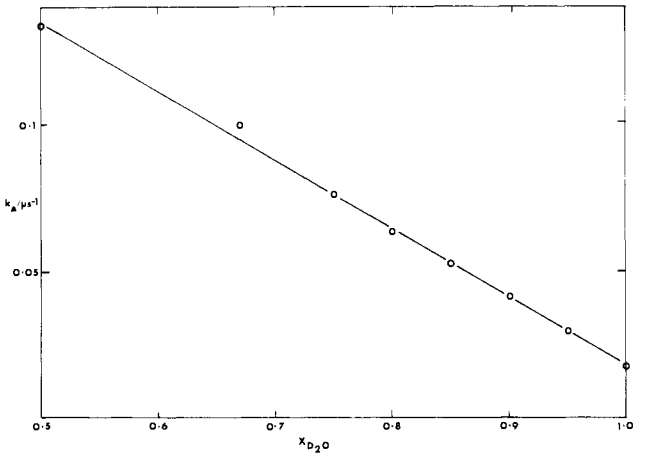

Figure 3. First-order decay rate constant of $O_2(^1\Delta_g)$ luminescence as a function of D_2O mole fraction in H_2O. The correlation coefficient from a linear regression analysis was 0.999.

imately this initial intensity were employed throughout. All lifetimes measured were corrected for this time constant according to

$$\tau_\Delta^2 = \tau_m^2 - \tau_r^2 \quad (1)$$

where τ_m is the reciprocal of the measured first-order decay constant (k_m) of the luminescence. In H_2O and D_2O solutions containing sensitizer [tetrakis(4-sulfonatophenyl)porphine, TPPS], the signal showed an intense early component followed by the weaker (ca. one-tenth) delayed luminescence of $O_2(^1\Delta_g)$. The initial amplitude of the fast component was about 5 times that observed to be scattered when pure H_2O (or D_2O) only was in the target cuvette in normal geometry. This intense early component was relatively very much less when CH_3OH (or CD_3OD) was the solvent and absent when dimethyl hematoporphyrinate (HPDME) was used as sensitizer in dielectric liquids such as benzene. Its origin in aqueous media is not certain but it is clearly related to the presence of TPPS in the target.

Figure 2, top and bottom, shows the luminescence time profiles from a TPPS (A_{532} 0.6) solutions in oxygen-saturated H_2O and D_2O, respectively. The nonexponential behavior is clearly apparent, unlike the profile of the scattered light. An iterative least-squares analysis was used to separate two first-order components.[19] No evidence was found of any second-order behavior of the early part of the decay. The lifetime of the early component was near 0.8 μs, which is the instrument response lifetime. The slower component (ca. one-tenth of the total signal amplitude) showed $k_m = 0.22\ \mu s^{-1}$ ($\tau_m = 4.5\ \mu s$). On correction for instrument response (eq 1) this yields $\tau_\Delta^{H_2O} = 4.4\ \mu s$.[20] This slow component was removed by saturating with nitrogen gas and is assigned to the infrared luminescence from $O_2(^1\Delta_g)$.

To verify that this residual luminescence was in fact not due to a system artifact, we examined a series of mixtures of H_2O and D_2O containing TPPS (A_{532} 0.64). Whereas the decay constant of the early component remained unchanged, that of the slow component was linearly dependent on the molar composition of the solvent systems (Figure 3). At $X_{D_2O} = 1$, $\tau_\Delta = 56\ \mu s$ was observed. The extrapolated value of k_Δ at $X_{H_2O} = 1$ was $2.54 \times 10^{-2}\ \mu s^{-1}$ or $\tau_\Delta = 3.9\ \mu s$ (correlation coefficient = 0.999), in close agreement with that observed directly. The value for $\tau_\Delta^{H_2O}$ measured here agrees well with a value (4 μs) obtained earlier by an indirect photobleaching method[21] but is somewhat larger than the value of 2 μs reported by Merkel and Kearns,[22] again by extrapolation from indirect measurements. The present data lead to a value of $\tau_\Delta^{D_2O}/\tau_\Delta^{H_2O} = 13$.

In conclusion, the ease, convenience and precision of time-resolved infrared luminescence measurements of τ_Δ allows the generation of a reliable data base from which a critical examination of the current theory[22] of solvent and isotope effects can proceed.

Acknowledgment. Dr. I. B. C. Matheson made important contributions in the early part of this work. Partial support of this work was from NIH Grant GM24235. Work at the Center for Fast Kinetics Research is supported by NIH Grant RR00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas at Austin.

Registry No. H_2O, 7732-18-5; O_2, 7782-44-7.

(18) At a referee's suggestion we measured the rise time of the detector response to a 10-μs duration square-wave light pulse from a red light emitting diode. The rising edge of the output wave form was exponential with an e^{-1} rise time of 0.82 μs, in good agreement with the scattered laser light measurement.

(19) Foyt, D. C. *Comput. Chem.* **1981**, *5*, 49.

(20) This value, as correctly pointed out by a referee, contains a contribution from the formation time of $O_2(^1\Delta_g)$. The lifetime of the triplet state of TPPS in oxygen-saturated water was 0.39 μs. Allowing for this in a manner similar to eq 1 made no significant difference to the value of 4.4 μs. Error limits of ±10% are applicable to all data reported here.

(21) Lindig, B. A.; Rodgers, M. A. J. *J. Phys. Chem.* **1979**, *83*, 1683.
(22) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244.

Molybdenum Catalysts for Allylic Alkylation

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The ability to selectively activate relatively inert leaving groups toward substitution using palladium templates has generated a number of useful synthetic reactions and sequences.[1-6] The extraordinary chemo- and regioselectivity and stereocontrol exhibited by these templates led us to search for complementary reactivity, especially with respect to stereochemical control. The high coordination number of molybdenum, the ready availability of π-allylmolybdenum complexes, and the paucity of information regarding their susceptibility toward nucleophilic attack turned our attention toward π-allylmolybdenum complexes.[7] In this paper, we report stoichiometric and catalytic allylic substitution reactions involving molybdenum complexes and the sensitivity of regioselectivity toward the nature of the ligands on molybdenum.

Except for a single example of the alkylation of the cationic complex $CpMo(CO)(NO)(\pi\text{-allyl})^+$ with an enamine[8] to yield

(1) For reviews see: Trost, B. M. *Pure Appl. Chem.* **1981**, *53*, 2357; *Aldrichimica Acta* **1981**, *14*, 43; *Acc. Chem. Res.* **1980**, *13*, 385; *Tetrahedron* **1977**, *33*, 2615. Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: Berlin, 1980.
(2) For activation of allylic sulfones and neutral alkylations via epoxides see: Trost, B. M.; Schmuff, N.; Miller M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979. Trost, B. M.; Molander, G. A. *Ibid.* **1981**, *103*, 5969.
(3) For cyclization and macrocyclization see: Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1977**, 99, 3867; **1979**, *101*, 1595; **1980**, *102*, 4743.
(4) For isomerizations see: Trost, B. M.; Runge, T. A.; Jungheim, L. N. *J. Am. Chem. Soc.* **1981**, *103*, 2485, 7550, 7559.
(5) For eliminations see: Trost, B. M.; Fortunak, J. *J. Am. Chem. Soc.* **1980**, *102*, 2841; *Tetrahedron Lett.* **1981**, *22*, 3459. Trost, B. M.; Verhoeven, T. R.; Fortunak, J. *Ibid.* **1979**, 3201. Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Ibid.* **1978**, 2075. Mandai, T.; Gotah, J.; Otera, J.; Kawada, M. *Chem. Lett.* **1980**, 313. Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623.
(6) For cycloadditions see: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429, 6432; **1980**, *102*, 6359; **1981**, *103*, 5972. For a related reaction see: Binger, P.; Germer, A. *Chem. Ber.* **1981**, *114*, 3325 and earlier references cited therein.
(7) For nucleophilic attack using iron and cobalt complexes see: Roustan, J. L.; Merour, J. Y.; Houlihan, F. *Tetrahedron Lett.* **1979**, 3721.
(8) Adams, R. D.; Chodosh, D. F.; Rosan, A. M.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 2570. Also see: Bailey, N. A.; McCleverty, J. S. *J. Chem. Soc., Chem. Commun.* **1974**, 592.

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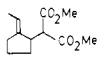
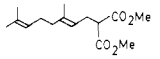
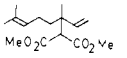
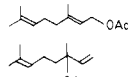
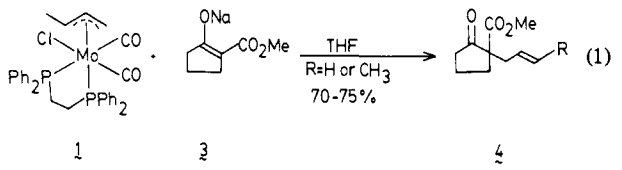
Table I. Regioselectivity of the Mo-Catalyzed Allylic Alkylation[a]

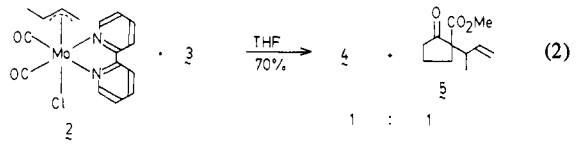
entry	allylic acetate	nucleophile[b]	catalyst[c]	time, h	product		yield, %[e]
							
1	R = H	B	Mo(bpy)	16	R = H		93
2	R = CH_3	B	Mo(c)	10	R = CH_3 95	5	75
3	R = Ph				R = Ph		
a		B	Mo(bpy)	36	30	70	75
b			Mo(c)	8	95	5	73
4							
a		B	Mo(bpy)	72			70[f]
b			Mo(c)	6			82
5							
a		A	Mo(bpy)	72	67	33	45 (55)[f]
b			Mo(c)	48	15	85	69 (75)[f]
							
6		A	Mo(c)	48	6 15[g]	7 85	65
7							
a		A	Mo(c)	3	6 15[g]	7 85	84
b		A[h]	Mo(c)	1.25	6 4	7 96	84

[a] Reactions normally performed with 5-20 mol % of catalyst in refluxing toluene. [b] Nucleophile: A = $NaCH(CO_2CH_3)_2$; B = **3**. Both are generated by treatment of the respective carbon acids with sodium hydride. [c] Mo(c) = $Mo(CO)_6$; Mo(bpy) = Mo(2,2'-bipyridyl)$(CO)_4$; Mo(pe) = Mo[1,2-bis(diphenylphosphino)ethane]$(CO)_4$. [d] All products have been identified either by spectral and/or chromatographic comparison to authentic samples or by spectral methods including elemental composition in the case of new compounds. [e] Isolated yields of pure products. [f] Yield based upon recovered starting material. [g] This product is a 4:1 mixture of the depicted *E* to *Z* isomers. [h] The nucleophile was generated by treating dimethyl malonate with 0.9 equiv of *O,N*-bis(trimethylsilyl)acetamide.

a stable olefin complex, attack of carbon nucleophiles on simple molybdenum complexes is unreported.[9] We first examined the neutral complexes **1**[10] and **2** (eq 1 and 2).[11] The reaction of the



(1)

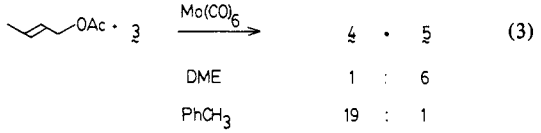


(2)

dppe complexes **1**, R = H, and **1**, R = CH_3, proceeded smoothly to give **4** with high selectivity (>95:5 for R = CH_3). In contrast to the case of palladium, the bipyridyl complex **2** reacts at a rate quite similar to that of **1**. Furthermore, this switch in ligands from dppe to bpy had a substantial effect on the resultant regioselectivity. While it is premature to rationalize the source of this effect, it is noteworthy that the bpy and dppe complexes have different preferred geometries[10,11] and that bpy is a stronger σ-donating ligand than dppe.

For maximum synthetic effectiveness, a catalytic process was immediately sought. Reaction of allylic acetates with the anion of dimethyl malonate or 2-carbomethoxycyclopentanone in the presence of Mo(bpy)$(CO)_4$[Mo(bpy),[12] Mo(dppe)$(CO)_4$[Mo(pe)],[13] Mo(TMEDA)$(CO)_4$, and $Mo(CO)_6$[Mo(c)] lead to the desired alkylation products with the Mo(bpy) and Mo(c) being preferred (see Table I). The slow rate of alkylation and poor conversions with Mo(pe) and the TMEDA complex limited our exploration of these catalysts for the moment. Perusal of this table reveals the complementary regiochemical behavior of the Mo(bpy) vs. the Mo(c) catalyst when intrinsic structural features are not overwhelming as in entries 2, 3, and 5. For entry 4, the preference for the endocyclic double bond reinforces the bias for attack at a primary carbon, leading to the same product for both catalysts. While the source of this regioselectivity remains unproven, it can be rationalized as a result of a delicate interplay between the bias for attack of a nucleophile at the sterically less congested carbon of the π-allyl fragment and the stability of the initially produced olefin–molybdenum(0) complex—two effects that oppose one another. A further complication in this interpretation results from the uncertainty in the mechanism of attack of the nucleophile either directly at carbon or initially at molybdenum.[9]

Solvents have a marked effect on this reaction in terms of rate and regioselectivity. Ethereal solvents like THF, diglyme, and dioxane decelerate the reaction relative to toluene—presumably due to their coordinating ability for the metal, thereby reducing its electrophilicity. Reaction of crotyl acetate with Mo(c) in DME led not only to a slower reaction but to a reversal of the regioselectivity (eq 3). We attribute the difference to generation of



(3)

(9) Treatment of **2** with the anion of pentan-2-4-dione is reported to result in ligand exchange. See: Brisdon, B. J.; Griffin, G. F. *J. Chem. Soc., Dalton Trans.* **1975**, 1999.

(10) For **1**, R = H, see: tom Dieck, H.; Friedel, H. *J. Organomet. Chem.* **1968**, *14* 375. Faller, J. W. Haitko, D. A.; Adams R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865. Complex **1**, R = CH_3, made in analogous fashion.

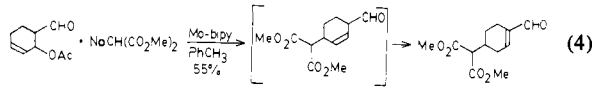
(11) Cf.: Hull, C. G.; Stiddard, M. H. B. *J. Organomet. Chem.* **1967**, *9*, 519. Brisdon, B. J.; Day, A *Ibid.* **1981**, *221*, 279 and reference cited therein. Also see ref 9 and 10.

(12) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 2323. Stiddard, H. M. B. *J. Chem. Soc.* **1962**, 4712.

(13) Chatt, J.; Watson, H. R. *J. Chem. Soc.* **1961**, 4980. Zingales, F.; Canziani, F. *Gazz. Chim. Ital.* **1962**, *92*, 343. Grim, S. O.; Wheatland, D. A.; McAllister, P. *Inorg. Chem.* **1968**, *7*, 161.

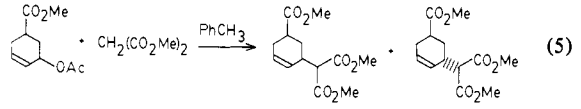
a new catalyst in DME, i.e., $Mo(DME)(CO)_4$.[14] DME, being a strong σ-donating ligand like bpy, shows a similar selectivity pattern. Use of *O,N*-bis(trimethylsilyl)acetamide as the base to generate the nucleophile in lieu of sodium hydride and a noteworthy improvement in the regioselectivity (cf. entry 7a,b in the table) from 85:15 (tertiary to primary) to 96:4. The source of this effect may derive from this base acting as a ligand toward molybdenum.

Chemo- and regioselectivity are highlighted in the successful alkylation of 3-acetoxy-4-carboxaldehydocyclohex-1-ene (eq 4)



(4)

in which the polar group directs the incoming nucleophile to the more distal carbon.[15] This example also illustrates the preference for alkylation over elimination. While the stereochemistry of the reaction could not be discerned in this case due to the migration of the double bond, it could be determined in the case of 3-acetoxy-5-carbomethoxycyclohex-1-ene (eq 5). The Mo(bpy)



(5)

base			
NaH	Mo(bpy)	85	15
NaH	Mo(c)	50	50
$CH_3C(OTMS)=NTMs$	Mo(c)	>95	<5

catalyst gives predominantly the same product that derives from the corresponding palladium reaction when NaH is used as base. Strikingly, the Mo(c) catalyst produces a 1:1 ratio of the *E* and *Z* isomers under the above conditions but only the product of net retention when *O,N*-bis(trimethylsilyl)acetamide is used as base. While a double retention or a double inversion accounts for formation of the product of net retention, the latter appears most reasonable. Following the reaction by VPC as well as a control experiment reveals that the mixed stereochemistry does not result from isomerization of the starting acetate. While the source of this stereochemical result remains to be elucidated,[16] the ability to change the stereochemical course of the reaction by ligand variation should prove useful.

Allylic alkylation catalyzed by molybdenum forms a useful and frequently complementary alternative to the palladium-catalyzed reaction. For example, regioselectivity appears more sensitive to ligand variation in the case of Mo. Higher selectivity for attack at a primary vs. secondary carbon of a π-allyl fragment occurs with Mo. It also appears that more flexibility in stereocontrol may exist. On the other hand, these reactions require higher temperatures and longer times. More thorough evaluation of this Mo chemistry will be required to delineate its full potential.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. We thank the NSERC of Canada for a graduate fellowship for M.L.

Registry No. 3, 1830-92-8; **4** (R = H), 74036-93-4; **4** (R = CH_3), 82352-40-7; **5**, 82352-41-8; (*E*)-**6**, 72444-93-0; (*Z*)-**6**, 60729-61-5; **7**, 60729-63-7; 6-formyl-2-cyclohexenyl acetate, 61088-60-6; 4-(dimethoxycarbonylmethyl)-1-cyclohexenecarboxaldehyde, 82352-42-9; methyl *cis*-α,5-dimethoxycarbonyl-3-cyclohex-1-eneacetate, 64841-68-5; methyl *trans*-α,5-dimethoxycarbonyl-3-cyclohex-1-eneacetate, 74545-66-7; 2-propenyl acetate, 591-87-7; 2-butenyl acetate, 628-08-0; 3-phenyl-2-propenyl acetate, 103-54-8; 2-methylenecyclohexyl acetate, 53723-50-5; 1-(cyclopentenyl)ethyl acetate, 74545-46-3; 3,7-dimethyl-2,6-octadienyl acetate, 16409-44-2; 1-ethenyl-1,5-dimethyl-4-hexenyl acetate, 115-95-7; methyl 1-(2-propenyl)-2-oxocyclopentanecarboxylate, 74036-93-4; methyl 1-(2-butenyl)-2-oxocyclopentanecarboxylate, 82352-40-7; methyl 1-(1-methyl-2-propenyl)-2-oxocyclopentanecarboxylate, 82352-41-8; methyl 1-(3-phenyl-2-propenyl)-2-oxocyclopentanecarboxylate, 82352-43-0; methyl 1-(1-phenyl-2-propenyl)-2-oxocyclopentanecarboxylate, 82352-44-1; methyl 1-(1-cyclohexenylmethyl)-2-oxocyclopentanecarboxylate, 82352-45-2; methyl 3-cyclopropenyl-2-methoxycarbonylbutanoate, 74545-48-5; methyl 2-(2-ethylidenecyclohexyl)-2-methoxycarbonylacetate, 82352-46-3; $NaCH(CO_2CH_3)_2$, 18424-76-5; Mo(bpy), 15668-64-1; Mo(c), 13939-06-5; Mo(pc), 15444-66-3.

(14) Dawans, F.; Dewailly, J.; Meunier-Piret, J.; Piret, P. *J. Organomet. Chem.* **1974**, *76*, 53.
(15) Cf.: Trost, B. M.; Klun, T. P. *J. Am. Chem. Soc.* **1979**, *101*, 6756; **1981**, *103*, 1864. Also see ref 2.
(16) Three rationales can account for this observation: (1) competing retention and inversion pathways in the oxidative addition; (2) competing retention and inversion pathways in the reductive elimination; (3) loss of stereochemistry in the intermediate π-allyl complex.

Structure of a Photodimer Determined by Natural-Abundance ^{13}C–^{13}C Coupling

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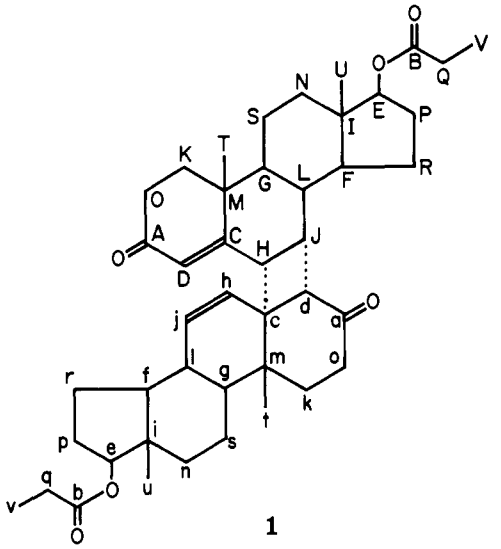
Received May 21, 1982

Photodimerization of $\Delta^{4,6}$-diene-3-keto steroids[1,2] has been shown to involve cyclobutane formation between the α,β double bond of one monomer unit and the γ,δ double bond of the second, giving a single product in essentially quantitative conversion. Unfortunately it has not proved possible to make a clear-cut distinction between the head-to-tail (formula **1**) and the opposite



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head-to-head structures. A theoretical treatment of this problem[3] concluded that the head-to-tail isomer should be preferred because of the calculated dipolar character of the reactive excited state. Over the years, a variety of attempts has failed to distinguish these two possibilities.[4-8] These methods include attempts to bridge across the two halves in 17-hydroxy derivatives,[4] measurements of dipole moments,[5] conventional NMR spectroscopy, attempts at dimerization in the solid state so that topochemical considerations of monomer crystal packing could be applied,[6] and x-ray

(1) Throndsen, H. C.; Cainelli, G.; Arigoni, D.; Jeger, O. *Helv. Chim. Acta* **1962**, *45*, 2342–2346.
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(4) Glover, D. Ph.D. Thesis, Carnegie Institute of Technology, **1969**.
(5) Orchin, M., private communication of results of T. Weil.
(6) This approach was suggested by Professor G. M. J. Schmidt.
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