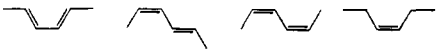
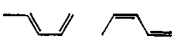
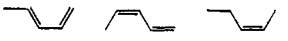
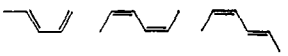
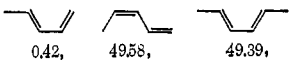
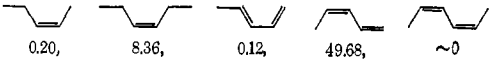
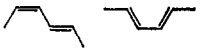
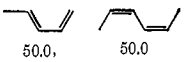
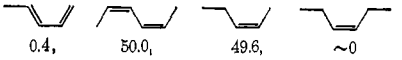
Table I. Selective $M(CO)_6$ Photoassisted Hydrogenation of 1,3 Diene Mixtures

$M(CO)_6$ (M)	Starting mixture, %	Total diene, M	Reaction[a] time, hr	Mixture after reaction, %
$Cr(CO)_6$ (0.001)	 49.27, 1.05, 49.67	0.1	1.0	 43.46, 0.93, 49.57, 6.04
$Cr(CO)_6$ (0.001)	 49.16, 50.83	0.2	0.5	 46.88, 51.63, 1.49
			1.0	45.22, 50.68, 4.10
			1.5	43.37, 50.43, 6.20
			2.0	40.70, 50.58, 8.72
$Cr(CO)_6$ (0.002)	 50.00, 49.79, 0.21	0.1	2.0	 11.31, 38.69, ~0, 49.34, 0.65,
$Cr(CO)_6$ (0.002)	 0.42, 49.58, 49.39,	0.1	2.0	 0.20, 8.36, 0.12, 49.68, ~0
	 0.61			 2.14, 39.50
$Cr(CO)_6$ (0.01)	 50.0, 50.0	0.1	22.0[b]	 0.4, 50.0, 49.6, ~0

[a] Reaction carried out at 10° with continuous uv irradiation in the presence of 1 atm of H_2, in benzene. [b] Reaction for first 2 hr at 10° then allowed to warm to 25°.

selectivity obtained here makes this system one of superlative specificity. In particular, none of the known[5] homogeneous hydrogenation catalysts have been shown to have the degree of selectivity exhibited by the $Cr(CO)_6$ photoassisted catalysis. Conformational effects in Diels–Alder reactions[6] of 1,3 dienes and in the triplet photosensitized dimerizations[7] and isomerizations[8] are known to involve the s-trans $\rightleftharpoons$ s-cis equilibrium, but this work represents the first report of a substantial conformational effect on diene reactivity in a metal photoassisted reaction. Preliminary results reveal that both $Mo(CO)_6$ and $W(CO)_6$ are effective as photocatalysts albeit with different rates, but they still yield selective H_2 addition to s-cis 1,3 dienes. However, both $Mo(CO)_6$ and $W(CO)_6$ suffer from the ability to assist isomerization of 1,3 dienes[9] and alkenes.[10]

While detailed mechanistic considerations may seem premature at this time we find that the role, in part, of the uv light in reaction 1 appears to be to generate a thermally active hydrogenation catalyst. This point was unequivocally established by several hours of dark reaction at 25° after an initial photolysis of 1 hr. Thermal hydrogenation proceeded, converting 2-methyl-1,3-butadiene to 2-methyl-2-butene, and the number of diene molecules hydrogenated is larger than the number of $Cr(CO)_6$ molecules initially present, Table II. Thus, the [$Cr(CO)_6$–H_2–light] system represents a case of true *photocatalysis*, a situation where a catalytic reaction is triggered by light and the number of molecules ultimately undergoing reaction does not depend on the number of photons absorbed.

Table II. Chromium Carbonyl Photocatalyzed Hydrogenation of 2-Methyl-1,3-butadiene[a]

Time irradiated at 10°, hr	Time thermolyzed at 25°, hr	% hydrogenation
1	0	6.5
1	18	14.3
1	0	6.0
1	15	14.9

[a] $Cr(CO)_6$ initially 2×10^{-3} M, diene initially 10^{-1} M, and hydrogenation product from continuous photolysis and dark thermolysis is 2-methyl-2-butene.

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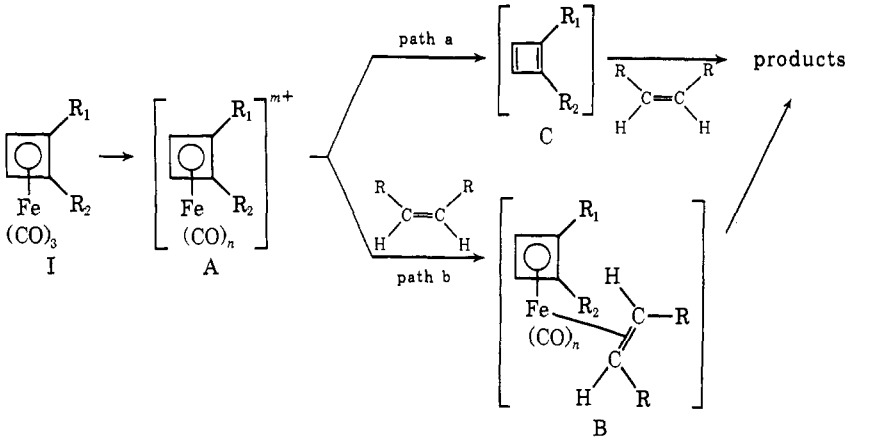
(5) R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, **73**, 21 (1973).
(6) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, p 263.
(7) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, pp 212–216.
(8) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **93**, 5302 (1971).
(9) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 6068 (1970).
(10) M. Wrighton, unpublished results.

Cyclobutadiene as an Intermediate in the Oxidative Decomposition of Cyclobutadienyliron Tricarbonyl

Sir:

Rapid advances have been made recently in the study of the chemistry of cyclobutadiene. Although cyclobutadiene and its derivatives can be generated photochemically and observed at low temperature[1,2] the best potential precursors for cyclobutadiene remain the

(1) O. L. Chapman, D. DeLaCruz, R. Roth, and J. Pacansky, *J. Amer. Chem. Soc.*, **95**, 1337 (1973).
(2) C. Y. Lin and A Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972).



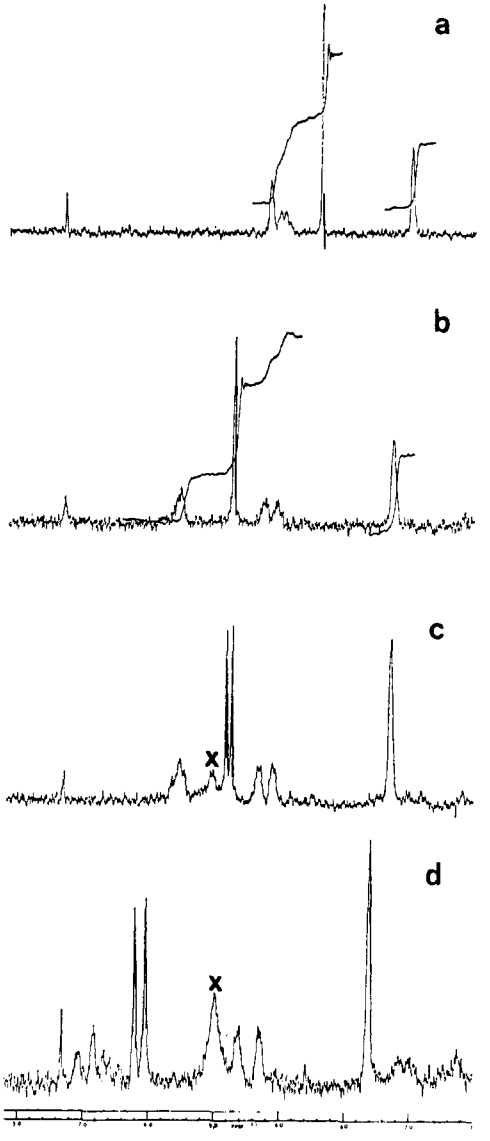
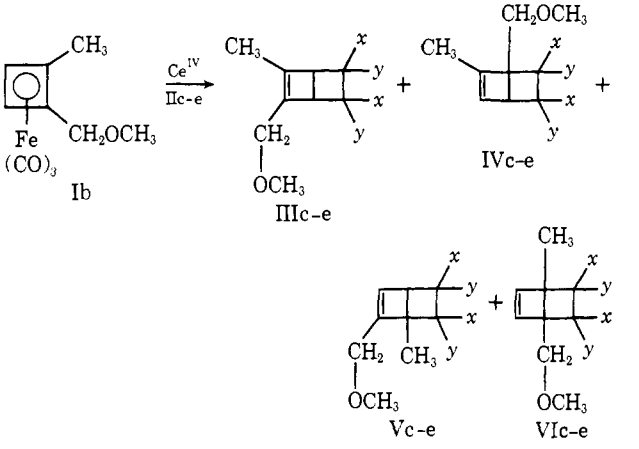


Figure 1.

transition metal derivatives.[3,4] Pettit and his coworkers have observed products arising from cyclobutadienoid intermediates from the oxidative decomposition of cyclobutadienyliron tricarbonyl. Stereochemical studies of these reactions have suggested the electronic state and reactivities of cyclobutadiene.[5,6]

These results are only meaningful if it can be demonstrated that cyclobutadiene is free of the metal's influence when it reacts with the trapping agent. Although various schemes for the mechanism of the oxidative decomposition of cyclobutadienyliron tricarbonyl (I) were ruled out by Pettit,[7] one scheme (path b) that is consistent with his results is as follows. In path b, the initial oxidation product is trapped before the release of the ligand and the cyclobutadiene reacts in the coordination sphere of the metal. If $R_1 \neq R_2$ then complex I and the products resulting from its decomposition in the presence of a symmetrical dienophile are chiral. The intermediate C in path a is achiral, and the intermediate B and related structures in path b are chiral. Consequently, starting with optically active A, path a has to lead to racemic and path b to optically active products.

Consequently, optically active Ib was prepared by the methods reported earlier.[8,9] Decomposition of Ib in acetone solution with ceric ammonium nitrate in the presence of symmetrical dienophiles, tetracyanoethylene, benzoquinone, and *N*-phenylmaleimide produced a mixture of the adducts. In each case, structure



c = TCNE
d = benzoquinone
e = *N*-phenylmaleimide

(3) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965); L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).
(4) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967).
(5) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966).
(6) P. Reeves, J. Henery, and R. Pettit, *ibid.*, **91**, 5890 (1969).
(7) P. Reeves, T. Devon, and R. Pettit, *ibid.*, **91**, 5888 (1969).
(8) R. Grubbs, *ibid.*, **92**, 6693 (1970).
(9) R. Grubbs and R. A. Grey, *J. Chem. Soc., Chem. Commun.*, 76 (1973).

III was the predominant isomer. The product mixture arising from Ib that was 79–42% optically pure[10] showed no rotation at 578 nm (±0.003°). The CD spectrum of each mixture was identical (±0.2 millidegrees) with the base line from 400 to 250 nm (each mixture absorbed in this region). Compound IIIc separated from an ether solution of the reaction mixture.

As can be seen in Figure 1, the nmr spectrum of this compound in the presence of tris[3-(heptafluorobutyryl)-*d*-camphorato]europium(III) [Eu(hfbc)$_3$] showed a splitting of the enantiomeric methoxyl groups. IIc was produced from racemic, 46.3% optically pure (+)- and 38.6% optically pure (−)-Ib. The relative areas of the methoxyl signals arising from the two enantiomers were identical (±2%) in all cases.

The shifted spectra [Eu(hfbc)$_3$] of the mixture of benzoquinine adducts prepared from optically active Ib were identical (±5%) with similar spectra of the products from racemic Ib. If only half of the complex was decomposed in the presence of tetracyanoethylene, half of the initial rotation vanished. The recovered complex had not racemized. Consequently, at least greater than 95% of the cyclobutadiene ligand reacts after it has gained a plane of symmetry. This indicates that the metal was not close enough to the ligand to change its symmetry from that of the free ligand and should, therefore, have little effect on the free ligand's electronic state or reactivity.

Acknowledgments. We wish to thank the National Science Foundation for partial support of this work through an Institutional Grant administered by Michigan State University and Dr. D. G. Farnum for many helpful discussions.

(10) For example, $[\alpha]_{578}$ 0.184°, 213 mg/6 ml of ether, 46.3% optically pure, and $[\alpha]_{578}$ −0.072°, 100 mg/6 ml of ether, 38.6% optically pure.

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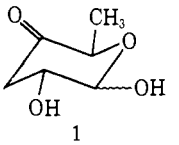
Synthesis of 3,6-Dideoxy-D-*erythro*-hexos-4-ulose and Identification as the 3,6-Dideoxy-4-ketohexose from *Pasteurella pseudotuberculosis*

Sir:

The 3,6-dideoxyhexoses are biologically important carbohydrates which contribute to the serological specificity of many immunologically active lipopolysaccharides.[1] Elucidation of the biochemical pathways for the formation of these sugars has been the subject of several recent investigations.[2,3] Abequose (3,6-dideoxy-D-*xylo*-hexose), paratose (3,6-dideoxy-D-*ribo*-hexose), and ascarylose (3,6-dideoxy-L-*arabino*-hexose) were shown to originate from CDP–6-deoxy-D-*xylo*-hexos-4-ulose (6-deoxy-4-keto-D-glucose) which in turn was formed from CDP–D-glucose.[4,5] The intermediate for the formation of paratose, abequose, and ascarylose from CDP–6-deoxy-4-keto-D-glucose was suggested to be 3,6-dideoxy-D-*erythro*-hexos-4-ulose (3,6-dideoxy-4-keto-D-glucose (**1**)) as its cytidine diphosphate nucleotide conjugate.[6] We now describe the synthesis of the free sugar **1** and its identification with the ketohexose isolated from *Pasteurella pseudotuberculosis* type V strain VO and thus unequivocally establish the structure of this important intermediate in the conversion of D-glucose into the 3,6-dideoxyhexoses. A recent report[7] of the occurrence of the L isomer of **1** (3,6-dideoxy-L-*erythro*-hexos-4-ulose) as part of the antibiotic cinerubine B provides added significance to the synthesis of **1**.



1

The synthesis of keto sugar **1** was accomplished starting from the known methyl 3-deoxy-4,6-*O*-benzylidene-α-D-*ribo*-hexopyranoside[8] (**2**) as summarized in Scheme I.[9] Free sugar **1**, which was obtained as an amorphous solid (nmr in DMSO-d_6–D_2O showed that **1** consisted of the α and β anomers in equal amounts) after lyophilization of the solvent, was converted to a crystalline derivative **15** for comparative studies with the natural product. This was achieved by converting **1** back to **14** by its treatment with 2,2-diethoxypropane in acetone in the presence of *p*-toluenesulfonic acid and the subsequent conversion of **14** to the crystalline oxime **15** in an overall yield of 25%.

The natural product uniformly labeled with ^{14}C was obtained by the following method. Enzymes E1, E3, and CDP glucose oxidoreductase were prepared from extracts of *Pasteurella pseudotuberculosis* type V strain VO as previously described.[2] CDP–6-deoxy-4-keto-D-glucose-*U*-^{14}C was prepared by treating CDP–glucose-*U*-^{14}C with CDP–glucose oxidoreductase in the presence of NAD^+.[10] After a small aliquot was treated with nucleotide pyrophosphatase and alkaline phosphatase, analysis by thin layer chromatography on silica gel F-254 using ethyl acetate–acetic acid–methanol–water (60:15:15:10) showed that the reaction had gone to about 95% completion. This material, without further purification, was treated with enzymes E1 and E3 in the presence of pyridoxamine 5′-phosphate and NADPH to obtain the CDP–3,6-dideoxy-4-ketohexose.[2,11] Analysis of the reaction by tlc on cellulose MN 300 using isobutyric acid–1 *M* ammonium hydroxide (5:3) showed that the reaction was more than 95% complete. The nucleotide was then purified by column chromatography on Bio-Rad AG1-X_4 (200–400 mesh) Cl^-, followed by gel filtration

(1) O. Luderitz, A. M. Staub, and O. Westphal, *Bacteriol. Rev.*, 30, 192 (1966).
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(6) S. Matsuhashi and J. L. Strominger, *ibid.*, 242, 3494 (1967).
(7) W. Richle, E. K. Winkler, D. M. Hawley, M. Dobler, and W. Keller-Schierlein, *Helv. Chim. Acta*, 55, 467 (1972).
(8) T. D. Inch and G. J. Lewis, *Carbohyd. Res.*, 15, 1 (1970); E. J. Hedgley, W. G. Overend, and R. A. C. Ronnie, *J. Chem. Soc.*, 4701 (1963).
(9) The melting points are uncorrected. The specific rotations were obtained in chloroform solutions with a concentration of *ca.* 1 g/100 ml. All new compounds, except **1**, gave satisfactory elemental analysis.
(10) CDP-D-glucose-*U*-^{14}C, 200 mCi/mmol, was purchased from ICN. Pyridoxamine 5′-phosphate hydrochloride, NAD^+, NADPH, nucleotide pyrophosphatase, and *Escherichia coli* alkaline phosphatase were purchased from Sigma Chemical Co.
(11) P. Gonzalez-Porque and J. L. Strominger, *Proc. Nat. Acad. Sci. U. S.*, 69, 1625 (1972).