sulfoxide → sulfone (entry 11), cyclic olefin → ketol (entry 12). Of these various transformations, only 6, 7, and 12 have not been observed previously. However, although each of the other oxidations shown in the table can be achieved in other ways, none of these has previously employed experimental conditions as simple or general as those reported here for oxidations by zinc permanganate.

With the completion of this preliminary survey of monofunctional organic substrates, the potential of zinc permanganate oxidation can now be applied to more complex polyfunctional molecules. The mechanisms of these reactions are also of interest; preliminary studies indicate that these mechanisms will differ in some respects from those observed for potassium permanganate oxidations in solution.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada and Merck, Sharp and Dohme Research Laboratories, Rahway, NJ. C.F.I. thanks Queen's University and the Province of Ontario for the award of an Alcan Fellowship and an Ontario Graduate Scholarship.

Registry No. PhC≡CPh, 501-65-5; $PhCH_2NHBoc$, 42116-44-9; $PhSCH_3$, 100-68-5; PhCOCOPh, 134-81-6; PhCOPh, 119-61-9; $PhCOCH_3$, 98-86-2; PhCONHBoc, 88000-67-3; $PhSO_2CH_3$, 3112-85-4; $Zn(MnO_4)_2$, 23414-72-4; $Mg(MnO_4)_2$, 10377-62-5; $KMnO_4$, 7722-64-7; $BaMnO_4$, 7787-35-1; MgO, 1309-48-4; ZnO, 1314-13-2; tetrahydrofuran, 109-99-9; benzophenone ethylene ketal, 4359-34-6; acetophenone ethylene ketal, 3674-77-9; cyclohexanone, 108-94-1; *N*-phenylsulfonylpyrrolidine, 5033-22-7; tetrahydropyran, 142-68-7; butyrolactone, 96-48-0; valerolactone, 542-28-9; adipic acid, 124-04-9; *N*-phenylsulfonylpyrrolidin-2-one, 88000-68-4; 3-phthalimidocyclohexene, 1541-26-0; *trans*-2-hydroxy-3-phthalimidocyclohexanone, 88015-25-2.

Tungsten-Catalyzed Allylic Alkylations. New Avenues for Selectivity

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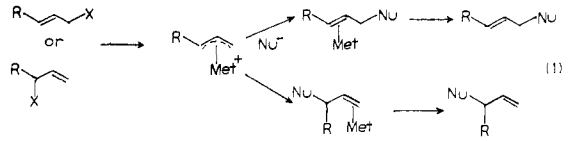
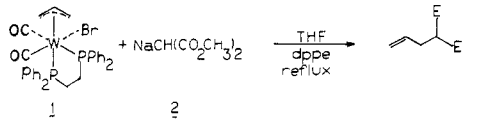
Transition-metal templates offer an opportunity to provide new dimensions for selectivity in organic reactions. In examining the question of regioselectivity of allylic alkylations,[1-4] we were intrigued by the possibility of enhanced selectivity for attack at the more substituted end of a π-allyl metal intermediate (eq 1). Five



(1)

factors may be envisioned to affect the regioselectivity—(1) steric demands of the nucleophile, (2) steric demands of the π-allyl substituents, (3) charge distribution of the π-allyl intermediate, (4) steric and electronic demands of the metal template, and (5) reactivity of the nucleophile. Rationalizing that factors 3 and 4 favor attack at the more substituted end, we envisioned that the steric demands imposed by a tungsten template may favor alkylation at the more substituted end. In this paper we wish to record (1) the development of a tungsten catalyst for allylic alkylation and (2) the unusual regio- and chemoselectivity of such alkylations.

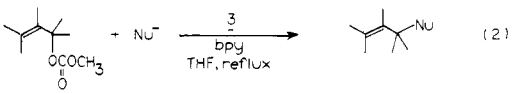
To establish the feasibility of nucleophilic attack on a π-allyltungsten complex,[5,6] we subjected **1**[5a,f] to dimethyl sodiomalonate (**2**) in refluxing THF; however, no alkylation occurred. On the other hand, addition of 1 equiv of dppe[7] to the refluxing mixture led to the alkylation product in 65% yield. We attribute the role



1 2

of the additional phosphine to ionization of **1**; the resultant cationic complex should be more susceptible to nucleophilic attack.

In order to develop a catalytic reaction, we used allyl acetate and **2** as the test reaction. We found that $W(CO)_6$ failed to catalyze the reaction[8] but that $(CH_3CN)_3W(CO)_3$[9] (**3**) led to a slow reaction (31% in 16 h). Addition of phosphines poisoned the catalyst. On the other hand, use of a stronger σ-donor type ligand such as bpy[7] to facilitate opening a coordination site on the tungsten led to a significant improvement (65% in 18 h). A more general reaction (see eq 2) resulted when carbonate, a slightly

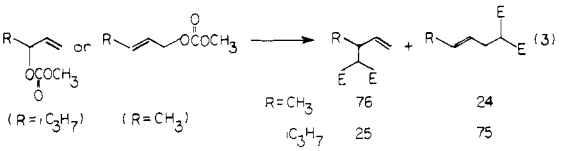


(2)

better leaving group than acetate, was substituted for acetate (81% in 12 h).

The allyl substrates that proved most interesting were those bearing one aryl group and are summarized in Table I. In each and every case, alkylation occurred predominantly to exclusively at the more substituted end regardless of the nucleophile. As expected, increasing the steric demands of the nucleophile did lead to some diminished regioselectivity (cf. entries 1, 4, and 5). Both electron-donating and electron-withdrawing aromatic rings succeed. In contrast to the molybdenum-catalyzed reactions,[2] sulfone-stabilized anions are good nucleophiles.

If both initial regioisomeric products are 1,2-disubstituted olefin–metal complexes, then a slightly diminished selectivity for the benzylic position occurs (entry 6). The effect of the aromatic ring on regioselectivity is discerned by comparing the results of the table to an alkyl-substituted π-allyl group as in eq 3. In the



(3)

latter cases steric demands of the nucleophile compete with the steric demands of the metal template to dominate the regioselectivity. Thus, the activation by the aryl group for displacement at a benzylic position conspires with the steric demands of the

(1) For reveiws, see: Trost, B. M. *Tetrahedron* **1977**, *33*, 2615; *Acc. Chem. Res.* **1980**, *13*, 385. Trost, B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 779. Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: Berlin, 1980.

(2) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543; **1983**, *105*, 3343.

(3) Roustan, J. L.; Merour, J. Y.; Houlihan, F. *Tetrahedron Lett.* **1979**, 3721. Roustan, J. L.; Houlihan, F. *Can. J. Chem.* **1979**, *57*, 2790.

(4) Cuvigny, T.; Julia, M. *J. Organomet. Chem.* **1983**, *250*, C21.

(5) For their preparation, see: (a) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865. (b) Brisdon, B. J.; Cartwright, M.; Edwards, D. A.; Paddick, K. E. *Inorg. Chim. Acta* **1980**, *40*, 191. (c) Behrens, H.; Lindner, E.; Lehnert, G. *J. Organomet. Chem.* **1970**, *22*, 665. (d) Brisdon, B. J.; Edwards, D. A. *Ibid.* **1978**, *156*, 427. (e) Stiddard, M. H. B.; Hull, C. G. *Ibid.* **1967**, *9*, 519. (f) Brisdon, B. J. *Ibid.* **1977**, *125*, 225. (g) Brisdon, B. J.; Griffin, G. F. *Ibid.* **1974**, *76*, C47. (h) Dawans, F.; Dervailly, J.; Meirnier-Piret, J.; Piret, P. *Ibid.* **1974**, *76*, 53. (i) Stiddard, M. H. B.; Holloway, C. E.; Kelly, J. D. *J. Chem. Soc. A* **1969**, 931. (j) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588, 3183.

(6) For a report of attack by hydride and Grignard reagents on a bis(cyclopentadienyl)-π-allyltungsten complex, see: Green, M. L. H.; Ephritikhine, M.; Francis, B. R.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc. Dalton Trans.* **1977**, 1131.

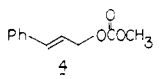
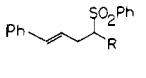
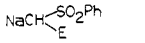
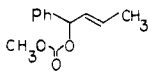
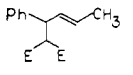
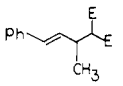
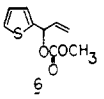
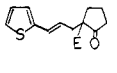
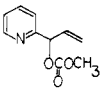
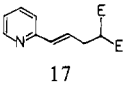
(7) Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane, bpy = 2,2'-bipyridyl, E = CO_2CH_3.

(8) For a stoichiometric reaction of allyl trifluoroacetate and $W(CO)_6$, see ref 5h.

(9) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865 and references cited therein.

0002-7863/83/1505-7757$01.50/0

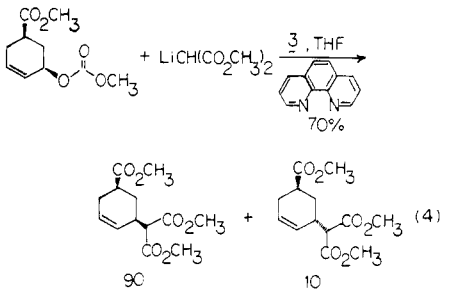
Table I. Tungsten-Catalyzed Alkylation of Aryl-Bearing Allylic Substrates

entry	allyl substrate	nucleophile[a]	time, h	product[b]	% [c]
1	 4	$NaCHE_2$	4		91[d]
2	4	$NaCH_3CE_2$	17		92[d]
3	4		15	  	87[d,e]
4	4		5	R=E 72[f] 28	78
5	4	$NaCH(SO_2Ph)_2$	9	R=$PhSO_2$ 53 47	67
6		$NaCHE_2$	4	 90  10	88
7	 5	$NaCHE_2$	6		81[d]
8	5	$NaCHE_2$	2		86
9	 6	$NaCHE_2$	4		70[g]
10	6		16.5	 84[h]  16	76
11		$NaCH_3CE_2$	14.5	 83  17	60

[a] The nucleophile was generated by treating the carbon acid with sodium hydride in THF. All reactions were run with 15 mol % $(CH_3CN)_3W(CO)_3$ and 15 mol % bpy[9] in refluxing THF. [b] All products have been fully characterized. [c] Isolated yields of pure products. [d] ≥98% a single regioisomer. [e] Threo/erythro 38/62. [f] Threo/erythro 42/58. [g] ≥95% a single regioisomer. [h] Threo/erythro 60/40.

metal template to give high regioselectivity in the aryl-substituted series with the tungsten catalyst.[10]

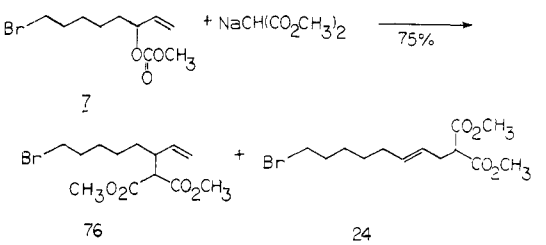
The stereochemistry of this reaction follows the same course as observed with molybdenum[2] and palladium[1] catalysts (eq 4).



90 10 (4)

The small crossover observed is not due to isomerization of either the starting carbonate nor the product under the reaction conditions.[11]

The chemoselectivity of the tungsten-catalyzed alkylation is quite noteworthy. The bromocarbonate **7** exhibits only displacement of the allyl carbonate. The fact that linalyl methyl



7

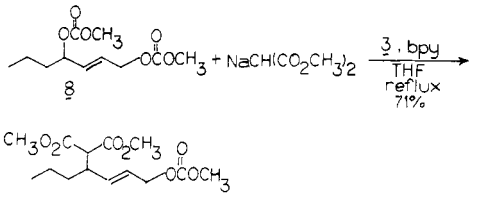
76 24

carbonate alkylates smoothly but geranyl methyl carbonate gives only a trace of alkylation products after 47 h suggested that the dependence of the ionization step on the degree of substitution

(10) By a frontier orbital argument, it is suggested that the coefficient in the LUMO at the benzylic position would be larger than that at the terminus in the π-allyltungsten complex intermediate. More effective overlap with the incoming nucleophile should then occur at the benzylic position. Thus, in the absence of overriding steric effects, it would be argued that attack would occur preferentially at the benzylic position. Since the exact structure of the intermediate is unknown at this time, performance of MO calculations to elucidate this point is difficult. A MNDO calculation on phenylallyl cation reveals that the coefficient in the LUMO and the charge density at the benzylic position are 0.672 and +0.33 (P_z charge is +0.43); whereas the corresponding values for the terminus are 0.508 and +0.22 (P_z is +0.37). These data are in accord with preferential nucleophilic attack at the benzylic position.

(11) Since the overall stereochemistry does not differentiate between a double inversion and a double retention, it is premature to speculate upon the mechanism of the small loss in stereochemistry. It should be noted that in a control experiment, reaction of the *Z* carbonate with **2** in the presence of bpy for 72 h led up to 12% of the *E* product as expected for a direct S_N2 displacement. The possibility that some of the net inverted product in the catalyzed reaction could arise by competition of a noncatalyzed displacement cannot be excluded.

of the carbon bearing the leaving group was sufficiently great to be useful synthetically. Indeed, the dicarbonate **8** permits easy replacement of the secondary carbonate without affecting the primary carbonate for the limited reaction times employed (5 h).



The high regioselectivity of this alkylation presumably reflects the effect of polar substituents to direct the incoming nucleophile to the more distal allyl terminus—an observation we have noted in the other metal-catalyzed reactions.[12,13]

The ability of metals other than palladium, notably less expensive ones, to catalyze allylic displacements offers additional dimensions of selectivity. The tungsten catalyst is less reactive than either the molybdenum[2] or especially the palladium catalysts.[1] However, the electronic and steric demands of this catalyst permit a level of control of regiochemistry not available with the previous metal systems. The timed release of leaving groups as shown in **8** shows how subtle the differences can be and yet be differentiated by this selective template. The use of timed release of leaving groups can be particularly useful in complex synthesis.[13]

Acknowledgment. We thank the National Science Foundation for their generous support of our programs.

Registry No. 1, 62891-99-0; **2**, 18424-76-5; **3**, 16800-47-8; **4**, 87802-71-9; **5**, 87802-72-0; **6**, 87802-73-1; **7**, 87802-74-2; **8**, 87802-75-3; $CH_3OC(O)OCH(Ph)CH{=}CHCH_3$, 87802-76-4; $NaCH_3CE_2$, 62116-54-5; $NaCH(SO_2Ph)E$, 60729-65-9; $NaCH(SO_2Ph)_2$, 34782-39-3; $PhCH(CHE_2)CH{=}CH_2$, 87802-78-6; $PhCH(C(CH_3)E_2)CH{=}CH_2$, 87802-79-7; $PlCH(CH(SO_2Ph)E)CH{=}CH_2$ (isomer 1), 87802-81-1; $PhCH{=}CHCH_2CH(SO_2Ph)E$, 87802-82-2; $PhCH(CH(SO_2Ph)_2)CH{=}CH_2$, 87802-83-3; $PhCH{=}CHCH_2CH(SO_2Ph)E$, 87802-84-4; $PhCH(CHE_2)CH{=}CHCH_3$, 87802-85-5; $PhCH{=}CHCH(CH_3)CHE_2$, 87802-86-6; $CH_2{=}CHCH_2CHE_2$, 40637-56-7; bpy, 366-18-7; *i*-$C_3H_7CH(OC(O)OCH_3)CH{=}CH_2$, 87802-94-6; $CH_3CH{=}CHCH_2O$-$C(O)OCH_3$, 87802-95-7; $CH_3CH(CHE_2)CH{=}CH_2$, 61979-92-8; $CH_3CH{=}CHCH_2CHE_2$, 61979-94-0; *i*-$C_3H_7CH(CHE_2)CH{=}CH_2$, 87802-96-8; *i*-$C_3H_7CH{=}CHCH_2CHE_2$, 87802-97-9; $LiCH(CO_2CH_3)_2$, 74826-01-0; $Br(CH_2)_5CH(CHE_2)CH{=}CH_2$, 87802-99-1; Br-$(CH_2)_5CH{=}CH{-}CH_2CHE_2$, 87803-00-7; $CH_3CH_2CH_2CH(CHE_2)$-$CH{=}CHCH_2OC(O)OCH$, 87803-01-8; $PhCH(CH(SO_2Ph)E)CH{=}CH_2$ (isomer 2), 87803-03-0; 2-(1-((methoxycarbonyl)oxy)-2-propen-1-yl)pyridine, 87802-77-5; methyl 2-hydroxycyclopenten-1-carboxylate sodium salt, 63178-03-0; methyl 1-(1-phenyl-2-propen-1-yl)-2-oxocyclopentan-1-carboxylate (isomer 1), 87802-80-0; dimethyl (3-(2-furyl)-1-buten-4,4-dicarboxylate, 87802-87-7; dimethyl 3-(2-furyl)-1-penten-4,4-dicarboxylate, 87802-88-8; dimethyl 3-(2-thienyl)-1-buten-4,4-dicarboxylate, 87802-89-9; methyl 1-(1-(2-thienyl)-2-propen-1-yl)-2-oxocyclopentan-1-carboxylate (isomer 1), 87802-90-2; methyl 1-(3-(2-thienyl)-2-propen-1-yl)-3-oxocyclopentan-1-carboxylate, 87802-91-3; dimethyl 3-(2-pyridyl)-1-buten-4,4-diocarboxylate, 87802-92-4; dimethyl 1-(2-pyridyl)-1-buten-4,4-dicarboxylate, 87802-93-5; allyl acetate, 591-87-7; methyl *cis*-6-((methoxycarbonyl)oxy)cyclohexen-4-carboxylate, 87802-98-0; 1,10-phenanthralene, 66-71-7; methyl *cis*-6-(bis(methoxycarbonyl)methyl)cyclohexen-4-carboxylate, 64841-68-5; methyl *trans*-6-(bis(methoxycarbonyl)methyl)cyclohexen-4-carboxylate, 74545-66-7; methyl 1-(1-phenyl-2-propen-1-yl)-2-oxocyclopentan-2-carboxylate (isomer 2), 87803-02-9; methyl 1-(1-(2-thienyl)-2-propen-1-yl)-2-oxocyclopentan-1-carboxylate (isomer 2), 87803-04-1.

(12) Cf.: Trost, B. M.; Klun, T. P. *J. Am. Chem. Soc.* **1979**, *101*, 6756. Trost, B. M.; Schmuff, N.; Miller, M. *Ibid.* **1980**, *102*, 5979. Trost, B. M.; Molander, G. A. *Ibid.* **1981**, *103*, 5969. Also see: Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575. Valpey, R. S.; Miller, D. J.; Ester, J. M.; Godleski, S. A. *J. Org. Chem.* **1982**, *47*, 4717.

(13) Genet, J. P.; Balabane, M.; Backvall, J. E.; Nystrom, J. E. *Tetrahedron Lett.* **1983**, *24*, 2745. Genet, J. P.; Balabane, M.; Charbonnier, F. *Ibid.* **1982**, *23*, 5027. Tanigawa, Y.; Nishimura, K.; Kawasaki, A.; Murahashi, S. I. *Ibid.* **1982**, *23*, 5549. Backvall, J. E.; Nordberg, R. E.; Nystrom, J. E. *Ibid.* **1982**, *23*, 1617. Genet, J. P.; Balabane, M.; Legras, Y. *Ibid.* **1981**, *23*, 331. Backvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959. Genet, J. P.; Piau, F. *J. Org. Chem.* **1981**, *46*, 2414. Genet, J. P.; Piau, F.; Ficini, J. *Tetrahedron Lett.* **1980**, *21*, 3183.

Cyclization of the *N*-Butyl-5-methyl-1-hex-4-enaminyl Radical and the Use of *N*-Lithio-*N*-butyl-5-methyl-1-hex-4-enamine as a Mechanistic Probe for Electron-Transfer Processes

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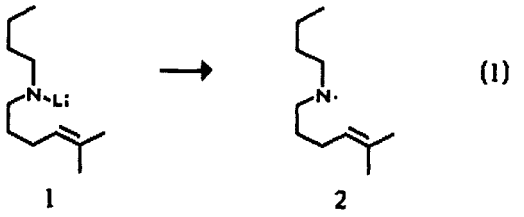
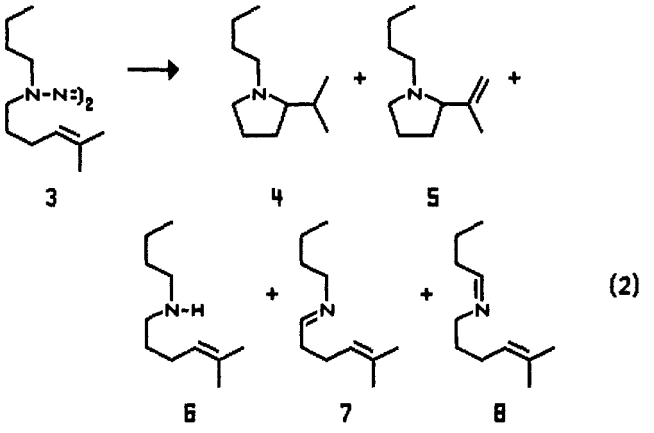
Evidence has been presented that lithium dialkylamides can react with selected substrates by an electron-transfer process rather than a conventional two-electron process.[2] Generally mechanistic conclusions have been reached by studying the reduced substrates of these reactions. An alternative approach would be to study the oxidized product, an aminyl radical, which was designed to undergo a characteristic skeletal rearrangement.[3,4] In this communication we report that *N*-lithio-*N*-butyl-5-methyl-1-hex-4-enamine (**1**) can be used as a mechanistic probe.[5] Oxidation of **1** gives radical **2** (eq 1) which has been found to cyclize.



(1)

1 **2**

To study the cyclization reaction, we generated radical **2** by photolysis or thermolysis of tetrazene **3**.[8] In reactions in various solvents both cyclic and acyclic products were obtained[8] (eq 2);



(2)

3 **4** **5** **6** **7** **8**

(1) Camille and Henry Dreyfus Teacher-Scholar, 1980–1985.

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(5) Ring openings of cyclopropyl- and cyclobutylaminyl radicals have been reported[6a] as has the cyclization of a pentenylaminyl radical.[6b] However, the corresponding lithium amide derivatives undergo complicating *anionic* rearrangements.[7]

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(8) The supplementary material contains a brief description of the syntheses of **6**, **3**, and **4**, references for the syntheses, the method used to identify the products in eq 2, and the method used to determine the yield of **10** from the reactions of **1** with **9**.

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