proton is positioned within the deshielding cone of the adjacent pyridone carbonyl group and is diagnostic for the formation of the phenanthridinone system.

Table I presents some of the phenanthridinone products rendered readily available via this methodology. Entries 4 and 5 are particularly significant in terms of their application to alkaloid synthesis. Appropriate modifications of these examples could be envisioned to lead to rapid construction of target natural products such as lycorine[4a] and chelidonine,[4b] respectively. In general these cycloaddition reactions proceeded without complications on a range of substrates; however, steric hindrance appears to suppress bond formation as evidenced by the failure of the isocyanate derived from the α,β-unsaturated acid depicted in entry 7 to undergo cycloaddition with benzyne under these conditions. This particular substrate is of interest since it could represent a potentially attractive model for entry into the crinine-type amaryllidaceae alkaloids.

It is noteworthy that during the course of this investigation a number of other conditions for mild benzyne generation were examined in detail and found to be, in general, inferior to the 1-aminobenzotriazole oxidation method for the application at hand.[9] A detailed mechanistic scenario for the process reported herein is obscure at this point. Benzynes are well known to participate in [4 + 2] cycloaddition processes with a wide range of diene addends[6,9] and our experience to date indicates that vinyl isocyanates tend to react in a polar, step-wise fashion with most reaction partners to yield net [4 + 2] products.[2] In this regard it is interesting to note that in some reactions studied to date, trace quantities of a possible β-lactam species (ν_{max} 1790 cm^{-1}) have been observed in crude reaction mixtures and pathways involving sequential [2 + 2] cycloaddition–rearrangement steps, although unlikely, cannot be rigorously excluded at this juncture.[13,14] Efforts to shed light on the mechanistic subtleties of these reactions are currently underway in our laboratory as is the application of the methodology to alkaloid total synthesis.

Acknowledgment. We thank the National Science Foundation (CHE-8719185) for their generous support of this work.

Supplementary Material Available: Experimental details and full spectroscopic and physical characterization of all new products (3 pages). Ordering information is given on any current masthead page.

(9) For other methods of benzyne preparation, see: Bryce, M. R.; Vernon, J. M. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1981; Vol. 28, pp 183–229.
(10) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807.
(11) Vebrel, J.; Carrie, R. *Bull. Soc. Chim. Fr.* **1982**, 161.
(12) Holmer, H. L.; Trevoy, L. W. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 300.
(13) Chlorosulfonyl isocyanate is known to react with dienes in a sequence involving initial [2 + 2] cycloaddition followed by rearrangement. (a) Moriconi, E. J.; Meyer, W. C. *J. Org. Chem.* **1971**, *36*, 2841. (b) Haug, T.; Lohse, F.; Metzger, K.; Batzer, H. *Helv. Chim. Acta* **1968**, *51*, 2069.
(14) Benzoazetinone species have been identified as transients in other reactions, but isolation of these unstable materials has been achieved only under select circumstances: (a) Bashir, N.; Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1973**, 868. (b) Olofson, R. A.; Vander Meer, R. K.; Hoskin, D. H.; Bernheim, M. Y.; Stournas, S.; Morrison, D. S. *J. Org. Chem.* **1984**, *49*, 3367.

Synthesis of α'-Acyloxy Enones from Enones Using Manganese(III) Acetate in Combination with Manganese(II) Carboxylates or Carboxylic Acids

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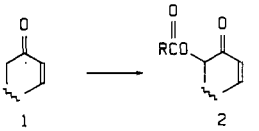
Received May 8, 1989

Summary: The oxidation of enones using manganese(III) reagents prepared from manganese(III) acetate in the presence of various carboxylic acids or manganese(II) salts of these carboxylic acids provided a convenient synthesis of α'-acyloxy enones.

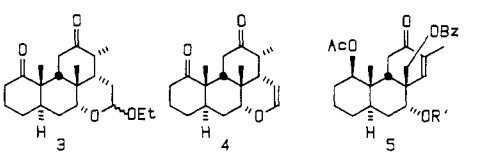
Sir: In the course of devising an enantioselective route to the quassinoids,[1] we required an effective procedure for the α'-oxidation of enones **1** to α'-acyloxy enones **2** as shown in Scheme I. Previously, we experienced difficulty with the simultaneous C-2 and C-11 oxidation[2] of a bis(enolate) derived from the tetracyclic diketones **3** and **4** in Scheme II to either a bis(α-ketol) or a bis(diosphenol) as well as difficulty with other multistep procedures[3] that would effect these oxidations. We next considered the sequential oxidation of the C-2 and C-11 positions in which application of manganese(III) acetate[4,5] would effect the C-11 oxidation of the tricyclic enone **5** in Scheme II. After finding that this C-11 oxidation process was compatible with a limited range of C-1 protecting groups[2] such as the C-1β acetate in **5**, we questioned whether we could dif-

Scheme I



1 2

Scheme II



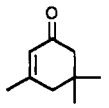
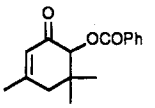
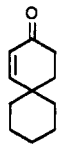
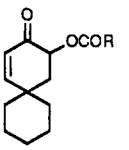
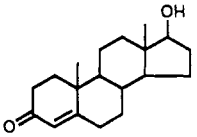
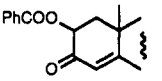
3 4 5

(1) Polonsky, J. *Fortsch. Chem. Org. Naturst.* **1973**, *30*, 101; **1985**, *47*, 221.
(2) Gross, R. S.; Kawada, K.; Kim, M.; Watt, D. S. *Synth. Commun.*, in press.

[†] Middle East Technical University.
[‡] University of Kentucky.

0022-3263/89/1954-4020$01.50/0

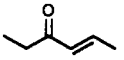
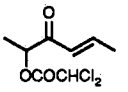
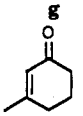
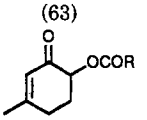
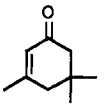
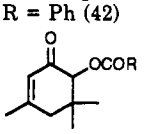
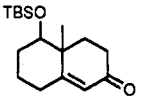
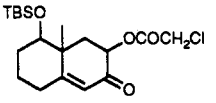
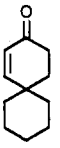
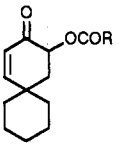
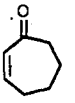
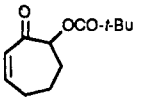
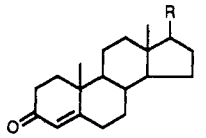
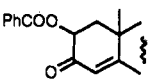
Table I. Oxidation of Enones Using Manganese(III) Acetate in the Presence of Manganese(II) Carboxylates in Benzene at 80 °C

enone 1	$Mn(OCOR)_2$	time, h	product 2 (yield, %)
			
a	$Mn(OCOPh)_2$	24	(62)
			
b	$Mn(OCOCH_2Cl)_2$	30	R = CH_2Cl (77)
c	$Mn(OCOEt)_2$	30	R = Et (71)
d	$Mn(OCOt\text{-}Bu)_2$	28	R = t-Bu (78)
e	$Mn(OCOPh)_2$	24	R = Ph (88)
			
	$Mn(OCOPh)_2$	30	(62)

ferentiate between acetoxy groups in a C-1β,11β diacetate. This concern led us to evaluate the use of other manganese(III) carboxylates as a means of introducing C-11 acyloxy groups that might be readily differentiated from the C-1β acetate group. We report a general procedure for the synthesis of α'-acyloxy enones **2** from enones **1** using manganese(III) acetate *in combination with* either manganese(II) carboxylates or carboxylic acids.

Initial efforts focused on the application of manganese(III) chloroacetate, propionate, pivalate, and benzoate that were prepared according to the procedure of Vaerman and Bertrand.[6] In each case, the oxidation of an enone **1** with these manganese(III) compounds furnished only unchanged starting material, although the corresponding manganese(III) acetate prepared using this same procedure[6] or other procedures[7] was an effective oxidant for the α'-acetoxylation of enones. The use, however, of 6 equiv of manganese(III) acetate *in combination with* 6 equiv of manganese(II) carboxylate[8-11] led to the desired α'-acyloxy enones **2** in good yield as summarized in Table I. Oxi-

Table II. Oxidation of Enones Using Manganese(III) Acetate in the Presence of Carboxylic Acids in Benzene at 80 °C

enone 1	RCO_2H	time, h	product 2 (yield, %)
			
g	Cl_2CHCO_2H	18	(63)
			
h	$PhCH_2CO_2H$	20	R = CH_2Ph (10)
i	$PhCO_2H$	6	R = Ph (42)
			
j	$ClCH_2CO_2H$	18	R = CH_2Cl (75)
k	$CH_3O_2C(CH_2)_2CO_2H$	18	R = $(CH_2)_2CO_2CH_3$ (88)
			
l	$ClCH_2CO_2H$	18	(72)
			
b	$ClCH_2CO_2H$	6	R = CH_2Cl (72)
m	Cl_2CHCO_2H	16	R = $CHCl_2$ (62)
c	$EtCO_2H$	18	R = Et (69)
n	$i\text{-}PrCO_2H$	9	R = i-Pr (75)
d	$t\text{-}BuCO_2H$	12	R = t-Bu (74)
o	(S)-(+)-$C_2H_5CH(CH_3)CO_2H$	48	R = (S)-(+)-$C_2H_5CHCH_3$ (62)
e	$PhCO_2H$	15	R = Ph (86)
p	$p\text{-}CH_3O\text{-}C_6H_4CO_2H$	18	R = C_6H_4-p-OCH_3 (62)
			
q	t-$BuCO_2H$	6	
			
r R = $COCH_3$	$PhCO_2H$	18	(54)
s R = $COCH_2OAc$	$PhCO_2H$	6	(41)
t R = 	$PhCO_2H$	16	(51)

(3) For example, we were unable to effect direct oxidation of **3** or **4** to the bis(diosphenol) using selenium dioxide [Sharpless, K. B.; Gordon, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 300] or NaH, KH, or LDA/oxygen [Barton, D. H. R.; Pradhan, S. K.; Sternhell, S.; Templeton, J. F. *J. Chem. Soc.* **1961**, 255. Rao, D. V.; Stuber, F. A.; Ulrich, H. *J. Org. Chem.* **1979**, *44*, 456. Gardner, J. N.; Carlon, F. E.; Gnoj, O. *Ibid.* **1968**, *33*, 3294]. We were also unable to effect conversion to the bis(diosphenol) indirectly via the 2,11-dibromide [Kornblum, N.; Frazier, H. W. *J. Am. Chem. Soc.* **1966**, *88*, 865. Bauer, D. P.; Macomber, R. S. *J. Org. Chem.* **1975**, *40*, 1990], the 2,11-bis(phenyl sulfide) [Trost, B. M.; Massiot, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 4405], the 2,11-bis(benzyl carbonate) [Gore, M. P.; Vederas, J. C. *J. Org. Chem.* **1986**, *51*, 3700], the bis[(*N*,*N*-dimethylamino)methylene] derivative at the C-2 and C-11 positions of **3** and **4** using Bredereck's alkoxybis(dimethylamino)methanes [Wasserman, H. H.; Ives, J. L. *J. Org. Chem.* **1985**, *50*, 3573], via the bis(hydroxymethylene) using ethyl formate, or via the bis(enone) using *p*-anisaldehyde [Bridgeman, J. E.; Jones, E. H. R.; Meakins, G. D.; Wicha, J. *J. Chem. Soc., Chem. Commun.* **1967**, 898. Bridgeman, J. E.; Buthchers, C. E.; Jones, E. R. H.; Kasal, A.; Meakins, G. D.; Woodgate, P. D. *J. Chem. Soc. C* **1970**, 244]. We were also unable to effect conversion to the bis(α-ketol) using LDA/MoOPh [Vedejs, E.; Engler, D. A.; Telshchow, J. E. *J. Org. Chem.* **1978**, *43*, 188].

(4) Dunlap, N. K.; Sabol, M. R.; Watt, D. S. *Tetrahedron Lett.* **1984**, *25*, 5839.

(5) (a) Danishefsky, S.; Bednarski, M. *Tetrahedron Lett.* **1985**, *26*, 3411. (b) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1986**, *108*, 7060.

(6) Vaerman, J. M.; Bertrand, J. N. M. Ger. Pat. 2,124,876, 1972, *Chem. Abstr.* **1972**, *77*, 100812z.

(7) (a) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 138. (b) Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry*; Open Court Publishing Co.: La Salle, IL, 1981; Chapter 1.

(8) For $Mn(OCOCH_2Cl)_2$, see: (a) Espersen, W. G.; Martin, R. B. *J. Phys. Chem.* **1976**, *80*, 161. (b) Fogel, L.; Rubinszetino'wna, T.; Taumano'wa, A. *Roczniki Chem.* **1929**, *9*, 348.

(9) For $Mn(OCOC_2H_5)_2$, see: Gurumurthy, C. V.; Govindarao, V. M. H. *Indian J. Chem.* **1968**, *6*, 326; *Chem. Abstr.* **1968**, *69*, 91484z.

(10) For $Mn(OCOC(CH_3)_3)_2$, see: Pasynskii, A. A.; Idrisov, T. C.; Suvorova, K. M.; Kalinnikow, V. T. *Soviet J. Coord. Chem.* **1976**, *2*, 813.

(11) For $Mn(OCOC_6H_5)_2$, see: Mauvernay, R. Y. French Pat. 1,210,497, 1960; *Chem. Abstr.* **1961**, *55*, 17582c.

dations conducted with 6 equiv of manganese(III) acetate in combination with 12 equiv of a carboxylic acid also proved to be a particularly convenient procedure, as summarized in Table II. An examination of these examples revealed that this process was compatible with enones 1 having hydroxyl, ester, ketal, and *tert*-butyldimethylsilyl ether functionality and was also compatible with carboxylic acids having a variety of alkyl substitution patterns or halogen substituents on the α carbon of the carboxylic acid. The process was not compatible with carboxylic acids having benzylic hydrogens (e.g., phenylacetic acid), α-hydroxy (e.g., lactic acid, mandelic acid), or α-methoxy substituents, and the process, in the few cases that were examined, exhibited little asymmetric induction using chiral carboxylic acids (e.g., (*S*)-(+)-2-methylbutyric acid). Despite these limitations, this oxidation accommodated a variety of different enone 1 and carboxylic acid components and the efficient regioselective coupling at the α'-position[12] is noteworthy.

The following general procedure was employed for oxidations using manganese(III) acetate in combination with carboxylic acids. A mixture of 15 mmol of manganese(III) acetate and 30 mmol of carboxylic acid in 50 mL of benzene was refluxed for 45 min under a Dean–Stark trap. The mixture was cooled to 25 °C, and 2.5 mmol of enone[13] 1 was added. The mixture was refluxed until the dark brown color disappeared (6–18 h). The mixture was cooled to 25 °C, diluted with ethyl acetate, washed successively with 1 M hydrochloric acid solution, aqueous saturated sodium bicarbonate solution, and brine, and dried over anhydrous magnesium sulfate. The crude products were chromatographed on silica gel to afford the α'-acyloxy enones 2 having IR, NMR, and mass spectral data in support of the assigned structures. In the case of oxidations using manganese(III) acetate in combination with manganese(II) carboxylates, 15 mmol of the manganese(II) carboxylate was substituted for the 30 mmol of carboxylic acid in the above procedure.

Acknowledgment. We thank the National Institutes of Health (Grant GM-36256) for their generous financial support, the North Atlantic Treaty Organization for a travel grant (No. 0346/88), the University of Kentucky for the purchase of Bond Issue Equipment, and the University of Kentucky Mass Spectrometry Center for exact mass determinations.

Supplementary Material Available: Characterization data for compounds **2a–t** (7 pages). Ordering information is given on any current masthead page.

(12) For an exception to this α'-regioselectivity, see: Ahmad, M. S.; Ahmad, S. Z.; Ansari, I. A. *J. Chem. Res. (S)* **1984**, 374.

(13) All enones were commercially available with the exception of spiro[5.5]undec-1-en-3-one, which was prepared according to: Kane, V. V. *Synth. Commun.* **1976**, *6*, 237.

Reductive Tandem Cyclization of Allyl Pentenyl Ketones

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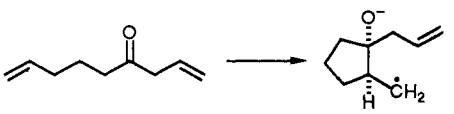
Received April 10, 1989

Summary: Bicyclo[3.3.0]octanols were synthesized in one step, by cathodic reduction of linear allyl pentenyl ketones.

Sir: Cathodic cyclization[1,2] of 6-hepten-2-ones and related compounds provides a remarkable example of a high yield, highly stereoselective electrochemical process. This selectivity, which is not duplicated by chemical reductions, arises from a delicate balance of kinetic factors which allow stereospecific ketyl addition to an unactivated alkene to succeed in competition with proton and electron transfers, and reversible cyclization which destroys stereochemistry.[2] In this study we set out to expand the synthetic scope of this method, investigating a "tandem" bicyclization process. It was hypothesized that an initial ketyl cyclization would give a substituted 5-hexenyl radical 1, appropriate for a radical cyclization onto the allyl moiety. This hypothesis



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was attractive for bicyclization because reactants of this type are readily available and because the ketyl cyclization stereochemistry will lead to a cis-ring juncture. The products are interesting because bicyclo[3.3.0]octanol systems of this type are found in a number of natural products.

Although tandem cyclizations are known[3] for certain dienyl halides with tin hydride reagents, they are not known for reduction of dienones. The closest example[4]

Table I. Reduction of 2 at a Hg Pool Cathode (DMF Solvent, 0.1 M Bu_4NBF_4 Supporting Electrolyte)[a]

conditions	cosolvent	cell	product distribution,[b] % 4	5
controlled potential[c]	none	2 compt	54	0
controlled potential[c]	0.2 MH_2O	2 compt	49	3
controlled current[d]	none	2 compt	52	0
controlled current[d]	none	1 compt	22	0
controlled current[d]	0.2 M *i*-PrOH	1 compt	48	8

[a] The amount of reactant 1 was 28–90 mmol and the amount of charge transferred was in the range of 1.7–2.5 F mol^{-1}. [b] Determined by calibrated GC. [c] −2.80 V (SCE). [d] 4–8.5 mA cm^{-2}.

(1) Shono, T.; Mitani, M. *J. Am. Chem. Soc.* **1971**, *93*, 5284. Shono, T.; Nishiguchi, I.; Ohmizu, H. *Chem. Lett.* **1976**, 1233. Shono, T.; Nishiguchi, I.; Ohmizu, H.; Mitani, M. *J. Am. Chem. Soc.* **1978**, *100*, 545. Shono, T.; Kise, N.; Suzumoto, T.; Morimoto, T. *J. Am. Chem. Soc.* **1986**, *108*, 4676.

(2) Kariv-Miller, E.; Pacut, R. I.; Lehman, G. K. *Top. Curr. Chem.* **1988**, *148*, 97. Swartz, J. E.; Mahachi, T. J.; Kariv-Miller, E. *J. Am. Chem. Soc.* **1988**, *110*, 3622. Swartz, J. E.; Kariv-Miller, E.; Harrold, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 1211.

(3) Curran, D. P. *Synthesis* **1988**, 47, 489. Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553.

(4) Fevig, T. L.; Elliot, R. L.; Curran, D. P. *J. Am. Chem. Soc.* **1988**, *110*, 5064.

0022-3263/89/1954-4022$01.50/0