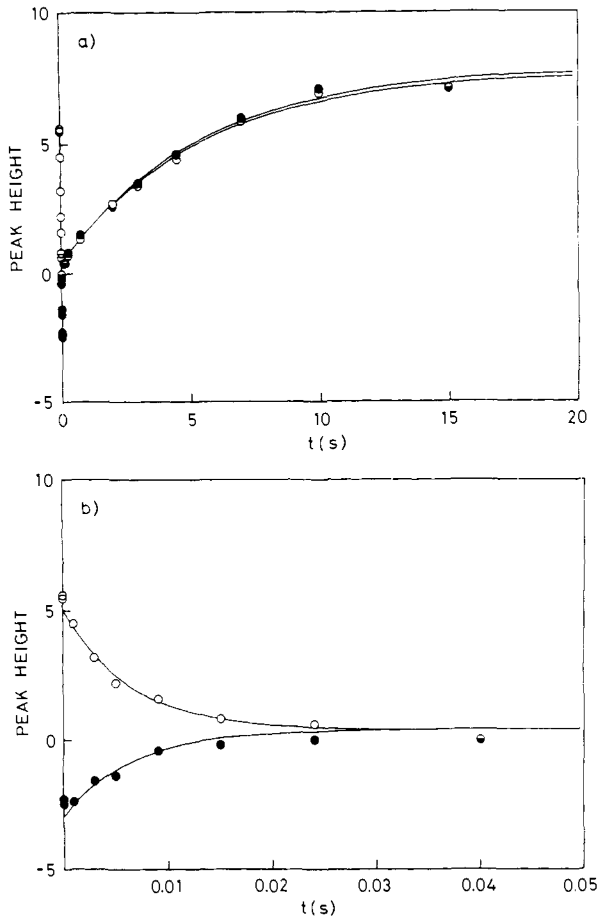

Figure 2. Plot of peak heights (arbitrary units) against time for the peaks illustrated in Figure 1 ((○) trans, (●) cis). The peak heights were obtained directly from the spectra. Plot b is an x-axis expansion of plot a. The solid lines are generated by the equations given in ref 16 and are fitted to the experimental data by an interative routine. Numerical analysis yields values of $k_i = 94.0 \pm 8.3\ \text{s}^{-1}$ and an exchange averaged value of $1/T_1(^{119}\text{Sn}) = 0.19 \pm 0.02\ \text{s}^{-1}$.

is most accurate around the coalescence point, becoming less sensitive to the rate of exchange as the line shape approaches either the slow or fast exchange limits.[14] Values of the tin-119 longitudinal relaxation rate, $1/T_1(^{119}\text{Sn})$, measured on the *cis*- and *trans*-$SnCl_4{\cdot}Me_2S$ adducts were determined at 285 K to be 0.24 ± 0.02 and 0.22 ± 0.02 s^{-1}, respectively, using an inversion recovery pulse sequence ($T_1 \neq T_2$ for these compounds because of the scalar coupling contribution to T_2). Since these values are considerably less than the exchange rate at the trans site, as measured by ^1H NMR line-shape analysis, we felt that this system was an ideal candidate for a magnetization transfer experiment.

Figure 1 illustrates the effect of selectively inverting the ^{119}Sn NMR resonance of the cis isomer in a 0.2 m $SnCl_4{\cdot}2Me_2S$ solution in CD_2Cl_2 at 285 K by using a modification of the so-called "1-2-1" pulse train.[15] From the decrease in intensity of the trans isomer signal, it is clear that magnetization is being transferred between the two sites, providing unambiguous evidence of a cis-trans isomerization process.

Figure 2 shows the plot of peak height against time for both signals. In the absence of cross relaxation, the return to equilibrium of the magnetization may be described by the equations given by Led and Gesmar.[16] The experimental data were fitted to these equations by an iterative, nonlinear least-squares routine to yield a value of k_i of 94 ± 8 s^{-1}. Proton NMR line-shape analysis[10] provides a value of $1/\tau_t = k_i + (k_t/2)$ of 101 ± 4 s^{-1} at the same temperature. It is clear from the comparison of the results of magnetization transfer and line-broadening experiments that the cis-trans isomerization rate is much greater than that of bound ligand/free ligand exchange at the trans site. This is contrary to the working hypothesis assumed previously.[10]

Acknowledgment. We thank M. J. Forster and Dr. P. J. Nichols for discussions and for their invaluable help with the numerical analysis and the Swiss National Science Foundation for financial support through Grant 2.256-0.81.

Registry No. *cis*-$SnCl_4{\cdot}2Me_2S$, 63038-92-6; *trans*-$SnCl_4{\cdot}2Me_2S$, 62182-06-3; Me_2S, 75-18-3; ^{119}Sn, 14314-35-3.

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[14] Mann, B. E. *J. Magn. Reson.* **1976**, *21*, 17-23.

[15] Sklenar, V.; Starcuk, Z. *J. Magn. Reson.* **1982**, *50*, 495-501.

[16] Led, J. J.; Gesmar, H. *J. Magn. Reson.* **1982**, *49*, 444-463.

Effective, Thermal Three-Carbon + Two-Carbon Cycloaddition for Cyclopentenone Formation: Formal 1,3-Dipolar Cycloaddition of Cyclopropenone Ketals

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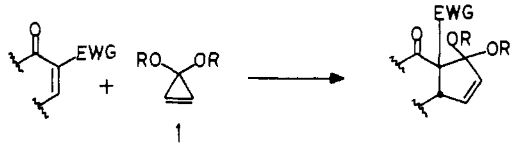
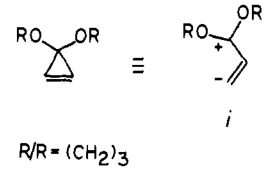
Received October 11, 1983

Increasing efforts have been expended to develop general 3-carbon + 2-carbon cycloadditions for functionalized cyclopentane formation with the expectation that such a process could prove to be an effective complement to the [4 + 2] Diels-Alder reaction used for the regio- and stereocontrolled preparation of functionalized six-membered rings. A number of approaches have been explored and a summary of the work to date has been compiled.[2] Although a number of multistep procedures are available for the introduction of cyclopentane systems, their direct formation by a single cycloaddition is rare.[3,4] Transition-metal-promoted reactions have emerged as the single most explored approach to the effective mediation of such 3-carbon + 2-carbon addition reactions.[2,4]

Herein, we describe a preliminary study of the *thermal* reaction of cyclopropenone ketals **1**[5] with electron-deficient olefins,[6] eq 1,



(1)



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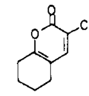
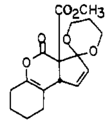
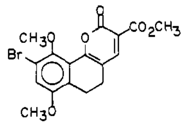
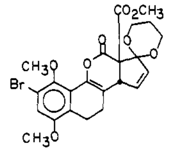
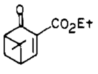
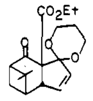
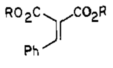
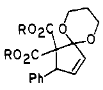
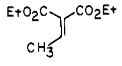
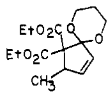
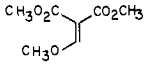
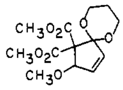
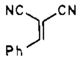
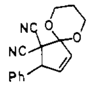
[1] (a) Searle Scholar Recipient, 1981-1984. Recipient of a National Institutes of Health career development award, 1983-1988 (CA 00898). (b) National Institutes of Health predoctoral fellow (GM 07775).

[2] Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315, 2326.

[3] For recent work, see: (a) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. (b) Mayr, H.; Seitz, B.; Halberstadt-Kausch, I. K. *J. Org. Chem.* **1981**, *46*, 1041. (c) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* **1981**, *37*, 4371 and references cited therein.

[4] (a) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61 and references cited therein. (b) Fierz, G.; Chidgey, R.; Hoffmann, M. H. R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 410. (c) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B. *J. Chem. Soc., Perkin Trans. 1* **1982**, *285*, 301. (d) Binger, P. *Synthesis* **1973**, 427. Binger, P.; Germer, A. *Chem. Ber.* **1981**, *114*, 3325. Binger, P.; Schuchardt, U. *Ibid.* **1981**, *114*, 3313. Noyori, R.; Yamakawa, M.; Takaya, H. *Tetrahedron Lett.* **1978**, 4823 and references cited therein.

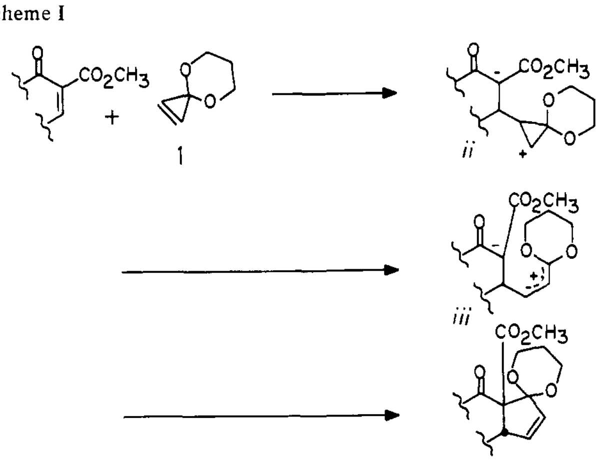
Table I. Reaction of Cyclopropenone Ketal 1 with Electron-Deficient Olefins

substrate	conditions[a] equiv of 1, temp in °C (time, h)	product[b]	yield,[c] %
 2[e]	1.0-2.0,[d] 80 (12)	 10	42
 3[e]	2.0, 80 (3)	 11	11[c] (70%)[f]
 4[g]	1.0, 75 (13)	 12	45
 5, R = Et 6, R = CH_3	1.5, 75 (13)	 13, R = Et 14, R = CH_3	13, 53
	1.5, 75 (10)		14, 48, 60
	2.5, 75 (32)[h]		14, 60
 7	1.5, 75 (15)	 15	57
 8	2.0, 80 (5)	 16	84
 9	2.0, 80 (4)	 17	86

[a] All reactions were run in benzene (0.5–2.0 M in substrate) under nitrogen unless otherwise noted. [b] All products exhibited the expected ^{1}H NMR, ^{13}C NMR, IR, and MS characteristics consistent with the assigned structure. Satisfactory CHN analysis or HRMS information was obtained for each adduct. [c] All yields are based on purified product isolated by chromatography (SiO_2) or crystallization. [d] 1.0 equiv of 1 (80 °C, 3 h) then an additional 1.0 equiv of 1 (80 °C, 9 h). [e] Prepared by the procedure described in ref 6. [f] Yield of product determined by ^{1}H NMR using an internal standard. [g] See ref 9. [h] Addition of 1 (1.5 equiv, 20 h, 75 °C) to 6 (1.1 M in toluene) followed by treatment with additional 1 (1.0 equiv, 12 h, 75 °C).

in which the cyclopropenone ketals serve as effective equivalents of the 1,3-dipole i in a regiospecific 3-carbon + 2-carbon cycloaddition. The results of this study are detailed in Table I. Treatment of systems containing an electron-deficient olefin, **2–9**, with cyclopropenone 1,3-propanediyl ketal[5c] (**1**, benzene, 70–80 °C, 2–32 h) provided cleanly the 1:1 adducts **10–17**. The structure of the cyclopentenone ketal product is clear from complete spectral analysis of the adducts and reveals that the addition is regiospecific.[7,5e] X-ray crystallographic analysis of adduct **13** confirmed the structural assignment.[7] The cis ring fusion in the adducts **10–12** is assumed.

Scheme I



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(5) (a) Baucom, K. B.; Butler, G. B. *J. Org. Chem.* **1972**, *37*, 1730. (b) Albert, R. M.; Butler, G. B. *Ibid.* **1977**, *42*, 674. (c) Butler, G. B.; Herring, K. H.; Lewis, P. L.; Sharpe, V. V., III; Veazey, R. L. *Ibid.* **1977**, *42*, 679. (d) Breslow, R.; Pecoraro, J.; Sugimoto, T. *Org. Syn.* **1977**, *57*, 41. (e) In addition, we have found that 3,3-dimethoxycyclopropene behaves similar to 1 in its reaction with electron-deficient olefins.

(6) The rate of the inverse electron demand Diels–Alder reaction is guided by $\mathrm{LUMO_{diene}}$–$\mathrm{HOMO_{dienophile}}$ interactions, and factors that raise the $\mathrm{HOMO_{dienophile}}$ energy level, thus lowering the $\mathrm{LUMO_{diene}}$–$\mathrm{HOMO_{dienophile}}$ energy separation, accelerate the rate of [4 + 2] cycloaddition. Thus, electron-rich or strained olefins serve as useful 2π components of inverse electron demand Diels–Alder reactions. In connection with a survey of the inverse electron demand Diels–Alder reactions of 3-carbomethoxy-2-pyrones (cf: Boger, D. L.; Mullican, M. D. *Tetrahedron Lett.* **1982**, *23*, 4551; **1983**, *24*, 4939), we examined their reaction with cyclopropenone ketals, strained olefins, with the expectation that they would function similar to electron-rich olefins. 3,3-Dimethoxycyclopropene has been shown to function as a 2π component in Diels–Alder reactions with neutral and electron-rich dienes.[5b,e]

(7) Full crystallographic details, including a view of the molecular structure, are provided as supplementary material (15 pages). The structure determination was performed by Crystalytics Co., Lincoln, NE.

A mechanism that accounts for the observed behavior of the cyclopropenone ketals is detailed in Scheme I. Nucleophilic attack of the strained cyclopropene olefin onto the electron-deficient olefin, rearrangement of the cyclopropyl cation to the allyl cation, and subsequent collapse of the dipole affords the observed products. The results of an initial study on the reactivity and behavior of cyclopropenone ketals by Albert and Butler[5b] and preliminary results of our own[8] are suggestive that such a mechanism is operative.

Investigations to determine the full scope of these observations are in progress.

Acknowledgment. This work was assisted financially by the Chicago Community Trust Co./Searle Scholars Program, the National Institutes of Health (CA 00898, GM 07775), and donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. Cynthia S. Day of Crystalytics Co. for the prompt experimental treatment in the X-ray structure determination in **13**.

Registry No. 1, 60935-21-9; **2**, 85531-80-2; **3**, 88442-03-9; **4**, 88442-04-0; **5**, 5292-53-5; **6**, 6626-84-2; **7**, 1462-12-0; **8**, 22398-14-7; **9**, 2700-22-3; **10**, 88442-05-1; (±)-**11**, 88442-06-2; **12**, 88442-07-3; **13**, 88442-08-4; **14**, 88442-09-5; **15**, 88442-10-8; **16**, 88442-11-9; **17**, 88442-12-0.

Supplementary Material Available: Complete spectral information on **10–17** is listed and full details of the X-ray structure determination of **13** are provided (20 pages). Ordering information is given on any current masthead.

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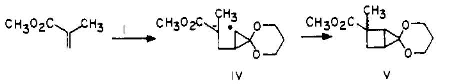
(8) Treatment of methyl methacrylate with **1** (benzene or dioxane, 70–75 °C, 12–24 h) apparently affords v, a highly unstable product that is the result



of [2 + 2] cycloaddition. This suggests that the dipolar intermediates ii are sufficiently stable and long-lived compared to iv to allow the cyclopropyl cation to allyl cation rearrangement (ii → iii) to precede collapse of the dipolar intermediates.

(9) Prepared from nopinone by the three-step procedure: (1) NaH, CO(OEt)$_2$, THF; (2) NaH, THF, PhSeBr; (3) H_2O_2, CH_2Cl_2–H_2O. We thank M. Patel for providing us with this sample.

Synthesis of Ligand-Free Transition-Metal Dihydrides in Low-Temperature Matrices: Manganese Dihydride, MnH_2

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Received July 21, 1983

There is a growing interest in ligand-free transition-metal dihydrides. This can be traced to their potential for modeling H_2 chemisorption on metal surfaces,[1] for probing H_2 oxidative-addition reactions in homogeneous catalysis,[2] and for identifying metal hydride species in solar spectra from sunspots and stars.[3]

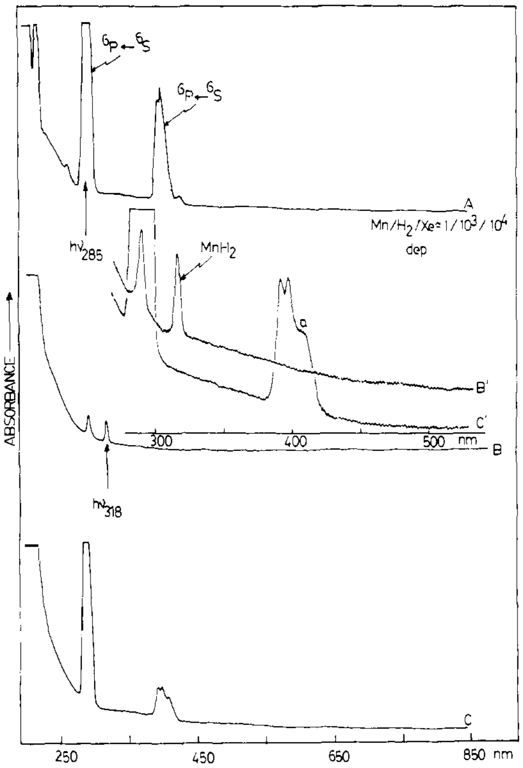

Figure 1. Optical spectra of (A) freshly deposited $Mn/H_2/Xe \simeq 1/10^3/10^4$ matrices at 10–12 K: (B) following 60 min of 285-nm photolysis of (A), (C) following 15 min of 318-nm photolysis of (B). B′ and C′ are approximately times 3 ordinate expansions of B and C, respectively.

The inherent molecular simplicity of MH_2 also makes them ideally suitable models for detailed spectroscopic and structural investigations backed by quantum chemical calculations.[4]

The available experimental data for ligand-free transition-metal dihydrides is, however, extremely sparse, probably because of their transient nature, high reactivity, and lack of convenient syntheses. Only metal atom–hydrogen atom matrix cocondensations have previously been demonstrated to lead to MH_x species. This method yields mixtures of metal hydrides ($x = 1, 2, 3$; M = Cr, Mn) coisolated with H and H_2 products.[5] Aside from spectroscopic complications, such mixtures would make subsequent studies of the chemistry of the ligand-free MH_x species with other coadded ligands, like CO, N_2, C_2H_4, difficult.

In this communication we wish to report on a new method for fabricating ligand-free transition-metal dihydrides in low-temperature matrices, completely devoid of H atoms and other MH_x products. The method involves resonance excitation of metal atoms coisolated with H_2 in rare gas matrices at 10–12 K. In this paper the metal atom photochemical technique is demonstrated by reference to Mn atoms in 10% H_2/Xe matrices. This choice was predicated on the inherent simplicity of the electronic ground state of Mn atoms $^6S_{5/2}(3d^54s^2)$ and its associated atomic resonance spectrum[6] (Figure 1A) as well as the existence of an earlier literature claim for the matrix synthesis of MnH_2 from Mn atom–H atom cocondensations in Xe, therefore permitting cross comparisons between the two different approaches. The use of high H_2 concentrations in Xe was designed to favor the formation of the highest possible stoichiometry manganese hydride, while

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(1) Bates, G.; Katzer, J. R.; Schmit, G. C. A. "Chemistry of Catalytic Processes"; McGraw-Hill: New York, 1979; "The Nature of the Surface Chemical Bond"; Rhodin, T. N., Ertl, G., Eds.; North-Holland: Amsterdam, 1979; and references cited therein.

(2) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA. Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; and references cited therein.

(3) Wing, R. F.; Cohen, J.; Brautt, J. W. *Astrophys. J.* **1977**, *216*, 659. Mould, J. R.; Wyckoff, S. *M.N.R.A.S.* **1978**, *182*, 63 and references cited therein.

(4) Blomberg, M. R. A.; Siegbahm, Per. E. M. *J. Chem. Phys.* **1983**, *78*, 5682. Tyrrell, J.; Youakim, A. *J. Phys. Chem.* **1980**, *84*, 3568; 1981, *85*, 3614, and references cited therein.

(5) Van Zee, R. J.; DeVore, T. C.; Wilkerson, J. L.; Weltner, W., Jr. *J. Chem. Phys.* **1978**, *69*, 1869. Van Zee, R. J.; DeVore, T. C.; Weltner, W., Jr. *J. Chem. Phys.* **1979** *71*, 2051.

(6) Klotzbücher, W.; Ozin, G. A. *Inorg. Chem.* **1980**, *19*, 3776 and references cited therein.

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