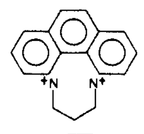
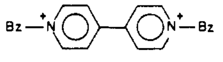
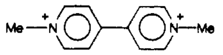
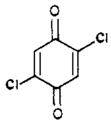
Table I. Electron-Transfer Rate Constants for Reduction of Electron Acceptors, A, by Photogenerated $Pd(CNMe)_3{}^{\bullet +}$ Radicals

A		$E°(A/A^{\bullet -})$ vs. SCE, V	k_e, M^{-1} s^{-1}
	(PPQ^{2+})	−0.13	2×10^8
	(BV^{2+})	−0.36	1×10^8
	(MV^{2+})	−0.45	3×10^7
	(DCBQ)	−0.18	3×10^7

by $\epsilon_{405} = 50\,000$ M^{-1} cm^{-1}, and recombination of $Pd(CNMe)_3{}^{\bullet +}$ to give **1** occurs with a rate constant, $k_r = 1 \times 10^9$ M^{-1} s^{-1}. The rate of $Pd(CNMe)_3{}^{\bullet +}$ recombination thus approaches, within an order of magnitude, the diffusion-controlled limit in acetonitrile solution.[12] The rate of $Pd(CNMe)_3{}^{\bullet +}$ recombination is essentially unaffected by solvent and shows similar rates in MeCN and CH_2Cl_2 solutions.

A significant finding of this study is that the absorbance of the d^9 $Pd(CNMe)_3{}^+$ radical is both more intense and significantly red-shifted compared to either the σ–σ^* excitation of **1** or to the MLCT band of d^8 $M(CNMe)_3(acetonitrile)^{2+}$ photoproduct.[9,13] We assign the unusually intense transient absorbance of the $Pd(CNMe)_3{}^+$ radical to an allowed d → p electronic transition. A rather similar conclusion was recently reached in the case of related d^{10} Pd(0) phosphine complexes.[14]

In the presence of electron acceptors, A (A = methylviologen (MV^{2+}), benzylviologen (BV^{2+}), *N,N′*-propylenephenanthrolinium (PPQ^{2+}), dichlorobenzoquinone (DCBQ)), photogenerated $Pd(CNMe)_3{}^+$ radicals engage in rapid electron-tranfer reactions. Flash photolysis of a 1.0×10^{-4} M acetonitrile solution of **1** in the presence of benzylviologen (BV^{2+}) leads to the synchronous first-order disappearance of $Pd(CNMe)_3{}^{\bullet +}$ and appearance of $BV^{\bullet +}$. The kinetically coupled disappearance of $Pd(CNMe)_3{}^{\bullet +}$ and appearance of $BV^{\bullet +}$ clearly imply that $Pd(CNMe)_3{}^+$ radicals participate in the electron-transfer process. The rates for electron transfers from $Pd(CNMe)_3{}^+$ radicals are quite rapid. The electron transfer rate, k_e, to BV^{2+} has been determined to be 1×10^8 M^{-1} s^{-1}. The metal-containing product in these reactions is the solvated, d^8 mononuclear complex $[Pd(CNMe)_3(NCMe)]^{2+}$. Table I summarizes the rate constants for reduction of several electron acceptors, PPQ^{2+}, BV^{2+}, MV^{2+}, and DCBQ, by photogenerated $Pd(CNMe)_3{}^+$ radicals. All electron-transfer rate constants, k_e, were determined by pseudo-first-order kinetics at several concentrations of the electron acceptor, A. For the three substituted viologens, rate constants show an expected decrease from 2×10^8 (PPQ^{2+}) to 3×10^7 M^{-1} s^{-1} (MV^{2+}) as the driving force for electron transfer decreases from $E°(PPQ^{2+/\bullet +}) = -0.13$ V to $E°(MV^{2+/\bullet +}) = -0.45$ V vs. SCE. Whether the acetonitrile solvent associates with the $Pd(CNMe)_3{}^{n+}$ fragment prior or subsequent to the electron-transfer event will be investigated in future studies. The rather potent reducing ability and rapid electron-transfer kinetics of the photogenerated $Pd(CNMe)_3{}^+$ radicals make them attractive candidates for other mediated photoreductions. Recently, photogenerated organometallic radicals have found application in the highly quantum efficient photodeposition of metal films for "laser writing" onto insulating and semiconducting supports.[15]

Acknowledgment. We thank NASA (NAG-3-586) and NSF (CHE84-11836) for support. We are particularly indebted to Dr. Guillermo Ferraudi of the Radiation Laboratory, University of Notre Dame, and Professor George McLendon of the University of Rochester for assistance, advice, and patience in collecting flash photolysis data.

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(12) The diffusion-limited rates for $Pd(CNMe)_3{}^+$ recombination are calculated to be $k_D = 1.1 \times 10^{10}$ M^{-1} s^{-1} (CH_3CN, 25 °C) and $k_D = 1.4 \times 10^9$ M^{-1} s^{-1} CH_2Cl_2, 25 °C). These values are obtained from the Smoluchowski and Stokes–Einstein equations, corrected for interionic repulsion,

$$k_D = \frac{8RT}{3\eta}\left(\frac{\delta}{e^{\delta} - 1}\right)$$

where $\delta = Z_A Z_B e^2/4\pi\epsilon kTd_{AB}$. See, for example: Wilkinson, F. *Chem. Kinetics and Reaction Mechanisms*; Van Nostrand Reinhold: New York, 1980.

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Stereocontrolled [*m* + *n*] Annulation Reactions. A [3 + 2] Cycloaddition of 3-Iodo-2-[(trimethylsilyl)methyl]propene onto 1,2-Diones

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The Diels–Alder reaction represents the most efficient means yet devised for the construction of six-membered carbocyclic rings.[2] The unprecedented stereochemical control achievable at multiple stereocenters, combined with predictable regiochemical control and a high degree of chemoselectivity, has made this process one of unparalleled utility in organic synthesis. The obvious need to extend equally efficient cycloaddition strategies to the construction of five-membered carbocyclic ring systems has led to many elegant studies of [3 + 2] annulation processes.[3] Perhaps the most widely utilized strategy in this regard is one in which dipolar synthons are utilized in conjunction with electron-deficient olefins to achieve net [3 + 2] annulation.[3,4]

Although some notable exceptions do exist,[3,5] these and other approaches often do not address the important problem of stereoselectivity in generation of functionalized cyclopentanoids via [3 + 2] annulation strategies. In an effort to develop general [*m* + *n*] approaches to carbocyclic ring systems that lead to stereocontrolled syntheses of five-, six-, and seven-membered rings, we considered the advantages of utilizing dianionic synthons[6] along with various dielectrophilic partners. Utilizing this conceptually novel approach to annulations, one is not necessarily constrained to generation of a single ring size. Furthermore, we perceived that significant stereochemical control could be achieved through intramolecular chelation control[7] by appropriate choice of a latent

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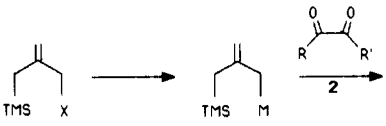
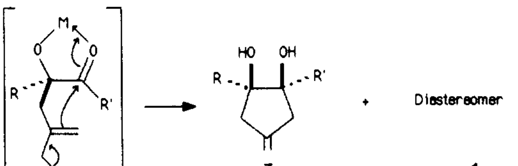
nucleophile in the dianionic synthon. Herein we report our initial efforts in this area, describing a successful stereocontrolled [3 + 2] annulation approach to cyclopentanoids utilizing 3-halo-2-[(trimethylsilyl)methyl]propenes (**1**) as dianionic synthons[8] and 1,2-diones (**2**) as the dielectrophilic partners.

Having chosen suitable partners for the cycloaddition process, several potential problems had to be addressed. First, a successful process required clean conversion of the allylic halide into an allylic organometallic, avoiding extensive Wurtz coupling. The allylic organometallic thus generated had to react chemoselectively with 1,2-diones to generate intermediate ketolates, avoiding overreaction leading to acyclic diallylated diols. Finally, we sought organometallics whose metal alkoxide would activate the carbonyl of intermediate ketolates toward addition by the latent nucleophile (allylsilane) and, in addition, *control the stereochemistry of the addition through intramolecular chelation control.*



1a X= Br
1b X= I



3 **4**

Initial efforts focused on use of Zn as a reductant.[9] Unfortunately, the Zn^{2+} generated was apparently not a strong enough Lewis acid to induce cyclization,[10] and addition of Bu_4NF (0.2 equiv) was required to effect cyclization in a one-pot conversion.

$$\mathbf{1a} + \underset{R,R' = CH_3}{\mathbf{2}} \xrightarrow[\substack{3.\ H_3O^+ \\ 78\%}]{\substack{1.\ Zn/THF \\ 2.\ Bu_4NF}} \mathbf{3}$$

Desiring a more efficient process, SnF_2 was employed to generate an allylstannane in the first step of the reaction.[11] This particular reagent has two inherent advantages. The first is that the Sn^{4+} species generated is a much stronger Lewis acid than the corresponding Zn^{2+} species. As a consequence, the electrophilicity of the complexed carbonyl in the intermediate ketolate[12] was expected to be greatly enhanced. Furthermore, the presence of fluoride ion was predicted to increase the nucleophilicity of the allylsilane.[13] With these factors working in concert, an efficient annulation process was anticipated. In fact, a number of 1,2-diones undergo clean [3 + 2] annulation in a highly stereoselective fashion, providing the corresponding 1,2-diols (Table I).[14] None of the intermediate ketols could be detected in the reaction mixtures at any time, indicating a rapid two-step sequence leading to product.

Table I. [3 + 2] Cycloaddition of 3-Iodo-2-[(trimethylsilyl)methyl]propene (**1b**) onto 1,2-Diones **2** Using Stannous Fluoride

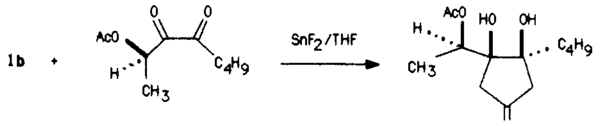
1,2-dione		% isolated yield (GC)	diastereo-selectivity[a]
R	R'		
CH_3	CH_3	72 (85)	>75:1
CH_3	CH_3CH_2	88	>32:1
CH_3	C_6H_5	72	>28:1
$CH_3(CH_2)_2$	$CH_3(CH_2)_2$	68	>25:1
$CH_3(CH_2)_3$	$Cl(CH_2)_4$	73	>50:1
$-(CH_2)_4-$		41	*b*
CH_3	$(CH_3)_2CH$	24	*b*
Ph	Ph	0[c]	

[a] These are minimum diastereoselectivities, reflecting the ratio of desired product **3** to the next most abundant product in the crude reaction mixture as determined by capillary gas chromatography. [b] A single diastereomer was formed. [c] Use of the Zn/fluoride procedure did not improve the yield.

$$\mathbf{1b} + \mathbf{2} \xrightarrow[\text{room temperature}]{SnF_2/THF} \mathbf{3}$$

The reaction appears to be sensitive to steric effects and perhaps to the propensity for 1,2-diones to exist in the monoenolic form (in particular 1,2-cyclohexanedione and perhaps 4-methyl-2,3-pentanedione under the reaction conditions).[15]

Excellent stereochemical control can be achieved at three contiguous carbons by utilizing a dione containing an adjacent heterosubstituted stereocenter. Allylstannanes derived from allylic halides and SnF_2 have been shown to undergo diastereofacial nucleophilic attack at such carbonyl centers through a Felkin–Ahn transition state.[11c,f] Furthermore, it has recently been demonstrated that α-oxygenated ketones react faster with a variety of organometallic nucleophiles than their corresponding unsubstituted derivatives.[16] In the addition of **1b** to 2-acetoxy-3,4-octanedione in the presence of SnF_2, therefore, we expected Felkin–Ahn addition of the initially formed allylstannane to the inductively activated carbonyl, followed by intramolecular chelation-controlled addition of the allylsilane to the second ketone carbonyl. In the event, two diastereomeric diols were isolated in 46% combined yield. Gas chromatographic analysis of the crude reaction mixture revealed that these diastereomers were formed in the ratio of 7.5:1, with no other diastereomers apparent in the GLC traces.[17]



We have demonstrated in this paper the power of combining dianionic synthons for annulation reactions with intramolecular chelation control of stereochemistry to develop highly stereocontrolled syntheses of cyclopentanoids. Future efforts devoted to construction of various five-, six-, and seven-membered rings

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utilizing these and other synthons will be reported shortly

Acknowledgment. We thank Curt Haltiwanger for the X-ray crystal structure determination. The National Institutes of Health (GM 35249) provided financial support for this research. An instrumentation grant from the National Institutes of Health (RR 01709) is also gratefully acknowledged.

Supplementary Material Available: General synthetic procedure, complete spectral data for all compounds synthesized, and a description of the structure determination (3 pages). Ordering information is given on any current masthead page.

Synthesis and Some Properties of Poly(diacetylene) (Polyenyne) Oligomers

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A large family of polymers with a polyenyne backbone is accessible through a solid-state polymerization of suitably substituted diacetylenes as depicted below:

$$\underset{\mathbf{1}}{RC\equiv C{-}C\equiv CR} \xrightarrow{h\nu} \underset{\mathbf{2}}{[{-}C\equiv CC(R){=}C(R){-}]_n} \quad (1)$$

In this process, a single crystal of a diacetylene is essentially converted to a single crystal of a poly(diacetylene)[1] ("PDA"), a phenomenon observed only in one other case, the preparation of $(SN)_x$.[2] There are no reported procedures for the synthesis of well-characterized polyenyne itself (**2**, R = H).[3] The PDA's (**2**, R = long-chain ester, urethane, etc.) have recently received much attention, not only from a mechanistic point of view (polymerization via a diradical followed by a propagating carbene)[1] but due to potentially important technological aspects such as nonlinear optical properties in the solid state[4] and unusual chromotropic[5] and dichroic[6] effects in solution.

Meanwhile, over the last decade it was shown that practically all polymers possessing an unsaturated, conjugated backbone could be converted to electrical conductors[7] with electrical conductivities on the order of 1 to 10^2 S cm^{-1} (pure, Na-doped poly(acetylene) has a conductivity of 10^3 S cm^{-1}, $S = \Omega^{-1}$). The PDA's are a glaring exception; acceptor doping was found to enhance their conductivity by only a few orders of magnitude and iodine formed only a very weak charge-transfer complex with a PDA containing relatively small R substituents.[8]

In order to (1) make a *direct* comparison between the solid-state properties of nondegernate ground state, conjugated backbone, conducting polymers (e.g., poly-*p*-phenylene, poly(thiophene), etc.) and polyenyne and (2) ascertain what aspect of the above unusual properties of PDA's were intrinsic to their polyenyne backbone, we decided to employ a strategy of modeling the macromolecule (**2**, R = H) with monodisperse, fully characterized oligomers. The ultimate goal is to obtain a monodisperse polyenyne with a 50-carbon atom ("C_{50}") backbone.[9]

Here we report the successful preparation of suitably substituted C_6, C_{10}, C_{14}, C_{22}, and C_{30} polyenyne oligomers[10] and some preliminary, surprising properties. Other properties are currently being determined.[11]

Scheme I

$$(CH_3)_3CC\equiv CZnCl + ICH{=}CHCl \xrightarrow{i} (CH_3)_3CC\equiv CCH{=}CHCl \quad (2)$$

$$(CH_3)_3CC\equiv CCH{=}CHCl + RC\equiv CMgX \xrightarrow{ii} \underset{C_6,\ R\,=\,t\text{-}Bu}{(CH_3)_3CC\equiv CCH{=}CHC\equiv CR} \quad (3)$$

$$i = (Ph_3P)_2PdCl_2,\ ii = dpppNiCl_2;\ R = t\text{-}Bu\ or Me_3Si$$

The compounds in Table I were prepared according to Scheme I.

This "universal" scheme shows the preparation of C_6 as a typical example of the sequence of reactions employed for oligomer syntheses. Application of this scheme to the preparation of, for example, C_{14} would require the Grignard reagent of reaction 3 to have R = Me_3Si [$(CH_3)_3Si$] followed by removal[12] of this group from the "C_6-Me_3Si" product, deprotonation of the alkyne with methyl Grignard, conversion to the alkynyl zinc reagent with $ZnCl_2$, and coupling of two parts of this reagent with one of *trans*-diiodoethylene in the presence of i. Full experimental details are available.[12,13]

As can be seen from the Table, all new compounds were easily characterizable (IR, ^1H and ^{13}C NMR, elemental analysis). The only exception was C_{14}, it discolored upon standing and elemental analysis gave poor agreement with expected values.

The choice of *tert*-butyl end groups was based on the very high stability-conferring ability of this residue (as contrasted, for example, with a methyl of phenyl end group) in the preparation of the longest isolable and characterizable polyyne.[14,15] Whereas this moiety could influence the electronic properties of the smaller oligomers, it was not expected to have an important effect on the

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[8] Bloor, D.; Hubble, C. L.; Ando, D. J. In "*Molecular Metals*"; Hatfield, W. E., Ed.; Plenum Press: New York, 1979; pp 243–247. One referee pointed out that due to unfavorable ionization potential poly-*p*-phenylene also does not react with iodine.

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