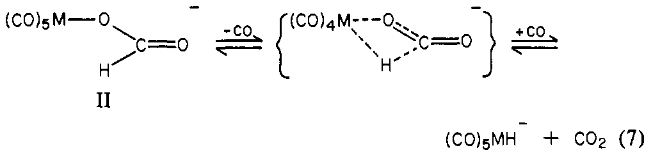
The reverse of CO_2 reduction as depicted in eq 4 proceeded under mild conditions (25-50 °C) for the case where M = Cr, i.e., $HCO_2Cr(CO)_5^-$ readily undergoes decarboxylation to $HCr(CO)_5^-$ and CO_2. Consistent with this finding it was possible to alternate between metalloformate and metallodithioformate derivatives by introducing CO_2 or CS_2 (eq 6). On the other hand,

$$HCO_2Cr(CO)_5^- + CS_2 \rightleftharpoons HCS_2Cr(CO)_5^- + CO_2 \quad (6)$$

decarboxylation of $HCO_2W(CO)_5^-$ occurred sluggishly at elevated temperatures (>80 °C). Moreover, it was found that the chromium pentacarbonyl formate derivative exchanges CO ligands with free ^{13}CO in solution much faster (~80% in 10 min) than the tungsten analogue (~50% in 3 h) at ambient temperature and in advance of the decarboxylation process. Hence CO lability appears to be a requisite step in the mechanism for rupture of the C-H bond in the formate ligand in systems involving coordinatively saturated metal centers (eq 7).[7-10] As required by the principle of microscopic reversibility, the reverse process, addition of CO_2 to $HM(CO)_5^-$ to afford $HCO_2M(CO)_5^-$(II), would also entail CO dissociation, a property indeed exhibited by $HM(CO)_5^-$ anions.



Both metalloformate (**II**) and metallocarboxylic acid (**I**) species are significant to a complete discussion of the water-gas shift reaction as catalyzed by metal carbonyls in alkaline solution. Carbon-13 labeling studies (vide supra) have established that the two structural isomers do not interconvert in an *intramolecular* manner. As demonstrated in this report the most prominent intermediate in the WGSR, $HM(CO)_5^-$, can react with a product of this reaction, CO_2, to provide $HCO_2M(CO)_5^-$. Although the concentration of CO_2 should be reduced due to trapping by $OH^- \rightarrow HCO_3^-$, the great facility with which $HM(CO)_5^-$ reacts with CO_2 suggests the latter to be competitive with bicarbonate formation. There are additional routes to formation of the $HCO_2M(CO)_5^-$ anions during catalysis of the WGSR. The reaction of $HM(CO)_5^-$ with a proton source affords H_2 and the unsaturated $[M(CO)_5]$ species which can be scavenged by HCO_2^- (from $OH^- + CO \rightleftharpoons HCO_2^-$) to yield $HCO_2M(CO)_5^-$. This latter derivative can also be obtained from reaction of formate ion with the $[M(CO)_5]$ intermediate resulting from CO dissociation in $M(CO)_5$ at elevated temperatures.[11] We have shown that both chromium and tungsten metalloformates are unstable toward decarboxylation, with the latter, however, being much more resistant and probably inhibitory to H_2 production. In any instance, of the two intermediates capable of affording H_2 and CO_2, the metallocarboxylic acid pathway is energetically more favorable, i.e., the process described in eq 2 was determined to occur under milder reaction conditions than the reversal of reaction 4. Similar observations have been reported for the decarboxylation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2COOH$.[7] These comments are totally consistent with the greater thermodynamic and kinetic stability of metal formates vs. metal carboxylic acid derivatives. Investigations aimed at providing more quantitative definitions of the various energy barriers are in progress.

Acknowledgment. The financial support of this research by the National Science Foundation [Grants CHE 80-09233 (D.J.D.) and CHE 79-23204 (M.Y.D)] is greatly appreciated.

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(6) Doyle, G. *J. Organomet. Chem.* **1975**, *84*, 323.

(7) Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297.

(8) In order to firmly establish the requirement for CO dissociation prior to decarboxylation in saturated metal centers, CO concentration dependence rate studies of decarboxylation are necessary and are under way.

(9) The solid-state structures of the acetatopentacarbonylmetalates of the group 6B metals,[10] as well as that of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$,[7] show the uncoordinated oxygen atom to be located in the direction of the carbonyl ligands. Hence, the initial species depicted in eq 7 would result from a 180° rotation about the metal-bound oxygen atom and formate carbon atom bond. Since this bond has been shown to have multibonding character in the $RCO_2M(CO)_5^-$ species,[10] the rotational barrier is expected to be of significance in these cases.

(10) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398.

(11) King, R. B.; King, A. D., Jr.; Yang, D. B. *ACS Symp. Series*, in press.

Diels-Alder Reactions Involving Cross-Conjugated Dienones. Effects of Substitution on Reactivity

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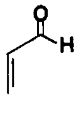
Unsaturated ketones are among the most commonly used dienophiles in Diels-Alder reactions.[1] As a general rule, the dienophilicity of enones is increasingly diminished as (a) the number of alkyl substituents attached to the double bond increases, (b) conformational effects become more severe, and (c) the hindrance afforded by remote substituents increases in the transition state of the reaction. Thus, while acrolein (**1**) is a moderately reactive dienophile, 3-methylcyclohexenone (**2**) fails to undergo Diels-Alder reactions under either thermal or Lewis acid-catalyzed conditions.[2,3]



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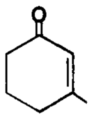

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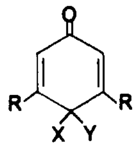

3

In principle, cross-conjugated cyclohexadienones **3** should be more reactive dienophiles than their corresponding cyclohexanone derivatives. Sterically, cyclohexadienones exist as shallow boats and, with the exception of the hindrance provided by the geminal substitution at C-4, are quite accessible to an approaching diene. Electronically, species such as **3** have lower lying LUMO's than their enone counterparts and are therefore predicted to be more reactive in Diels-Alder reactions.[4] For these reasons, we recently undertook a general study which examined the scope and limitations of Diels-Alder reactions involving cross-conjugated dienones. In particular, we have examined (a) the effects of double bond substitution on the reactivity of the dienone and (b) the effects of differential geminal substitution at C-4 with regard to "face selectivity" in Diels-Alder reactions. The preliminary results of our study are reported below.[5]

Formyl dienone **4a**[6] reacts with excess piperylene (**5**) slowly at room temperature and rapidly at 70 °C to yield a single adduct **6a**. Since we were unable to unequivocally assign the stereo-

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† Fellow of the Alfred P. Sloan Foundation, 1980-1984.

(1) (a) Sauer, J. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 211. (b) *Ibid.* **1967**, *6*, 16. (c) Hamer, J. "1,4-Cycloaddition Reactions"; Academic Press: New York, 1967. (d) Seltzer, S. *Adv. Alicycl. Chem.* **1968**, *2*, 1. (e) Opplozer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10.

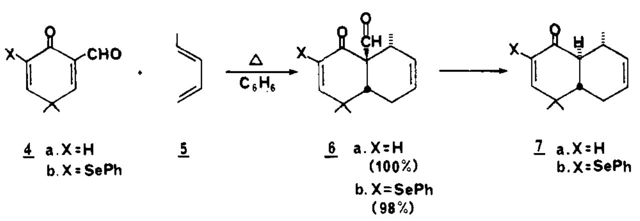
(2) Butz, L. W.; Rytina, A. W. *Org. React.* **1949**, *5*, 136.

(3) The inertness of **2** in Diels-Alder reactions is probably the result of both electronic factors (relatively high-lying LUMO) and steric factors.

(4) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

(5) Satisfactory spectral data and elemental analyses were obtained for all new compounds.

(6) Liotta, D.; Barnum, C.; Puleo, R.; Zima, G.; Bayer, C.; Kezar, H. S. *J. Org. Chem.*, in press.



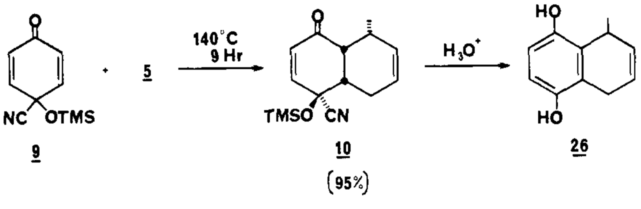
chemistry of **6a** by NMR techniques, we instead determined the X-ray crystal structure of adduct **6b**, produced in the reaction of phenylseleno derivative **4b**[6] with **5** (see Figure 1).[7]

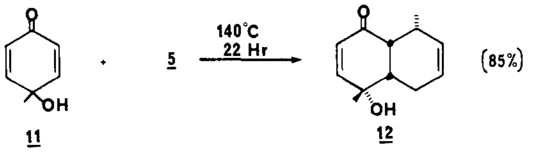
A number of important observations can be made on the basis of these results. First, reaction occurs at the more activated double bonds of **4a** and **4b** to produce the expected "ortho" adducts. Second, only the isomer in which the ortho substituents have a trans relationship is produced. Finally, both adducts **6a** and **6b** are readily deformylated with methanolic base to produce adducts **7a** and **7b**, respectively, in near quantitative yield. Thus, for cyclohexadienones, the formyl group not only serves as a good activating substituent but also one which is easily removed after adduct formation.

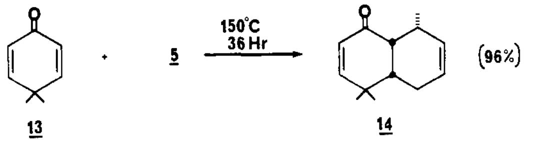
Of the observations made above, the one that is the most suprising is the second one, since the transition state required to produce the trans stereochemistry (Figure 2a) is more- hindered than the one leading to the cis stereochemistry (Figure 2b). However, this apparent anomoly is readily understood in terms of electronic factors. Examination of the LUMO coefficients (Figure 3) of the hypothetical formyl dienone **8** clearly indicates that the transition state depicted in Figure 2a incorporates larger stabilizing secondary orbital interactions than the transition state depicted in Figure 2b.

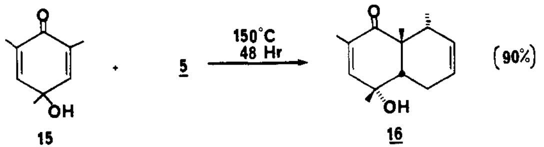
Although Diels-Alder reactions involving dienones possessing different geminal substituents [e.g., **3** ($X \neq Y$)] could form diastereomeric mixtures of adducts, only a single pair of enantiomers is produced in each of the reactions shown below.[8,9] This requires that these Diels-Alder reactions be highly face selective, i.e., the diene preferentially reacts with the dienophile on its less hindered face. Thus, if differences in inductive effects are neglected, the rates of adduct formation should qualitatively be determined by the steric bulk of the smaller of the two geminal sustituents. Consistent with this, increasingly more vigorous reaction conditions are required to obtain complete adduct formation for the series of reactions **9** + **5**, **11** + **5**, and **13** + **5**, respectively.

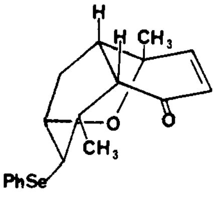
At present, the relative stereochemistry of the geminally substituted center of adduct **10** has been assigned on the basis of the steric model discussed above. Final confirmation of the stereochemistry of this adduct will probably require X-ray crystallographic determination. However, unequivocal chemical evidence for the relative stereochemistries of adducts **12** and **16** has been obtained by demonstrating that these adducts are capable of undergoing intramolecular selenoetherification reactions to form **17** and **18**, respectively.[10,11] Such reactions would be geometrically impossible if adducts **12** and **16** possessed epimeric stereochemistries at the geminally substituted centers.











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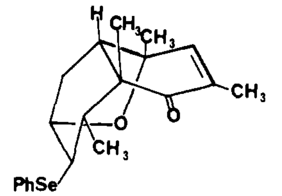
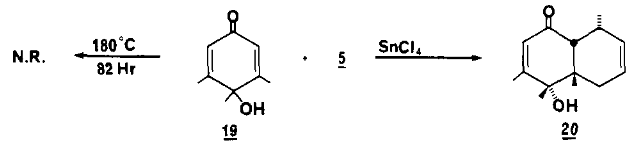
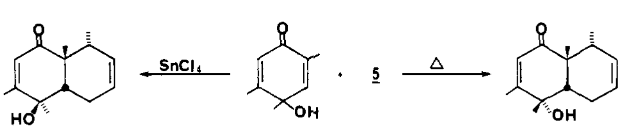


18

Diels-Alder reactions involving 2,6-disubstituted cyclohexadienones (e.g., **15** + **5**) proceed to a substantially slower rate than reactions involving their unsubstituted counterparts. Moreover, methyl substituents in the 3 and 5 positions of a dienone (e.g., **19** + **5**) retard the rate of thermal Diels-Alder reactions to such an extent that no adduct formation is observed even after heating reaction mixtures at elevated temperatures for prolonged periods of time. However, the desired adduct can be produced in 85% yield by allowing a mixture of **19** and **5** to react in the presence of $SnCl_4$ in acetonitrile at room temperature.[12,13]



Finally, we have observed that a complete reversal of face selectivity can be achieved in the reaction of **21** + **5**, depending



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[7] Brooks, L.; Rubin, B. *Acta Crystallogr.*, submitted.

[8] Compounds **9** and **15** were prepared according to the method of Evans. See: Evans, D. A.; Hoffman, J. M.; Truesdale, L. K. *J. Am. Chem. Soc.* **1973**, *95*, 5822. Compound **13** was prepared according to the method of Zimmerman. See: Zimmerman, H. E.; Hackett, P.; Juers, D. F.; McCall, J. M.; Schroder, B. *Ibid.* **1971**, *93*, 3653. Compounds **11**, **17**, **19**, and **21** were prepared according to the method of Fischer. See: Fischer, A.; Henderson, G. N. *Tetrahedron Lett. 1980*, 701.

[9] Although only one enantiomeric pair is observed, we cannot rule out the possibility that trace amounts of the other stereoisomers are produced.

[10] Nicolaou, K. C.; Lysenko, Z. *Tetrahedron Lett.* **1977**, 1257.

[11] PhSeCl alone does not react with unsaturated ketones. See: Zima, G.; Liotta, D. *Synth. Commun.* **1979**, *9*, 697.

[12] For an example of a Lewis acid-catalyzed Diels-Alder reaction involving a *p*-quinone, see: Dickinson, R. A.; Kubela, R.; MacAlpine, G. A.; Stojanac, Z.; Valenta, Z. *Can. J. Chem.* **1972**, *50*, 2377.

[13] Compounds **20** and **22** also undergo intramolecular selenoetherification reactions.

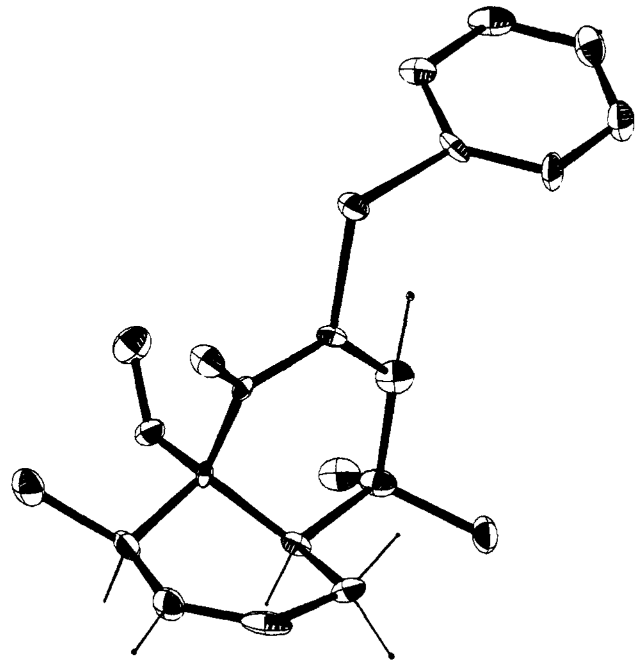


Figure 1. ORTEP representation of **6b**.

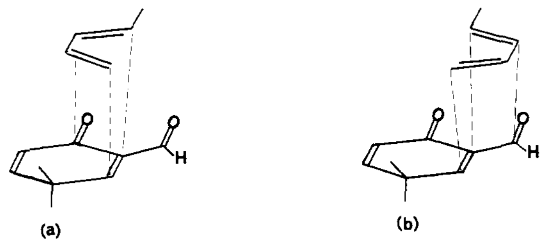
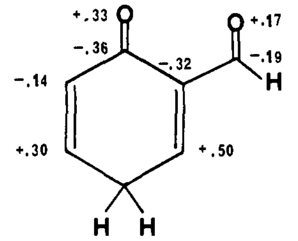


Figure 2. (a) Alder-Stein transtion state for **4a** + **5** involving secondary orbital interactions between the ketone carbonyl carbon and the diene. (b) Alder-Stein transtion state for **4a** + **5** involving secondary orbital interactions between the aldehyde carbonyl carbon and the diene.

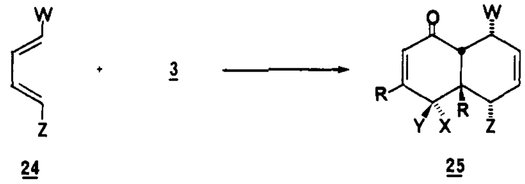


8

Figure 3. LUMO coefficients of **8**, as determined by using MINDO-3 calculations.

upon whether the process is done thermally or under Lewis acid-catalyzed conditions.[13,14] For the catalyzed process the observed diastereoselectivity presumably results from complexation of the hydroxyl group by $SnCl_4$, thereby transforming it into the larger of the two geminal substituents. This does not occur in the catalyzed reaction of **19** with **5** because complexation of the hydroxyl group with the Lewis acid is effectively prohibited by the adjacent methyl substituents.

The implications of these results are quite significant. *Intermolecular Diels-Alder reactions involving cross-conjugaed dienones could in a single reaction produce up to five asymmetric centers with one relative stereochemistry* (illustrated below for the general process **3** + **24** → **25**). Moreover, it may be possible



in selected cases to employ dienones as "enone equivalents" for Diels-Alder reactions which fail because of unreactive enones. Further studies involving the synthetic and mechanistic implications of this work will be the subject of future reports.

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

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[14] When compound **23** is allowed to react with PhSeCl, only products derived from simple addition to the unconjugated double bond are observed. For a discussion of these simple addition processes, see: Liotta, D.; Zima, G. *Tetrahedron Lett.* **1978**, 4977.

A Novel Synthesis of (±)-Cinnamodial

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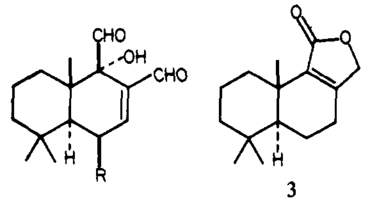
Received January 19, 1981

Cinnamodial (ugandensidial, **1**)[1] and warburganal (**2**), constituents of the genus *Warburgia ugandensis* (Canellaceae),[2] have been shown to possess potent insect antifeedant activity against the African army worm (*spodoptera* species),[3,4] as well as antimicrobial and molluscicidal properties.[3] Current interest in these substances is evidenced by the fact that five syntheses of warburganal have been reported within the past 2 years,[5] and, very recently, one of these[5c] has been extended to a synthesis of cinnamodial.[6] We now wish to describe a total synthesis of (±)-**1** which is different in concept from previous approaches to these sesquiterpene dialdehydes and which affords a convenient entry to related members of the drimane class,[7] including isodrimenin (**3**).



1, R = OAc
2, R = H

3

The plan for introducing the ene-dialdehyde functionality of **1** was based on the assumption that a furan could serve as a latent 1,4-dialdehyde synthon, and the initial phase of the synthesis was therefore directed toward the tricyclic furan **10**. The Diels-Alder adduct **4**[8] of 1-vinyl-2,6,6-trimethylcyclohexene and dimethyl acetylenedicarboxylate was treated with borane-THF, and the

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[1] C. J. W. Brooks and G. H. Draffan, *Tetrahedron*, **25**, 2887 (1969).

[2] I. Kubo, Y.-W. Lee, M. Pettei, F. Pilkiewicz, and K. Nakanishi, *J. Chem. Soc., Chem. Commun.*, 1013 (1976); see also I. Kubo, I. Miura, M. J. Pettei, Y.-W. Lee, F. Pilkiewicz, and K. Nakanishi, *Tetrahedon Lett.*, 4553 (1977).

[3] K. Nakanishi and I. Kubo, *Isr. J. Chem.*, **16**, 28 (1977).

[4] W. C. Ma and I. Kubo, *Entomol. Exp. Appl.*, **22**, 107 (1977).

[5] (a) A. Ohsuka and A. Matsukawa, *Chem. Lett.*, 635 (1979); (b) S. P. Tanis and K. Nakanishi, *J. Am. Chem. Soc.*, **101**, 4398 (1979); (c) T. Nakata, H. Akita, T. Naito, and T. Oishi, *J. Am. Chem. Soc.*, **101**, 4400 (1979); (d) A. S. Kende and T. J. Blacklock, *Tetrahedron Lett.*, 3119 (1980); (e) D. J. Goldsmith and H. S. Kezar, *ibid.*, 3543 (1980).

[6] T. Naito, T. Nakata, H. Akita, and T. Oishi, *Chem. Lett.*, 445 (1980).

[7] C. H. Heathcock in "The Total Synthesis of Natural Products", Vol. 2, J. W. ApSimon, Ed., Wiley-Interscience, New York, 1973, pp 338-353.

[8] J. C. Loperfido, *J. Org. Chem.*, **38**, 399 (1973).

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