cage. To satisfy the stoichiometry a cage efficiency of between 20% and 40% must be assumed.[15]

In conclusion, carboxyl radicals are certainly intermediates in both the catalyzed and uncatalyzed reactions of ascorbic acid with lauroyl peroxide. However, many mechanistic details of the uncatalyzed reaction are admittedly open to speculation.[16,17] Current research in these laboratories will shed light on the viability of eq 6-9.

Acknowledgment. This research was supported by the Goodyear Tire & Rubber Company, the donors of Petroleum Research Fund, administered by the American Chemical Society, and the Miami University Faculty Research Committee. We gratefully acknowledge the assistance of Professor Frederick Greene in the preparation of the revised manuscript.

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[16] Electron-rich arenes are proposed to induce the decomposition of benzoyl peroxide by a rate-limiting electron transfer: Walling, C.; Zhao, C.; *Tetrahedron* 1982, *38*, 1105.

[17] The decomposition of benzoyl peroxide with aniline produces free radicals but is believed not to proceed by a rate-limiting electron transfer: Pryor, W. A.; Hendrickson, W. H., Jr. *Tetrahedron Lett.* 1983, *24*, 1459.

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Received March 17, 1988

Construction of Quaternary Carbon Centers Using Organomolybdenum Chemistry. Synthesis of a Trichothecene Intermediate

Summary: Dicarbonyl(1,4-dimethyl-1,3-cyclohexadiene)(η^5-indenyl)molybdenum(1+) tetrafluoroborate was shown to react with a variety of carbon nucleophiles, including Grignard reagents and "hard" enolates, to generate (π-allyl)molybdenum complexes containing quaternary carbon centers; this methodology was employed to prepare the lactone 8, an intermediate for synthesis of trichodermin and trichodiene.

Sir: Development of methods for the construction of quaternary carbon centers remains an active area of research in contemporary organic chemistry, owing to the presence of such subunits in a diverse range of natural products.[1] Previous work in our laboratory was aimed at utilizing the reaction between dienyliron complexes, of general structure 1, and carbon nucleophiles to generate diene complexes 2 which are then converted to 4,4-disubstituted cyclohexenones.[2] However, a number of shortcomings of this methodology, most notably the rather narrow range of carbon nucleophiles that can be used, led us to investigate other organometallic systems which might complement the dienyliron complexes.

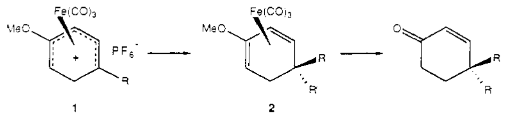
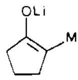
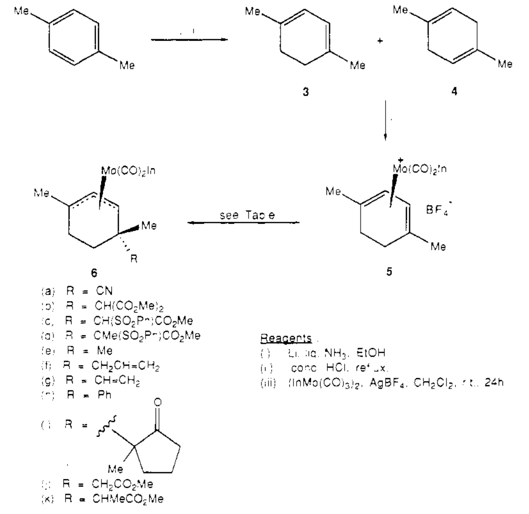


Table I. Reactions of Dicarbonyl(1,4-dimethyl-1,3-cyclohexadiene)(η^5-indenyl)molybdenum(1+) Cation (5) with Carbon Nucleophiles

entry	nucleophile[a]	product	yield, %
1	NaCN	**6a**	85
2	$NaCH(CO_2Me)_2$	**6b**	91
3	$NaCH(SO_2Ph)CO_2Me$	**6c**[b]	87
4	$NaCMe(SO_2Ph)CO_2Me$	**6d**[b]	81
5	MeMgBr	**6e**	92
6	$CH_2{=}CHCH_2MgBr$	**6f**	90
7	$CH_2{=}CHMgBr$	**6g**	37
8	PhMgBr	**6h**	30
9		**6i**[b]	83
10	$CH_2{=}C(OLi)OMe$	**6j**	81
11	$CHMe{=}C(OLi)OMe$	**6k**[b]	89

[a] All reactions were performed in tetrahydrofuran at -78 °C, except for entry 1, which was run in CH_3CN/H_2O (10:1) at 0 °C. [b] Obtained as an equimolar mixture of diastereomers.



The mixture of dienes 3 and 4 (3:1 ratio[3]) was readily converted by Green's method[4a] to the diene-molybdenum complex 5 (52% yield).[5] This reacts with a wide range of carbon nucleophiles to give (π-allyl)$Mo(CO)_2In$ (In = η^5-indenyl) complexes of structure 6 (Table I). The stereochemistry of 6 is assigned on the basis that nucleophile addition to previously prepared, but simpler, cyclohexadiene-molybdenum complexes occurs exclusively trans to the metal.[4b,6] Of direct relevance to the present work is the assignment of exo stereochemistry during nu-

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[1] For a review on this topic, see: Martin, S. F. *Tetrahedron* 1980, *36*, 419. For some recent examples, see: Meyers, A. I.; Harre, M.; Garland, R. *J. Am. Chem. Soc.* **1984**, *106*, 1146. Meyers, A. I.; Warner, K. T. *Tetrahedron Lett.* **1985**, *26*, 2047. Meyers, A. I.; Hanreich, R.; Wanner, K. T. *J. Am. Chem. Soc.* **1985**, *107*, 7776.

[2] Pearson, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Ed.; Pergamon: New York, 1982; Vol. 8, Chapter 58.

[3] Brady, W. T.; Norton, S. J.; Ko, J. *Synthesis* **1985**, 704.

[4] (a) Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365. (b) Green, M.; Greenfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18.

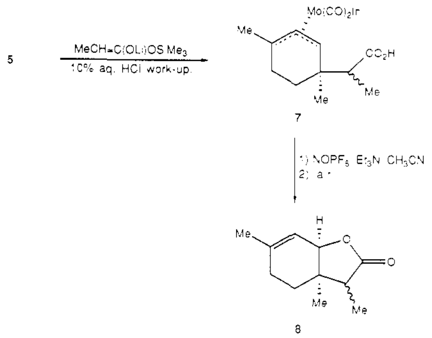
[5] All new compounds were obtained in racemic form and purified by chromatography and/or recrystallization. Yields are quoted for purified products, which were fully characterized by 200-MHz ^1H NMR and IR spectra and gave satisfactory high-resolution mass spectra and/or combustion analyses.

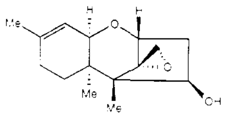
[6] Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.

0022-3263/88/1953-3395$01.50/0

cleophile addition to (η^5-indenyl)molybdenum–diene complexes reported by Green.[4b] Of particular note is the observation that "hard" carbanion nucleophiles, such as Grignard reagents and ketone or ester enolates (Table I, entries 5–11), react satisfactorily with **5**, in contrast to the behavior of the dienyliron system **1**, which undergoes deprotonation of the side chain (R) methylene group on treatment with such reagents.

This chemistry leads to an efficient entry into trichothecene synthesis. As an illustration of synthetic utility, reaction of complex **5** with the lithium enolate of trimethylsilyl propionate, followed by acidic workup, gave directly the carboxylic acid derivative **7** in 93% yield. This was readily converted in 87% yield by a one-pot procedure to the lactone **8**, which has previously been utilized as an intermediate for the total synthesis of (±)-trichodermin[7] (**9**) and (±)-trichodiene[8] (**10**). It is noteworthy that the present synthesis of **8** requires only five synthetic transformations from *p*-xylene, as compared to the "standard" organic route, which requires eight steps from 4-methylanisole[7] or 10 steps from 2,5-dimethylcyclohexanone.[9]





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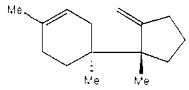

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Acknowledgment. We are grateful to the U.S. Public Health Service, National Institutes of Health, for generous financial support.

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[7] Colvin, E. W.; Malchenko, S.; Raphael, R. A.; Roberts, J. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1989.

[8] Welch, S. C.; Rao, A. S. C. P.; Wong, R. Y. *Synth. Commun.* **1976**, *6*, 443. Welch, S. C.; Rao, A. S. C. P.; Gibbs, C. G. *Synth. Commun.* **1976**, *6*, 485.

[9] Welch, S. C.; Wong, R. Y. *Tetrahedron Lett.* **1972**, 1853.

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Received May 12, 1988

Additions and Corrections

Vol. 52, 1987

Yong M. Choi,* Robert W. Emblidge, Norbert Kucharczyk, and R. Duane Sofia. Exceptionally Slow Reduction of Phenylmalonic Acid by Borane–THF via Cyclic (Phenylmalonoxy)borane.

Page 3926, right column, second line from the bottom, should read ... material **2** (+2.9 ppm), **5** ...

Page 3927, left column, seventh line from the top, should read ... to **5** (+26.1 ppm) ...

Edward C. Taylor* and Partha S. Ray. Pteridines. 51. A New and Unequivocal Route to C-6 Carbon-Substituted Pterins and Pteridines.

Page 3999, lines 20 and 21, column 2. The sentence that currently reads "The filter funnel was rinsed for 16 h under nitrogen" should read as follows: "The filter funnel was rinsed with 10 mL of dry methanol, and the reaction mixture was heated under reflux for 16 h under nitrogen".

Herbert A. Kirst,* Julie A. Wind, and Jonathan W. Paschal. Synthesis of Ring-Contracted Derivatives of Erythromycin.

Page 4361. In Table II, for position "12-CH$_3$" of compound **3**, the value should read 16.56, not 15.56.

Allen B. Reitz,* Alfonzo D. Jordan, Jr., and Bruce E. Maryanoff. Formation of Chiral Alkoxy Dienes in Wittig/Michael Reactions of 2,3,5-Tri-*O*-benzyl-D-arabinose.

Page 4801, column 2, line 27. The phrase "since a trans 5,6 ring junction is unfavorable" was inadvertently inserted in the last paragraph of discussion and should be deleted. The major and minor primary Diels–Alder products (**9** and its epimer by inversion of the 4 ring stereocenters) are endo adducts, and both would form a cis 5,6-ring system upon transacylation (to **8** and its epimer). The lack of transacylation in the minor adduct is due to steric constraints imposed by the benzyloxymethyl group. We thank Professor Ian Fleming of Cambridge for bringing this point to our attention.

Herbert C. Brown,* Won Suh Park, Byong Tae Cho, and P. Veeraraghavan Ramachandran. Selective Reductions. 40. A Critical Examination of the Relative Effectiveness of Various Reducing Agents for the Asymmetric Reduction of Different Classes of Ketones.

Page 5410, Table II, column E, eighth entry. The asymmetric reduction of *trans*-4-phenyl-3-buten-2-one by (−)-diisopinocampheylchloroborane at −25 °C provides alcohol of 81% optical purity, not the 12% reported.