{14}$	73
$n\text{-}C_{10}H_{21}Br$	24	$n\text{-}C_{10}H_{22}$	95
$c\text{-}C_6H_{11}Br$	10	$c\text{-}C_6H_{12}$	65
	0.5		95
	24	No reaction	
C_6H_5COCl	<0.1	C_6H_5CHO	40 (36[b])
$C_6H_5CH_2COCl$	<0.1	$C_6H_5CH_2CHO$	100[c]
$C_6H_{13}COCl$	<0.1	$C_6H_{13}CHO$	100[c]
$(CH_3)_3CBr$	12	$(CH_3)_3CH$	100
$C_6H_5CH_2Br$	<0.5	$C_6H_5CH_3$	90
$(-)\text{-}C_6H_5CH(Br)(CH_3)$	<0.5	$(\pm)\text{-}C_6H_5CHD(CH_3)$	64[d]
$C_4H_9CHBrCH_2Br$	2.5	$C_4H_9CH{=}CH_2$	100
C_6H_5Br	8.5	C_6H_6	43
$C_6H_5CH{=}CHBr$	5	$C_6H_5CH{=}CH_2$	46
$CH_3CH_2CH{=}(Br)CH_2CH_3$	>200	*cis*-3-Hexene	30[e]
		trans-3-Hexene	70[e]
$C_6H_5C(CH_3)_2CH_2Br$	48	$C_6H_5C(CH_3)_3$	83
	1		95
Cyclohexenone	1	No reaction	
$C_6H_{13}CO_2CH_3$	12	No reaction	

[a] Yields were determined by integration of NMR and gas chromatography peaks, except in cases indicated. [b] Isolated yield, *N,N'*-diphenylethylenediamine adduct. [c] Although spectroscopic monitoring indicates that yields of these aldehydes are essentially quantitative, we have so far experienced some difficulty isolating them. [d] Isolated (preparative VPC). [e] Corrected for unconverted starting material.

THF solutions of PPN^+-**1** exhibit two IR absorptions in the metal carbonyl region (1890 and 1780 cm^{-1}). The ^1H NMR spectrum in THF-d_8 shows a single resonance due to the cyclopentadienyl hydrogens at δ 4.57 ppm, and a very broad absorption centered[5] at δ −6.10 ppm due to the metal-bound hydrogen.

Table I gives the results of reduction experiments carried out on various organic halides, along with data on some unreactive substrates. Reactions were typically carried out at a 1:1 molar ratio of PPN^+-**1** to substrate by adding the organic halide to a THF solution of PPN^+-**1** at room temperature. The reactions may be easily monitored by observing the disap-

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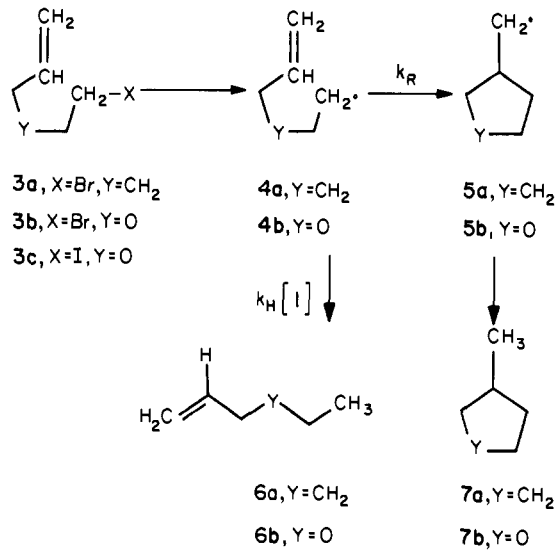
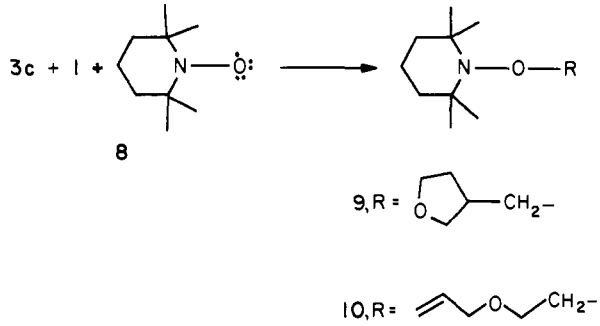
Chart II



pearance of the signals due to PPN^+-**1** in the IR or NMR. In the presence of added phosphine, the ultimate organometallic product of the reaction (vide infra) is $CpV(CO)_3PPh_3$; in its absence $CpV(CO)_3Br^-$ is isolated.

The following experiments support the hypothesis that organic *radicals* are intermediates in these reductions. First, the relative reactivities of various substrates are reminiscent of those observed in trialkyltin hydride reductions.[6] For example (1) reactivity increases in the order chlorides < bromides < iodides, with only very reactive chlorides (e.g., benzylic) reacting at all at room temperature; (2) ordinary alkyl *p*-toluenesulfonates (tosylates) react with PPN^+-**1** only at elevated temperatures; (3) primary, secondary, and tertiary bromides are all reduced at similar rates; (4) *gem*-dibromocyclopropanes are reduced rapidly to monobromocyclopropanes, which are then inert to further reduction at room temperature; (5) acyl and benzyl halides are reduced very rapidly. Second, no insertion, de-insertion or β-elimination (olefin) products are observed, even from tertiary halides. Third, stereochemical experiments are consistent with the radical mechanism: (1) reduction of optically active α-bromoethylbenzene with $(\eta^5\text{-}C_5H_5)V(CO)_3D^-$ produces *completely racemic* α-deuterioethylbenzene;[7] (2) reduction of pure *cis*- and *trans*-3-bromo-3-hexene gives the same mixture of *cis*- and *trans*-3-hexenes; (3) reduction of either stereoisomer of 7-bromo-7-chlorobicyclo[4.1.0^{1,6}]heptane replaces only the bromine atom and gives the same mixture of chloride products (exo/endo = 10). Fourth, reduction of 1,2-dibromohexane gives only 1-hexene, and *meso*- and *dl*-3,4-dibromohexanes are debrominated stereospecifically to *trans*- and *cis*-3-hexenes, respectively. Finally, reduction of neophyl bromide gives only *tert*-butylbenzene (indicating that carbonium-ion intermediates are unlikely) and reduction of *n*-alkyl bromides in the presence of substantial amounts of CD_3OD gives no deuterated hydrocarbon, ruling out the intermediacy of carbanions.

Rearrangement and trapping studies provide critical tests of the radical hypothesis. The cyclization of 1-hexenyl radical (**4a**; cf. Chart II) has been used to probe the behavior of radical intermediates in a number of systems, and so we first attempted to study the reduction of 6-bromo-1-hexene (**3a**). We were surprised to find that very little methylcyclopentane (**7a**) was formed, even at concentrations of halide and hydride as low as 0.02 M. Since the rate constant for cyclization of **4a** is[8] of the order of 1.0×10^5 s^{-1}, this experiment indicates that the radicals in the reduction must be very short-lived (consistent with this are the observations that no coupling or disproportionation products are formed, and the hydrogen which replaces the halide in these reactions always comes from the vanadium hydride, and never from solvent[7]). We therefore decided to examine the cyclization of the related radical **4b**, which proceeds an order of magnitude more rapidly[9,10] than **4a**. Substantial amounts of cyclization product were observed in this case, and product ratios at varying concentrations of **1** could be measured accurately. In this way, we have found that the ratio **6b** to **7b** is clearly linearly dependent upon the concentration of $CpV(CO)_3H^-$. The presence of free radicals is also confirmed by trapping studies. Nitroxyl **8** reacts with **1** too rapidly to allow its use as a trapping agent in the reduction of alkyl bromides. However, when **1** was injected into a solution of iodide **3c** and **8** (0.12 M), a 25% yield of adducts **9** and **10** were formed.[11] Assuming the partial mechanism outlined in Chart II, and an estimated value for k_R, we determine that the hydrogen transfer rate constant k_H must be $\sim 2 \times 10^7$ M^{-1} s^{-1}, an order of magnitude larger than that for tri-*n*-butyltin hydride.



We turn now to the question of how the radicals in these reactions are formed. Two reasonable mechanisms are shown in Chart III. One (mechanism IIIa) involves an adventitiously initiated chain process analogous to that observed in R_3SnH reductions,[6a] as well as certain other transition metal and main-group hydride reactions[12] and some oxidative addition reactions.[13] The second (mechanism IIIb) involves "outer-sphere" electron transfer[14] from metal anion to alkyl halide, cleaving the C-Br bond, followed by reaction of the resulting radical with oxidized hydride to give RH and $CpV(CO)_3$.

The outer-sphere electron transfer mechanism is excluded by the following observations. In the reduction of benzyl bromide, concurrent with the formation of toluene three new absorptions (1948, 1855, 1810 cm^{-1}) appear in the metal carbonyl region of the IR spectrum of the reaction solution.[15] Identical absorptions are produced[16] on photolysis of a solution of PPN^+Br^- and $CpV(CO)_4$ in THF. The material responsible for these absorptions, $[CpV(CO)_3Br]^-$ (PPN^+-**2**), may be isolated from both reactions and characterized by standard methods. However, if the photolysis and reduction reactions are carried out in the presence of excess PPh_3, the major product in the photolysis is $CpV(CO)_3PPh_3$ (only a small amount of $PPN^+[CpV(CO)_3Br]^-$ is produced),[17] but the *only*

Chart III

Mechanism IIIa

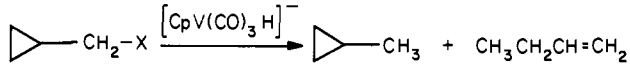
$$CpV(CO)_3H^- + In\cdot \rightleftharpoons In\text{-}H + CpV(CO)_3^{-}\cdot$$
$$CpV(CO)_3^{-}\cdot + RBr \rightarrow CpV(CO)_3Br^- + R\cdot$$
$$R\cdot + CpV(CO)_3H^- \rightarrow RH + CpV(CO)_3^{-}\cdot$$

Mechanism IIIb

$$CpV(CO)_3H^- + RBr \rightarrow CpV(CO)_3H + R\cdot + Br^-$$
$$CpV(CO)_3H + R\cdot \rightarrow RH + CpV(CO)_3$$
$$CpV(CO)_3 + L \rightarrow CpV(CO)_3L$$

kinetic product in the reduction reaction is $PPN^+[CpV(CO)_3Br]^-$. Assuming the photolysis proceeds via coordinatively unsaturated $CpV(CO)_3$, which reacts more quickly with PPh_3 than with Br^-, we conclude that the same intermediate (which appears in mechanism IIIb) *cannot* be involved in the reduction. *Thus, the bromine atom must be transferred directly from carbon to metal* during the reduction reaction.[18]

The chain mechanism IIIa provides the most reasonable way of accounting for the data discussed above. We have encountered only one system which appears to act anomalously: the reduction of cyclopropylcarbinyl bromide (**11a**). In THF, this halide gives significant amounts of *both* methylcyclopropane (33%) and 1-butene (67%). The ring-opening rate constant for cyclopropylcarbinyl radical has been estimated[19] as $\sim 1.0 \times 10^8\ s^{-1}$ at 25 °C; thus much less than 33% methylcyclopropane should be formed under our reaction conditions. Furthermore, although there is somewhat more scatter in the data than we observe with **3b**, the 1-butene/methylcyclopropane ratio is essentially *independent* of the vanadium hydride concentration. Although no difference in the **6b**/**7b** ratio is observed between reduction of bromide **3b** and iodide **3a**, cyclopropylcarbinyl iodide gives much more 1-butene (95%) than does the corresponding bromide. Most important, cyclopropylcarbinyl tosylate is reactive toward **1** *and gives >95% methylcyclopropane.* We conclude that a different mechanism must intervene in the case of **11.** It seems likely that the radical process oper-



11a, X = Br

11b, X = I

11c, X = OTs

ates with **11b**, giving almost exclusively 1-butene, but an alkylation–reductive elimination process operates nearly exclusively with **11c**, giving methylcyclopropane. In the bromide case (owing to the unusually high two-electron displacement reactivity of the cyclopropylcarbinyl center[20]), the two paths are competitive, giving methylcyclopropane by alkylation–reductive elimination and 1-butene by the radical chain mechanism.[21]

Acknowledgments. Support of this research by the National Science Foundation (Grant No. CHE-74-14711) and the Energy Research and Development Administration (Grant No. EX-76-G-03-1305) is gratefully acknowledged.

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(1) Only a few other vanadium hydrides are known. See, for example, (a) A. Davison and D. L. Reger, *J. Organomet. Chem.*, **23**, 491 (1970); (b) T. Kruck and H.-U. Hempel, *Angew. Chem., Int. Ed. Engl.*, **13**, 201 (1974); (c) J. E. Ellis and R. A. Faltynek, *J. Organomet. Chem.*, **93**, 205 (1975); (d) J. E. Ellis, R. A. Faltynek, and S. G. Hentges, *J. Am. Chem. Soc.*, **99**, 626 (1977).

(2) This hydride is isoelectronic with η^5-$C_5H_5W(CO)_3H$; cf. E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allg. Chem.*, **282**, 47 (1955).

(3) Ventron Chemical Co. For preparation, see (a) R. B. King and F. G. A. Stone, *Inorg. Synth.*, **7**, 99 (1963); (b) R. P. M. Werner, A. H. Bilbey, and S. A. Manastyrsky, *Inorg. Chem.*, **3**, 298 (1964).

(4) (a) E. O. Fischer and R. J. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 569 (1966); (b) E. O. Fischer and R. J. J. Schneider, *Chem. Ber.*, **103**, 3684 (1970). We have found, however, that the dianion salt precipitates as a mono-THF solvate.

(5) For NMR data on other transition metal hydrides, see (a) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972); (b) M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, **7**, 115 (1965).

(6) (a) H. G. Kuivila, *Acc. Chem. Res.*, **1**, 299 (1968); (b) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Am. Chem. Soc.*, **88**, 5361 (1966).

(7) $PPN^+[(\eta^5\text{-}C_5H_5)V(CO)_3D]^-$ (**PPN$^+$-1d**) is prepared by dissolving $Na_2^+[\eta^5\text{-}C_5H_5V(CO)_3]^{2-}$ in D_2O and precipitating the deuteride with PPN$^+$Cl. When **PPN$^+$-1d** is treated with *n*-octyl bromide in THF, the product is ≥97% octane-d_1. Likewise when **PPN$^+$-1** reacts with *n*-octyl bromide in THF-d_8, the octane product contains *no* deuterium. For data on the optical rotations of optically active deuterated ethylbenzene, see (a) A. Streitwiesser, J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron Lett.*, 338 (1959); (b) H. J. Dauben and L. L. McKoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).

(8) D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).

(9) The rate constant for cyclization of this radical (**4b**) has not been measured directly. However, Beckwith and his co-workers have shown that replacement of oxygen for C-3 in a number of substituted 6-hexenyl radicals consistently increases the rate of cyclization by at least an order of magnitude.[10a,b] We have carried out the reduction of **3a** with tri-*n*-butyltin hydride; using the known value[10c] for the tin hydride chain transfer rate constant ($1 \times 10^6\ s^{-1}$ for primary radicals), we estimate that the rate constant for cyclization **4b** is $\sim 1.0 \times 10^6\ s^{-1}$.

(10) (a) See, for example, (a) A. L. J. Beckwith, I. Blair, and G. Phillipou, *J. Am. Chem. Soc.*, **96**, 1613 (1974); (b) A. L. J. Beckwith and W. B. Gara, *J. Chem. Soc., Perkin Trans. 2*, 796 (1975); (c) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968).

(11) For a discussion of the use of **8** in trapping radicals formed during reduction of alkylmercuric halides by sodium borohydride, see C. L. Hill and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 870 (1974).

(12) See, for example, (a) B. L. Booth and B. L. Shaw, *J. Organomet. Chem.*, **43**, 369 (1972); (b) J. T. Groves and K. W. Ma, *J. Am. Chem. Soc.*, **96**, 6527 (1974).

(13) See, for example, A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 7832 (1974), and references cited there.

(14) For examples of apparent outer-sphere electron transfer reactions between transition metal complexes and alkyl halides, see (a) J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964); (b) T. A. Cooper, *ibid.*, **95**, 4158 (1972). A general discussion of electron transfer reactions in organometallic systems is given by (c) J. K. Kochi, *Acc. Chem. Res.*, **7**, 351 (1974).

(15) In the NMR, this material exhibited a single η^5-C_5H_5 resonance at δ 4.80 ppm.

(16) W. D. Jones and R. G. Bergman, unpublished results.

(17) Control experiments demonstrated that the phosphine complex observed in the photolysis is *not* a result of either thermal or photochemical displacement of Br^- from **2**. However, this substitution reaction does occur at a somewhat slower rate, and is responsible for the $CpV(CO)_3PPh_3$ isolated in preparative-scale reduction experiments.

(18) $[(\eta^5\text{-}C_5H_5)V(CO)_3Br]^-$ also reacts with PPN^+-1 present in solution to produce another complex, tentatively identified as a hydride-bridged vanadium dimer. Further properties of this material will be reported at a later date (W. D. Jones, R. J. Kinney, and R. G. Bergman, unpublished results).

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(20) See, for example, D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964); **30**, 23 (1965).

(21) For a somewhat related experience involving anions and cyclopropylcarbinyl halides, see (a) P. J. Krusic, P. J. Fagan, and J. San Filippo, Jr., *J. Am. Chem. Soc.*, **99**, 252 (1977); (b) B. W. Bangerter, R. P. Beatty, J. K. Kouba, and S. S. Wreford, *J. Org. Chem.*, **42**, 3247 (1977).

(22) National Science Foundation Predoctoral Fellow, 1971–1972; 1975–1977.

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Contribution No. 5518 from the Laboratories of Chemistry, California Institute of Technology Pasadena, California 91125

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Stereochemistry of 1,4-Conjugate Elimination Reactions

Sir:

In sharp contrast to the intensive studies of the stereochemical course of 1,2-elimination,[1] little is known of the stereochemistry of 1,4-conjugate elimination of allylic leaving groups. Theory predicts that concerted 1,4-conjugate eliminations which produce cisoid dienes should proceed syn,[2] but experimental evidence is sparse and conflicting. The 1,4-elimination component of benzene tetrachloride dehydrochlorination was deduced to be primarily anti,[3] though this conclusion was later disputed.[4] In the most convincing examples provided to date, Cristol et al. showed[5] that syn elimination heavily predominates in the base-catalyzed and thermal eliminations of the 9,10-dihydroanthracenes **1** and related compounds, but the conclusion was later reached that the base-catalyzed eliminations were nonconcerted, proceeding through an E1cB mechanism.[6] An enzyme-mediated example, the chorismate synthetase reaction (eq 1), has been proven to involve stereospecific anti 1,4-elimination.[7]

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