phenyls (Figure 1), stereoview of Figure 1 (Figure 2), ORTEP drawing of full asymmetric unit (Figure 3), schematic of atom numbering scheme (Figure 4), interatomic distance and angles (Table 1), structure factor list (Table 2), fractional coordinates (Table 3) (54 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) H. C. Clark and K. E. Hine, *J. Organomet. Chem.*, **105**, C32 (1976); N. C. Rice and J. D. Oliver, *ibid.*, **145**, 121 (1978). (b) B. L. Booth and A. D. Lloyd, *ibid.*, **35**, 195 (1972). (c) D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc. A*, 1765 (1968). (d) See also 3a and references therein.

(2) (a) A. Nakamura and S. Otsuka, *J. Mol. Catal.*, **1**, 285 (1975/6); (b) S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, 245 (1976).

(3) (a) M. Michman and S. Weksler-Nussbaum, *J. Chem. Soc., Perkin Trans. 2*, 872 (1978). (b) J. J. Eisch, R. J. Manfre, and D. A. Konar, *J. Organomet. Chem.*, **159**, C13 (1978). (c) We are sympathetic to (if not a little amused by) a referee's comment concerning the current IUPAC ("*E*/*Z*") rules[3d] for naming alkenes ("define for reader not up on lingo"), but we have felt obligated to utilize this system because it has become accepted for naming organic compounds. In order to minimize confusion, we have used *E*/*Z* nomenclature when referring to the stereochemistry of *compounds*, and cis/trans nomenclature for referring to the stereochemistry of addition *processes* (i.e., cis addition can in principle give either an *E* or *Z* product, depending upon the substituents involved). (d) IUPAC Commission on Nomenclature of Organic Chemistry, *Pure Appl. Chem.*, **45**, 11 (1976).

(4) F. A. Cotton, B. A. Frenz, and D. L. Hunter, *J. Am. Chem. Soc.*, **96**, 4820 (1974).

(5) **1** is air stable as a solid, but rapidly decomposes in solution. It is soluble in aromatic and ether solvents and insoluble in hydrocarbons. All of the reactions of **1** were carried out using standard inert atmosphere techniques in thoroughly dried solvents.

(6) These reactions are first order in **1** and alkyne. Using a mixture of 1 and **1**-d_3 it was possible to determine that k_H/k_D is ~1.2.

(7) The assignment of this doublet of doublets as the *o*-phenyl protons on the β-phenyl remains tentative. This unusual downfield absorption has also been observed in similar complexes containing PCy_3 instead of PPh_3.

(8) Space group $P\bar{1}$; a = 17.892, b = 12.339, c = 16.732 Å; α = 106.27, β = 73.17, γ = 110.77°; Z = 4. The two nickel and two phosphorus atoms were refined anisotropically; the other 80 non-H atoms were refined isotropically; R = 0.082, goodness of fit = 1.54 for all 5258 observed reflections ($2\theta \leq 38°$), R = 0.053 for 3198 reflections ($F_o > 3\sigma(F_o)$). Intensity data were collected on a Syntex $P2_1$ diffractometer with monochromatic Mo Kα radiation using θ–2θ scanning.

(9) **5** was prepared by the method of Yamamoto et al.[15] from $Ni(acac)_2$, PPh_3, and $AlPh_3{\cdot}Et_2O$ (1:1.05:0.33) and purified by extensively washing the crude product with ether: ^1H NMR (C_6H_6) δ 7.55, 7.0 (complex, PPh_3), 6.8 (complex, Ni–Ph), 5.30 (s, 1 H, acac–H), 1.72, 1.40 (s, 3 H each, acac–CH_3).

(10) This reaction proceeds at a rate comparable to the rates of reaction for **1** with PhC≡CPh and PhC≡CCH_3 ($t_{1/2}$ < 10 min at 23 °C).

(11) **1**-d_3 was prepared in the same manner as **1**, using $Al(CD_3)_2OCH_3$. Anal. Calcd for $C_{24}D_3H_{22}O_2NiP$; C, 65.79, H + D, 6.44. Found: C, 66.20, H + D, 6.66.

(12) J_{PH} = 5 Hz in the analogous complex Ni(acac)$(PCy_3)CH_3$, where the phosphine is not as labile (cf. ref 16).

(13) T. Yamamoto, T. Saruyama, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 589 (1976); *J. Am. Chem. Soc.*, **95**, 5073 (1973).

(14) The cis/trans addition ratio of 1.57 (±0.1), obtained in the reaction of **1**-d_3 (0.1 M) with PhC≡CCH_3 (0.1 M) in benzene-d_6 at room temperature, became 1.67 (±0.1) for 0.1 M added PPh_3 and 1.85 (±0.1) for 1.0 M added Ph_3 (both at 60 °C).

(15) K. Maruyama, T. Ito, and A. Yamamoto, *J. Organomet. Chem.*, **155**, 359 (1978).

(16) P. W. Jolly, K. Jonas, C. Krüger, and Y.-H. Tsay, *J. Organomet. Chem.*, **33**, 109 (1971).

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Received March 2, 1979

Electroreduction of Retinal. Formation of Pinacol in the Presence of Malonate Esters

Sir:

Reductive electrodimerization of α,β-unsaturated carbonyl compounds most frequently results in a mixture of dimeric products.[1-10] In contrast, we have accomplished the high-yield electrosynthesis of retinal pinacol (III) from the one-electron reduction of retinal (I) in acetonitrile. This electrosynthesis is successful only in the presence of carbon acids such as diethyl malonate (II); electrodimerization of retinal in solutions containing water, phenol, or acetic acid leads to a mixture of less-conjugated dimeric products. Thus, the use of malonate esters as proton donors demonstrates a new method for directing the pathway of electrodimerization. Procedures for coupling unsaturated carbonyl compounds are of particular significance—in the case of retinal, pinacolization provides a useful synthetic route to the C_{40} carotenoids.

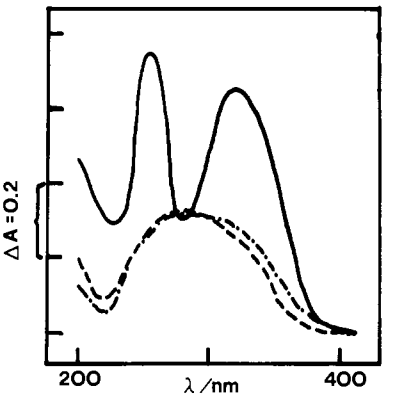

Figure 1. Spectra of dimeric products resulting from electrolysis of 2.05 mM retinal at the first reduction wave in the presence of different proton donors in an OTTLC. All solutions were 0.5 M TBAP in acetonitrile. Proton donor concentrations follow: (– · –) 1000-fold excess water; (– – –) 2-fold excess acetic acid; (—) 5-fold excess diethyl malonate.

High yield of the "head-to-head" coupling products can be obtained by chemical reduction of retinal with a zinc amalgam to form pinacol[11] or by reduction with a $LiAlH_4$–$TiCl_3$ reagent to form β-carotene.[12] However, previous electrochemical attempts to synthesize pinacols from retinal[9] and related compounds[7,8] have been markedly unsuccessful. Electroreduction of retinal in acetonitrile with tetra-*n*-butylammonium acetate yields 11% pinacol.[9] Electrochemical reduction of 3-methylcrotonaldehyde in pH 5.00 acetate buffer results in a pinacol yield of 10%.[7] Similar quantities of pinacol are obtained in the reduction of geranial and farnesal in aqueous, micelle, or ethanolic solutions.[8] Electroreductive pinacol formation has been achieved only when the β position is totally blocked (e.g., acetophenone[13]) or, in some cases, if there is steric hindrance at the β position (e.g., 71% yield of pinacol by electrodimerization of β-ionone[9]). Our unique electrochemical route for pinacolization of retinal demonstrates that judicious selection of proton donor results in high yield of the desired product in a rapid, one-step synthesis.

Using cyclic voltammetry with a hanging mercury drop electrode, as well as spectroelectrochemistry, we have examined the electrochemical behavior of retinal in acetonitrile with tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte.[14] Spectroelectrochemistry was performed with an optically transparent thin-layer cell (OTTLC) containing a gold minigrid working electrode.[14] Retinal (λ_{max} 375 nm) is reduced to the radical anion (λ_{max} 515 nm ($E_{p/2}$ −1.33 V)) in a quasi-reversible, one-electron process. With equal amounts of diethyl malonate and retinal, the latter undergoes an irreversible, one-electron reduction and the absorption spectrum after electrolysis shows peaks at 325 and 260 nm (Figure 1). The absorbance at 325 nm corresponds to that for retinal pinacol in 89% yield.[11] The peak at 260 nm is ascribed to the diethyl malonate anion (IV); a mixture of diethyl malonate and tetraethylammonium hydroxide in acetonitrile-TBAP has the same absorption maximum. Consumption of 1 mol of protons/mol of retinal reduced is confirmed by the appearance of a one-electron wave for oxidation of diethyl malonate anion that is equal in height to the reduction wave for retinal. The

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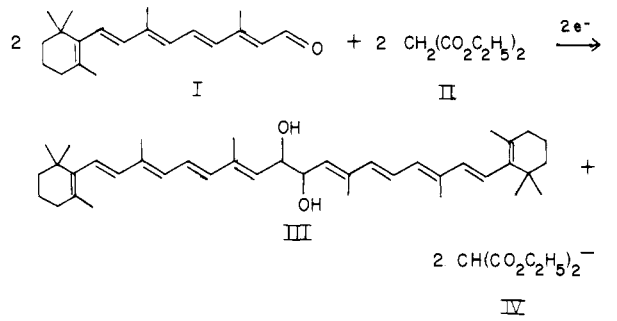
Scheme I



stoichiometry, electrochemistry, and spectral data are consistent with the formation of retinal pinacol (Scheme I). Pinacol formation is also achieved in the one-electron reduction of retinal in the presence of 100-fold molar excess of diethyl ethylmalonate.

Spectroelectrochemistry shows that the pinacol is but a minor product of reduction of retinal in the presence of added water, phenol, or acetic acid. This is evidenced by the absence of an absorption maximum at 325 nm in the product spectra (Figure 1). A mixture of dimeric products is formed which are not electroactive. As previously discussed, this is the expected result for electrodimerization of α,β-unsaturated compounds.

We have isolated and characterized the pinacol following bulk electrolysis of retinal in the presence of diethyl malonate. In these experiments, retinal (0.05 g) in acetonitrile with 0.1 M TBAP was reduced at a mercury pool cathode with a silver wire quasi-reference electrode and an isolated platinum auxiliary electrode. Electrolysis in the presence of a 10-fold molar excess of diethyl malonate at a potential 100 mV cathodic to the first observed half-wave potential consumes 1.09 ± 0.14 electrons/mol. A UV spectrum of the electrolysis products before extraction indicated the presence of 85% pinacol by weight. The products were extracted into ether, dried, and separated by thin-layer chromatography (TLC) using the method of Fung et al.;[16] butylated hydroxytoluene served as an antioxidant except for the spectral studies. The spectral data are all in direct agreement with that expected for retinal pinacol.[17] Isolated yield of the pinacol was 50% of the starting material. This yield reflects losses of the pinacol during TLC due to the sensitivity of retinal compounds to light and air oxidation.[18] Other identified products (which were present in <5% yield) include retinol, β-carotene, and retinal from incomplete electrolysis.

These results demonstrate that diethyl malonate and diethyl ethylmalonate work in a unique manner to foster electrodimerization of retinal at the carbonyl carbon. It can be concluded from our data that acid strength of the proton donor is not the predominant effect: water, a weak acid in acetonitrile, and acetic acid, which is a much stronger acid than diethyl malonate, both produce the same mixture of dimers with very little pinacol. A detailed study of the directed coupling is required to elucidate the reaction mechanism. We have observed the radical anion of retinal by cyclic voltammetry at 0.5 V/s under conditions where exhaustive electrolysis yields the pinacol, which infers that malonate esters form a weak complex with the radical anion and thus direct the coupling reaction toward pinacol formation. This report of preferential dimerization at the carbonyl carbon upon electroreduction of retinal is the first instance of selective pinacol formation by electrochemical means; whether malonate esters or different carbon acids promote pinacol formation with other α,β-unsaturated aldehydes will be the subject of future research.

Acknowledgment. The support of this study by the Research Corporation and Indiana University is gratefully recognized. Helpful discussions with G. P. Lahm and M. M. Baizer are also acknowledged.

References and Notes

(1) Baizer, M. M. In "Organic Electrochemistry, An Introduction and Guide"; M. M. Baizer, Ed.; Marcel Dekker: New York, 1973, pp 399–411.
(2) Evans, D. H. *Acc. Chem. Res.* **1977,** *10,* 313–319.
(3) Wiemann, J.; Bouguerra, M. L. *Ann. Chim. (Paris)* **1968,** *3,* 215–218.
(4) Wiemann, J; Sa-Le-Thi-Thuan; Lelandais, D.; Dedieu, M. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1969,** *269,* 30–33.
(5) Lamy, E; Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* **1973,** *42,* 189–221.
(6) Wawzonek, S.; Gundersen, A. *J. Electrochem. Soc.* **1964,** *111,* 324–328.
(7) Miller, D.; Mandell, L.; Day, R. A., Jr. *J. Org. Chem.* **1971,** *36,* 1683–1685.
(8) Johnston, J. C.; Faulkner, J. D.; Mandell, L.; Day, R. A., Jr. *J. Org. Chem.* **1976,** *41,* 2611–2614.
(9) Sioda, R. E.; Terem, B.; Utley, J. H. P.; Weedon, B. C. L. *J. Chem. Soc., Perkin Trans. 1* **1976,** 561–563.
(10) Rifi, M. R. In "Technique of Electroorganic Synthesis", Part II; Weinberg, N. L., Ed.; Wiley-Interscience: New York, 1975, pp 83–136.
(11) Reedy, A. J. British Patent 1 097 497, 1968.
(12) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974,** *96,* 4708–4709.
(13) Bewick, A.; Brown, D. J. *J. Chem. Soc., Perkin Trans. 2* **1977,** 99–102.
(14) For previous studies of the electrochemistry of retinal see: (a) Park, S.-M. *J. Electrochem. Soc.* **1978,** *125,* 216–222. (b) Mairanovskii, V. G.; Samokhvalov, G. I. *Electrokhimiya* **1966,** *2,* 62–68. (c) Powell, L. A.; Wightman, R. M., submitted for publication to *J. Electroanal. Chem.*
(15) (a) Murray, R. W.; Heineman, W. R.; O'Dom, G. W. *Anal. Chem.* **1967,** *39,* 1666–1668. (b) Heineman, W. R. *ibid.* **1978,** *50,* 390A–400A.
(16) Fung, Y. K.; Rahwan, R. G.; Sams, R. A. *J. Chromatogr.* **1978,** *147,* 528–531.
(17) Spectral analysis gives the following results: UV–visible λ_{max} 325 nm; mass spectrum *m/e* 570 (M^+), 552 (M^+-H_2O), 285 (symmetric cleavage); IR ($CHCl_3$) 3680, 3620, 1050 cm^{-1}. In the NMR spectrum, the appearance of two doublets each for the protons on C-14 (δ 4.36 (J = 7.2 Hz), 4.55 (J = 8.0 Hz)) and C-15 (δ 5.40 (J = 7.2 Hz), 5.50 (J = 8.0 Hz)) is due to the meso and (±) isomers of the pinacol. Though the remainder of the NMR spectrum for the pinacol also shows splitting of peaks due to diastereomers, it is similar to the spectrum of retinol. (See Planta, C. v.; Schwieter, U.; Chopard-dit-Jean, L.; Rüegg, R.; Kofler, M.; Isler, O. *Helv. Chim. Acta* **1962,** *45,* 548–561.)
(18) Lerner, D.-A.; Mani, J.-C.; Mousseron-Canet, M. *Bull. Soc. Chim. Fr.* **1970,** 1968–1974.

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New Synthetic Methods. Allylic Alkylation of Enol Thioethers

Sir:

To date, enol thioethers represent the least useful class of enol derivatives. Except for their hydrolysis to carbonyl partners or reduction to olefins, their synthetic applications have been almost ignored. The fact that they are as readily available from ketones[1] as enamines, enol acetates, or enol silyl ethers, as well as available directly by addition of sulfur-stabilized anions to carbonyl groups,[2] isomerization of allyl phenyl sulfides,[3a] various methods of sulfenylation of olefin systems,[3b] rearrangement of 1-phenylthio-1-vinylcyclopropanes,[4] metalation and alkylation of phenyl vinyl sulfide,[5] oxidative decarboxylation of α-thioacids,[6] etc., enhances interest in their elaboration as basic building blocks. The use of the aforementioned enol derivatives has focused on their ability to increase the nucleophilicity of the double bond. We wish to report that a new type of reactivity for enol derivatives is accessible via enol thioethers—nucleophilic alkylation at the allylic position which constitutes an equivalent of an enolonium ion.[7] Furthermore, combined with emerging new methods for direct elaboration of enol thioethers, this method becomes a potentially powerful approach in synthesis. Equation 1 outlines the sequence.

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