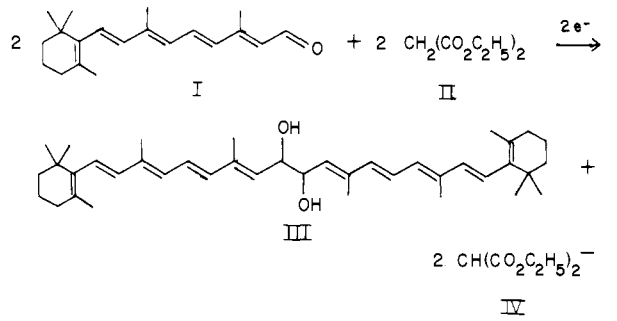
Scheme I



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.

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(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.)
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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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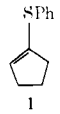
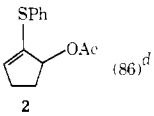
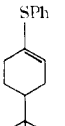
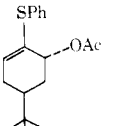
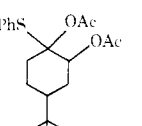
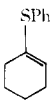
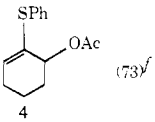
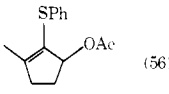
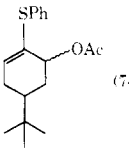
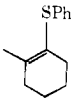
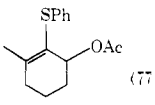
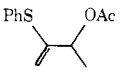
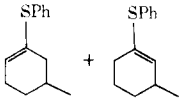
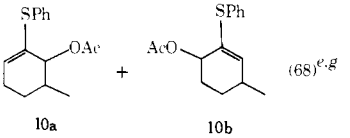
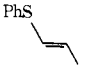
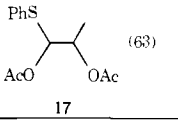
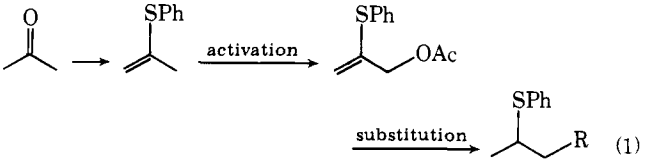
Table I. Allylic Acetoxylation of Vinyl Sulfides[a]

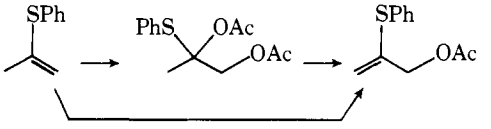
vinyl sulfide	product (% yield)[b,c]	vinyl sulfide	product (% yield)[b,c]
 1	 2 (86)[d]	 11	 12a (42)  13 (37)
 3	 4 (73)[f]		
 5	 6 (56)	11	 (74)[h]
 7	 8 (77)[g,i]	 14	 15 (17)[i]
 9a 9b	 10a 10b (68)[e,g]	 16	 17 (63)

[a] All reactions were run in THF at 0 °C (~1 h) to room temp (~4 h) with 1.1 equiv of $Pb(OAc)_4$ per equiv of sulfide. [b] Yields are for pure compound isolated by chromatography. [c] Products have been characterized spectroscopically and for elemental composition. [d] Yield of distilled product. [e] These products have been characterized spectroscopically only. [f] The crude reaction mixture was treated with boron trifluoride etherate in benzene prior to isolation. [g] The crude reaction mixture was treated with 5 M KOH and ether as a two-phase system. [h] The yield of allylic acetate **12** obtained from initial reaction plus that of **12** from treatment of the diacetate **13** with boron trifluoride or 5 M KOH/ether. E/Z = 1/2. [i] Reaction of 12–13 h at room temperature.

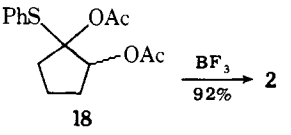


(1)

The key to the sequence is the ability to selectively activate the allylic position of a vinyl sulfide. Surprisingly,[8] lead tetraacetate effects such a transformation cleanly at room temperature or below in THF as summarized in eq 2 and Table I.[9]


(2)

Oxidation of sulfur is not observed. As implied in eq 2, the reaction appears to proceed at least in part through bis-acetoxylation followed by elimination. In the case of the six-membered ring compounds **3, 7, 9,** and **11,** the initial reaction mixture consisted of the 1,2-bis(acetate) (cf. **13**) in addition to the allyl acetate. For synthesis of the desired allylic acetate, the reaction mixture was worked up by treatment with either BF_3-ether or 5 N KOH-ether (with only a trace of concomitant hydrolysis). In the case of **11,** the diacetate **13** was isolated as a stereoisomeric mixture as indicated by four acetate (δ 1.88, 1.90, 1.93, 1.96) signals in almost equal intensity which was independently converted to a stereoisomeric mixture of allyl acetates **12** in contrast to isolation of only **12a** in the initial oxidation. Switching the solvent to methylene chloride enhances bisacetoxylation at the expense of allylic acetate formation. For example, treatment of 1-phenylthiocyclopentene (**1**) with lead tetraacetate in methylene chloride (1 h at 0 °C, 4 h at room temp) produces only a 10% isolated yield of **2** and a 60% isolated yield of **18** (mainly one isomer). The latter again



18

produces an excellent yield of allylic acetate upon treatment with boron trifluoride etherate at room temperature.

The enhanced selectivity and acceleration of the reaction of a double bond by sulfur is at first glance quite surprising. A rationale invokes initial complexation of lead tetraacetate with sulfur, e.g., **19.** Nucleophilic addition of acetate produces

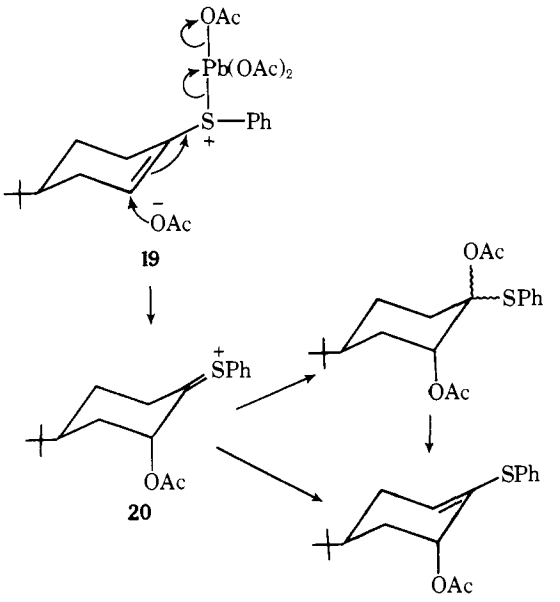
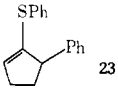
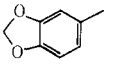
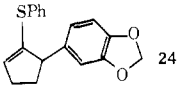
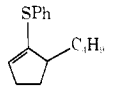
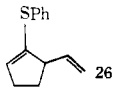
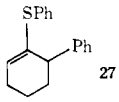
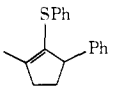
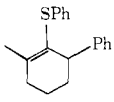
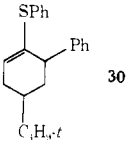
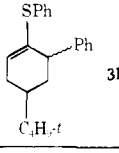
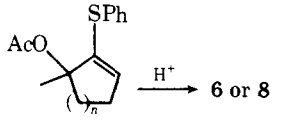


Table II. Coupling of Allylic Acetate with Organocuprates[a]

allylic acetate	R in R_2CuLi	temp, °C	product	% yield[b]
2	Ph	0	 **23**	86
2		−30	 **24**	72
2	*n*-C_4H_9	−50	 **25**	89
2	$CH{=}CH_2$	−78	 **26**	76
4	Ph	0	 **27**	85
6	Ph	0	 **28**	73
8	Ph	0	 **29**	77
12a	Ph	0	 **30**	71
12[c]	Ph	0	 **31**[d]	68

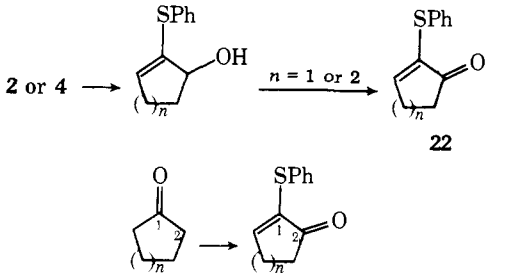
[a] The organocuprate was prepared by reacting 2 equiv of the organolithium with 1 equiv of recrystallized cuprous iodide or dimethyl sulfide-cuprous bromide in THF at −78 to 0 °C. Coupling was achieved by reacting 1 mmol of allylic acetate with 1.0 mmol of dialkylcuprate. [b] All yields are for isolated pure product. New compounds have been characterized spectroscopically and satisfactory elemental compositions determined. [c] *E*/*Z* = 1/2. [d] *E*/*Z* = 2/1.

the thionium ion **20** which can partition between deprotonation and capture by acetate. The conversion of **19** to **20** can be compared to the methanolysis of methoxyphenylvinylsulfonium fluoroborate to 1,2-dimethoxyethyl phenyl sulfide.[10] The isolation of only the *E* isomer **12a** in the initial oxidation which involves axial attack of acetate on **19** from **11** supports the above. This stereochemistry for **12a** is clearly indicated by the presence of an unresolved multiplet at δ 5.24 ($W_{1/2}$ = 7 Hz) indicative of an equatorial hydrogen for the methine proton geminal to acetoxy, whereas the *Z* isomer shows this proton at δ 5.42 ($W_{1/2}$ = 30 Hz) indicative of an axial hydrogen. The formation of only the tetrasubstituted olefins **6** and **8** would imply isomerization of the kinetically formed acetate **21** to the thermodynamically more stable product.[11]



21

The utility of this high-yield acetoxylation can be illustrated by the further transformations of the products. For example, hydrolysis of the acetate (K_2CO_3, CH_3OH, H_2O, room temp) followed by oxidation (PCC or preferably MnO_2, $CHCl_3$) gives the sulfenylated enones **22** which have proven to be valuable building blocks.[12] As illustrated in eq 3, the sequence becomes

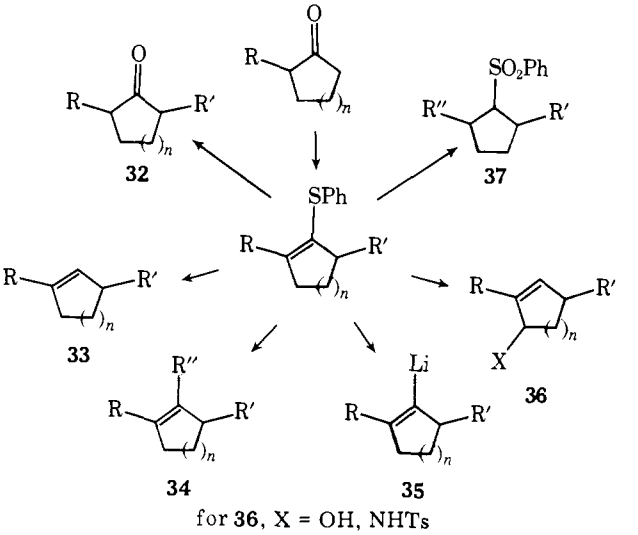


(3)

a 1,2-carbonyl transposition with incorporation of a reactive Michael acceptor system.

More significant is the coupling with cuprates as outlined in Table II. While alkyl cuprates behave normally, attention was focused on aryl and vinyl cuprates. In each case, coupling was excellent. As shown for **6** and **8** going to **28** and **29**, respectively, regioselectivity is complete and the reaction proceeds with inversion of stereochemistry (**12a** → **30**) as expected.[13] Since the products retain the enol thioether linkage, taking advantage of its use as a regiocontrolled enol derivative is possible. Hydrolysis to the ketone[14] **32** represents the overall use of a ketone as an enolonium ion equivalent. Desulfurization to **33** represents a regiocontrolled 1,3-disubstituted olefin synthesis. Some additional aspects of the potential of enol thioethers has only recently been probed. A phenylthio group has been replaced by an allyl or aryl group via organonickel chemistry (→**34**),[15] and transmetalation reactions have been noted (→**35**).[16] Conversion of the enol thioether into the corresponding sulfoxide or sulfilimine followed by double bond isomerization to the allyl derivative and sigmatropic rearrangement creates an allylic alcohol or amine **36**.[1a] Oxidation of the sulfide to the sulfone with 2 equiv of MCPBA proceeds cleanly and can be followed by nucleophilic addition of organometallic reagents (→**37**).[17] Combined with the present allylic alkylation, these methods highlight the flexibility of enol thioether as shown in Chart I.

Chart I



for **36**, X = OH, NHTs

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sulfide by treatment with thiophenol and dry HCl, oxidation with 1 equiv of MCPBA at 0 °C to room temp, and refluxing in $CHCl_3$, $PhCH_3$, or xylene. Also see Deljai, A.; Stefanac, Z.; Balenovic, K. *Tetrahedron Suppl., No. 8*, **1966**, 33. (d) Mukaiyama, T.; Saigo, K. *Chem. Lett.* **1973**, 479. (e) Boonstra, H. J.; Brandsma, L.; Wiegman, A. M.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 252, and earlier references therein. (f) From α-sulfenylated carbonyl partners; see ref 3a. Also see: Nakai, T.; Mimura, T. *Tetrahedron Lett.* **1979**, 531. Kano, S.; Yokomatsu, T.; Ono, T.; Hibino, S., Shibuya, S. *J. Chem. Soc., Chem. Commun.* **1978**, 414.
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(9) Typically the IR spectra of the allylic acetates show absorptions at 1740, 1585, 1480 cm^{-1} for the acetate and phenylthio groups. The NMR spectra show the protons for the acetate methyl group, acetoxy methine, and vinyl protons at δ 1.85 ± 0.05, 5.56 ± 0.40, and 6.05 ± 0.30.
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Mechanism of the Oxidation of Alkanes with Nitronium Tetrafluoroborate in Acetonitrile. Evidence for a Carbenium Ion Intermediate

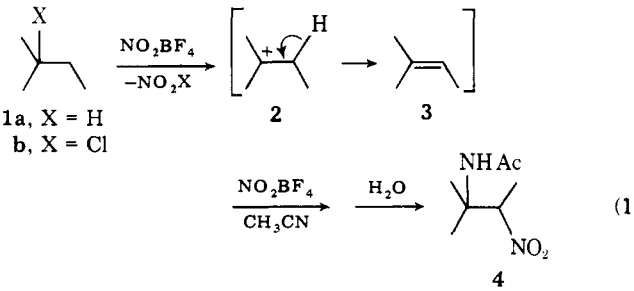
Sir:

It is becoming increasingly evident that electrophilic attack at a carbon σ bond is an important reaction despite the low reactivity often associated with completely saturated molecules. Since σ-bond cleavage via this type of mechanism has only recently been noted,[1] the scope and utility of this class of reactions remain to be defined. Protolytic reactions of alkanes by superacids,[2] nitration by nitronium salts,[3] Lewis acid catalyzed halogenation by elementary halogen,[4] hydroxylation with dry ozone,[5a] and oxyfunctionalization with ozone and hydrogen peroxide in superacid media[5b] are among the more interesting transformations involving σ bonds that have been reported to date.

Early efforts to oxidatively functionalize hydrocarbons frequently utilized the nitrogen oxides. Both solution and gas-phase chemistry at high temperatures often favored free-radical reactions.[6] At lower temperatures, heterolytic σ-bond cleavages are observed with NO_2PF_6 in methylene chloride–sulfolane solvent.[3] For example, the oxidation of ethane afforded both nitroethane and nitromethane, while adamantane afforded nitroadamantane in about 10% yield. In general, the heterolytic cleavage of carbon–hydrogen and other σ bonds requires a highly reactive electrophile, which is commonly generated in situ under harsh conditions. As a consequence, yields are often low and complex mixtures of products common.

We recently demonstrated that the reaction of alkyl halides and alkyl ethers with NO_2BF_4 in acetonitrile resulted in efficient abstraction of halide or alkoxide ion and formation of a nitrilium ion, which afforded the corresponding acetamide upon hydrolysis.[7a] Mechanistic studies[7b] with optically active *exo*- and *endo*-2-bromonorbornane provided convincing evidence that the reaction of NO_2^+ with the nonbonding electron pairs of the halogen forms a nitronium complex that effects heterolysis of the C–X bond. In the present study, we provide conclusive evidence that a related mechanism is operating in alkane oxidation. The reaction of selected hydrocarbons with NO_2BF_2 results in a formal hydride ion abstraction, leading to the formation of transient carbenium ion intermediates.

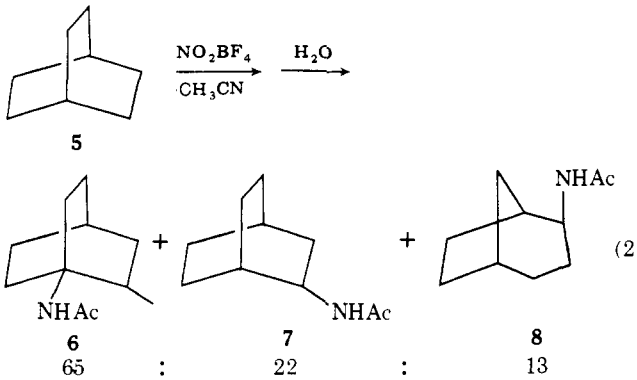
We have noted that tertiary alkyl halides frequently afforded highly substituted thermodynamically stable alkenes as intermediates upon reaction with NO_2BF_4. This observation prompted a comparative study between halide and hydride abstraction. A common carbenium ion (**2**) is implicated in the oxidation of 2-methylbutane (**1a**) and 2-chloro-2-methylbutane (**1b**). *Both* compounds afforded 2-acetamido-2-methyl-3-nitrobutane (**4**) (55%) as the major product. The vicinal nitroacetamide **4** was identical in every respect with the product obtained from the electrophilic addition of NO_2BF_4 to trimethylethylene (**3**) in acetonitrile.[8] The reaction sequence given in eq 1, involving alkene formation from a cationic



(1)

species, provides a rational explanation for these observations. These data cannot exclude a concerted elimination from a complex consisting of **1b** and NO_2^+. Significantly, the results do strongly suggest that parallel mechanisms are operating in both alkane[9] and alkyl halide oxidation.

A second mechanistic probe utilized bicyclo[2.2.2]octane (**5**), where cation generation of C-2 would lead to rearranged products. Treatment of **5** with NO_2BF_4 in acetonitrile (16 h) afforded acetamides **6**, **7**, and **8** in an overall isolated yield of 73% (eq 2).[10] The ratio of **7**:**8** is informative in that the sol-



(2)

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