

antimalarial candidate because structurally similar deoxoartemisinin has been shown to be more active than artemisinin both *in vitro* (8 times) and *in vivo*.¹¹ Third, since the cyclic enol ether 7 can be easily prepared and derivatized, other useful derivatives such as C-4 methylated trioxane are accessible by one additional step. These trioxanes, combined with their antimalarial activities, will be reported in a full paper when ready.

Acknowledgment. This paper was supported by NON DIRECTED RESEARCH FUND (04D0209), Korea Research Foundation.

References

- (a) Klayman, D. L. *Science* **1985**, *228*, 1049. (b) Duc, D. D.; DeVries, P. J.; Khanh, N. X.; Binh, L. N.; Kager, D. A.; Van Boxtel, C. J. *Am. J. Trop. Med. Hyg.* **1994**, *51*, 785.
- For recent reviews, see: (a) Zaman, S. S.; Sharma, R. P. *Heterocycles* **1991**, *32*, 1593. (b) Zhou, W.-S.; Xu, X.-X. *Acc. Chem. Res.* **1994**, *27*, 211.
- (a) Schmid, G.; Hofheinz, W. *J. Am. Chem. Soc.* **1983**, *105*, 624. (b) Xu, X.-X.; Zhu, J.; Huang, D. Z.; Zhou, W.-S. *Tetrahedron* **1986**, *42*, 819. (c) Avery, M. A.; Jennings-White, C.; Chong, W. K. M. *Tetrahedron Lett.* **1987**, *28*, 4629. (d) Avery, M. A.; Chong, W. K. M.; Jennings-White, C. *J. Am. Chem. Soc.* **1992**, *114*, 974.
- (a) Posner, G. H.; Oh, C. H.; Gerena, L.; Milhous, W. K. *Heteroatom Chemistry* **1995**, *6*, 105. (b) Jefford, C. W.; Velarde, J.; Bernardinelli, G. *Tetrahedron Lett.* **1989**, *30*, 4485. (c) Avery, M. A.; Jennings-White, C.; Chong, W. K. M. *J. Org. Chem.* **1989**, *54*, 1792. (d) Keper, J. A.; Philip, A.; Lee, Y. W.; Morey, M. C.; Carrol, F. I. *J. Med. Chem.* **1988**, *31*, 713.
- (a) Posner, G. H.; Oh, C. H.; Gerena, L.; Milhous, W. K. *J. Med. Chem.* **1992**, *35*, 2459. Posner, G. H.; Oh, C. H.; Webster, H. K.; Ager, JR. A. L.; Rossan, R. N. *Am. J. Trop. Med. Hyg.* **1994**, *50*, 522.
- Roth, R. J.; Acton, N. *J. Nat. Prod.* **1989**, *52*, 1183.
- (a) Jung, M.; Li, X.; Bustos, A.; Elsohly, H. N.; McChesney, J. D. *Tetrahedron Lett.* **1989**, *30*, 5973. (b) Binns, F.; Wallace, T. W. *Tetrahedron Lett.* **1989**, *30*, 1125.
- Baumstark, A. L. In *Advances in Oxygenated Processes*; JAI Press Inc.: 1988; vol 1, pp 31-84.
- All synthesized compounds have the following spectroscopic data. Compound 6: ¹H NMR (400 MHz, CDCl₃) δ 6.11 (s, 1H), 3.88 (m, 1H), 3.79 (m, 1H), 2.52-2.36 (m, 2H), 2.05-1.90 (m, 4H), 1.85-1.78 (m, 2H), 1.60-1.51 (m, 3H), 1.44 (m, 1H), 1.15 (m, 1H), 0.93 (m, 1H). Compound 7: ¹H NMR (400 MHz, CDCl₃) δ 6.17 (s, 1H), 3.87 (m, 1H), 3.78 (m, 1H), 2.58-2.42 (m, 2H), 2.15 (s, 3H), 2.04-1.91 (m, 2H), 1.88-1.72 (m, 5H), 1.59-1.32 (m, 3H), 1.16-1.05 (m, 1H), 0.96-0.86 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 208.99, 136.18, 120.00, 63.78, 41.58, 39.39, 35.11, 34.03,

33.18, 30.65, 29.93, 25.93, 25.11. Trioxane 3: ¹H NMR (400 MHz, CDCl₃) δ 5.19 (s, 1H), 3.96 (m, 1H), 3.75 (m, 1H), 2.49-2.34 (m, 2H), 2.01 (m, 1H), 1.85-1.52 (m, 8H), 1.44 (s, 3H), 1.41-1.28 (m, 1H), 1.2 (m, 1H), 1.13 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 104.04, 91.94, 79.93, 61.26, 46.10, 39.29, 36.41, 32.57, 28.35, 26.96, 26.67, 26.33, 25.00; FT-IR (neat, cm⁻¹) 3013, 2933, 2865, 1453, 1436, 1378, 1088, 1044; Anal. calcd for C₁₃H₂₀O₄: C, 64.98, H, 8.39. Found: C, 65.04; H, 8.45. Trioxane 3a: ¹H NMR (400 MHz, CDCl₃) δ 4.79 (s, 1H), 4.14 (m, 1H), 3.54 (m, 1H), 2.42 (td, *J*=14.0, 4.0 Hz, 1H), 2.11 (m, 1H), 1.98-1.81 (m, 3H), 1.75-1.67 (m, 2H), 1.45 (s, 3H), 1.42-1.129 (m, 5H), 1.26-1.18 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 104.30, 97.13, 77.84, 65.65, 43.74, 41.39, 35.14, 28.25, 27.17, 26.40, 26.19, 25.85, 25.21; FT-IR (CHCl₃, cm⁻¹) 2978, 2866, 1111, 1076, 1065, 1044, 1016.

- (a) Posner, G. H.; Oh, C. H. *J. Am. Chem. Soc.* **1992**, *114*, 8328. (b) Posner, G. H.; Cumming, J. N.; Ploypradith, P.; Oh, C. H. *J. Am. Chem. Soc.* **1995**, *117*, 5885.
- Jung, M.; Li, X.; Bustos, D. A.; Elsohly, H. N.; McChesney, J. D.; Milhous, W. K. *J. Med. Chem.* **1990**, *33*, 1516.
- Oh, C. H.; Cumming, J. N.; Wang, D.; Posner, G. H. *Tetrahedron* **1995**, manuscript in preparation.

Photopolymerization of Acrylic Acids Initiated by CCl₄/Group VIII Metallocene

Hee-Gweon Woo*, Soo-Yeon Yang, Hyun You, Yong-Kook Choi, Seong-Keun Kook, and Whan-Gi Kim†

Department of Chemistry,
Chonnam National University,
Kwangju 500-757, Korea
†Samyang Group R&D Center,
Taejeon 305-348, Korea

Received March 30, 1996

Photopolymerization technology applicable conveniently is extensively employed this day on a commercial scale in the areas of surface coatings, photoresists, adhesives, and holography.¹ Organometallic photochemistry has drawn a great deal of attention because irradiation of organometallic compounds can lead to catalytically and synthetically useful transformations.² In particular, a historically important class of cyclopentadienyl complexes has been plentifully prepared and their photochemical properties have been intensively investigated.³ Many halogenated organic compounds have been used as effective initiators for the photopolymerization of many vinyl derivatives.⁴ Practical problems with halogenated photoinitiators are the corrosion of reactor system and some side reactions caused by acid hydrogen halides which are produced as byproducts during the photopolymerization. The use of ferrocene (Cp₂Fe) as a photopolymerization promoter (to activate the halogenated photoinitiator) and as a halide-radical trap (to prevent the troublesome acid formation) in

combination with halogenated compounds in the photopolymerization of MMA has been described.⁵ To our knowledge, the other group VIII metallocenes such as cobaltocene (Cp₂Co) and nickelocene (Cp₂Ni) have never been used for this type of photopolymerization except our recent report on the photopolymerization of MMA initiated by CCl₄/group VIII metallocene.⁶ In this communication we wish to report the photopolymerization of acrylic acids such as acrylic acid (AA) and methacrylic acid (MA) initiated by CCl₄/group VIII metallocene to compare with the photopolymerization of MMA initiated by CCl₄/group VIII metallocene.

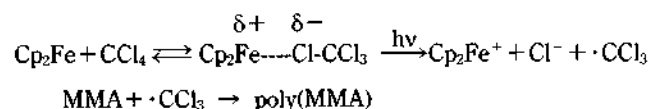
In a typical experiment, a quartz test tube (1 cm × 20 cm) was loaded with AA (1.44 g, 20 mmol), CCl₄ (0.19 mL, 2 mmol), Cp₂Fe (0.37 mg, 2 μmol), and benzene (2 mL). The mixture was degassed, sealed, and irradiated with 300 nm UV-light (monochromatic UV lamp intensity, 6.93 × 10¹⁸ hv mL⁻¹ min⁻¹) for 2 h. The resulting polymer was taken in methanol, precipitated in hexane, filtered off, and dried under vacuum to give 0.46 g (32%) of white solid.⁷ Cobaltocene and nickelocene instead of ferrocene were also used with CCl₄ for the photopolymerization. Other halocarbons such as CHCl₃ and Ph(C=O)CH₂Br were examined as a possible substitute for CCl₄. The results are listed in Table 1.

Similarly, the photopolymerization of MA was also carried out to give poly(MA)s as white solids.⁸ The results are given in Table 2.

We used a fixed mole ratio of monomer : halide : metallocene (10000 : 1000 : 1). CCl₄ was used here as both solvent and initiator. The amount of metallocene used was minimized in order to decrease the contamination of the polymers and the UV-masking action by the metallocene. We are studying their relative concentration effect on the photopolymerization and will be reported as a separate paper in the

future. All of the resulting polymers were soluble in DMF, DMSO, and methanol. Poly(MA)s were produced in higher yields than poly(AA)s in the photopolymerization, as opposed to the expectation based on the steric grounds. However, the molecular weights of poly(AA)s were higher than those of poly(MA)s. The photopolymerization yields of the acrylic acids initiated by CCl₄/group VIII metallocene were generally higher than those of MMA initiated by CCl₄/group VIII metallocene.⁶

Fujisaki *et al.* suggested that the photopolymerization of MMA may be initiated by ferrocene/CCl₄ system as follows.^{8b}



A charge-transfer (CT) complex formed between ferrocene and CCl₄ by the iron atom serving as an electron donor and the chlorine atom as an electron acceptor. The primary process of photochemical initiation of the polymerization could be the absorption of light by this CT complex which will then dissociate into trichloromethyl radical and ferricenium chloride. The trichloromethyl radical will finally initiate the photopolymerization. The CT complex formation seems to be a mandatory condition for the photopolymerization. As a control experiment, ferrocene or CCl₄ alone is practically ineffective on the photopolymerization. As shown in Table 1 and Table 2, Ph(C=O)CH₂Br was ineffectual probably because of inability of forming the CT complex with ferrocene. CHCl₃ was found to be less effective than CCl₄. Radicals are particularly strongly stabilized when both an electron-withdrawing and an electron-donating substituent are located at the radical site.⁹ Chlorine atom on the radical site could be more stabilizing the corresponding radical center than hydrogen atom. Although the direct C-Cl bond dissociation energy (73 kcal/mol) in CCl₄^{10a} is smaller than the C-Cl bond dissociation energy (84 kcal/mol) in CH₃Cl^{10b}. Such arguments were firmly supported by the worldwide replacement of chlorofluorocarbons (CFCs) by hydrochlorofluorocarbons (HCFCs) due to ozone depletion phenomena in the Arctic and Antarctic zones in winter.¹¹

The electron configuration is (e_{2g})⁴(a_{1g})² for Cp₂Fe (18 electrons), (e_{2g})⁴(a_{1g})²(e_{1g})¹ for Cp₂Co (19 electrons), and (e_{2g})⁴(a_{1g})²(e_{1g})² for Cp₂Ni (20 electrons). The highest occupied molecular orbitals e_{2g} and a_{1g} are only slightly bonding and therefore removing electrons from them does not greatly destabilize the metallocenes. The lowest unoccupied molecular orbital e_{1g} is not significantly antibonding so when electrons are added to create 19-electron and 20-electron species the stability loss is minimal. Nevertheless, an organometallic complex become most stable when it has 18 electron closed-shell configuration.¹² The group VIII metallocenes can be stepwise reduced or oxidized.¹³ The photoinitiating ability is linearly related to the magnitude of polymerization yield. We first anticipated the photoinitiating ability of the group VIII metallocenes should decrease in the order of Cp₂Ni > Cp₂Co > Cp₂Fe (an oxidation order), based on the 18 electron rule. However, the photoinitiating effect was found to decrease in the order of Cp₂Fe > Cp₂Ni > Cp₂Co. Ferrocene is known to be completely photoinert in nonhalogenated solvents.^{14a}

Table 1. Characterization of Photopolymerization of AA^a

initiator	% yield	intrinsic viscosity ^b [η]
CCl ₄ + Cp ₂ Fe	32	9.4
CCl ₄ + Cp ₂ Co	5	26.5
CCl ₄ + Cp ₂ Ni	12	13.4
CHCl ₃ + Cp ₂ Fe	15	—
Ph(C=O)CH ₂ Br + Cp ₂ Fe	0	—
Cp ₂ Fe	2	—
CCl ₄	2	—

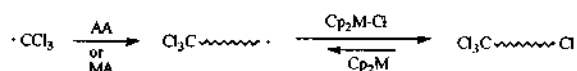
^aUV-irradiation for 2 h. ^bMeasured in DMF at 25 °C; unit, dL/g.

Table 2. Characterization of Photopolymerization of MA^a

initiator	% yield	intrinsic viscosity ^b [η]
CCl ₄ + Cp ₂ Fe	54	2.7
CCl ₄ + Cp ₂ Co	5	4.0
CCl ₄ + Cp ₂ Ni	24	3.9
CHCl ₃ + Cp ₂ Fe	20	—
Ph(C=O)CH ₂ Br + Cp ₂ Fe	0	—
Cp ₂ Fe	trace	—
CCl ₄	trace	—

^aUV-irradiation for 2 h. ^bMeasured in DMF at 25 °C; unit, dL/g.

On the other hand, Borrell and Henderson reported that those metallocenes with an even number of electrons (e.g., 18, 20) were less photoactive, but those with an odd number (e.g., 17, 19) were more photoactive in nonhalogenated solvents.^{14b} The photoinitiating order appears to coincide with the photostability order in nonhalogenated solvent. We also expected that the molecular weights should decrease in the same order as the order of polymerization yield. It is known that high-molecular-weight polymer is formed instantly and that the weight average molecular weight generally increases with increase of polymerization yield in the radical polymerization of vinyl monomers.¹ However, the molecular weights decreases in the order of $Cp_2Co > Cp_2Ni > Cp_2Fe$, exactly opposite to the order of polymerization yield. Ferrocene could accept a chlorine radical forming a ferricenium chloride, but, at the same time, the ferricenium chloride might want to go back by losing the chlorine radical to be stable 18-electron ferrocene. Thus, a growing polymer chain radical containing a CCl_3 as an end group could accept a chlorine radical to cap the radical end of polymer chain.



The capping order of metallocenium chloride could be directly related to the photostability order of metallocene itself, $Cp_2Fe > Cp_2Ni > Cp_2Co$. The polymer molecular weight should be, in turn, inversely proportional to the capping order. Typical redox radical telomerization promoted by transition-metal species shows a linear relationship between polymer molecular weight and monomer conversion.¹⁵ Living polymerization technique allows to precise control of polymer molecular weight distribution and structure. However, the bias of free radicals to undergo self-reaction at diffusion-controlled rates precludes conventionally *living* polymerization. Radical polymerization may be considered *living* if the following conditions are met: (1) the radicals must be long-lived and slow to initiate polymerization, (2) the interruption of chain growth should be occurred by radical combination and group transfer, and (3) the bond to the end group formed in the termination reaction must be labile. Rizzardo *et al.* reported alkoxamine-initiated living radical polymerization.¹⁶ Matyjaszewski *et al.* described the atom-transfer radical polymerization initiated by 1-phenylethyl chloride/CuCl/bipyridine combination.¹⁷ The radical polymerization by the initiator combination exhibits a *living* character with a negligible amount of irreversible transfer and termination and with a narrow molecular weight distribution, $\bar{M}_w/\bar{M}_n < 1.5$. In this case, polymer molecular weight linearly increases with monomer conversion. The intrinsic viscosity is directly related to the weight average molecular weight of polymer.¹⁸ Therefore, as shown in Table 1 and Table 2, the reverse linear relationship between polymer molecular weight and monomer conversion could suggest that our photopolymerization is not a *living* process. Thus, the present chlorine radical transfer from metallocenium chloride to polymer chain radical could be an irreversible termination process. A study improving our initiating system to be *living*, the capping process being reversible, is in progress and will be reported in the near future. Finally, we should admit that there is a chance metallocenium chlo-

ride might not be a spectator, but might act as a photoinitiator. In fact, cationic organometallic compounds of many types are known to be efficient photoinitiators of cationic polymerization.² We are checking such a possibility.

In conclusion, we have shown the photopolymerization of AA and MA initiated by Cp_2M ($M=Fe, Co, Ni$)/ CCl_4 combination. Lower-molecular-weight poly(MA)s were produced in higher yields than higher-molecular-weight poly(AA)s in the photopolymerization. It was found that while the polymerization yield decreases in the order of $Cp_2Fe > Cp_2Ni > Cp_2Co$, the molecular weight decreases in the order of $Cp_2Co > Cp_2Ni > Cp_2Fe$. An explanation for the reverse order has been provided.

Acknowledgment. This research was supported in part by the Korea Science and Engineering Foundation (1995) and in part by the Basic Science Research Institute program (BSRI 94-3429).

References

- (a) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991; Chapter 3. (b) Alcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice-Hall: New Jersey, 1992; Chapter 3.
- (a) *Photosensitive Metal-Organic Systems: Mechanistic Principles and Applications*; Kutal, C., Serpone, N., Eds.; ACS Advances in Chemistry Series No. 238; American Chemical Society: Washington, DC, 1993. (b) *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Gratzel, M., Eds.; Kluwer Academic Publisher: Dordrecht, Netherlands, 1993.
- Bock, C. R.; Koerner von Gustorf, E. A. *Adv. Photochem.* 1977, 10, 221.
- Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers: Theory and Applications*; Wiley: New York, 1987; Chapter 7.
- (a) Imoto, M.; Ouchi, T.; Tanaka, T. *J. Polym. Sci., Polym. Lett. Ed.* 1974, 12, 21. (b) Tsubakiyama, K.; Fujisaki, S. *J. Polym. Sci., Polym. Lett. Ed.* 1972, 10, 341. (c) McGinniss, V. D.; Stevenson, D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1974, 15(1), 302.
- Woo, H.-G.; Park, J.-Y.; Hong, L.-Y.; Yang, S.-Y.; You, H.; Ham, H.-S. *Bull. Korean Chem. Soc.*, in press.
- Poly(AA): IR (KBr pellet, cm^{-1}): 3300 br s (ν_{O-H}), 1720 s ($\nu_{C=O}$), 1250 s (ν_{C-O}); 1H NMR (δ , DMSO- d_6 , 300 MHz): 1.2-2.4 (br, 3H, CH-CH₂), 12.4 (br, 1H, COOH); Intrinsic viscosity: 9.4 dL/g.
- Poly(MA): IR (KBr pellet, cm^{-1}): 3400 br s (ν_{O-H}), 1720 s ($\nu_{C=O}$), 1200 s (ν_{C-O}); 1H NMR (δ , DMSO- d_6 , 300 MHz): 0.9-1.1 (br, 3H, C-CH₃), 1.8-2.1 (br, 2H, CH₂), 7.1-7.4 (br, ArH), 12.3 (br, 1H, COOH); Intrinsic viscosity: 2.7 dL/g.
- (a) Baldock, R. W.; Hudson, P.; Katritzky, A. R.; Soti, F. *J. Chem. Soc., Perkin Trans. 1* 1974, 1422. (b) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 917.
- (a) *CRC Handbook of Chemistry and Physics*, 57th ed.; Weast, R. C., Ed.; CRC Press: Ohio, 1976; p F-234. (b) Benson, S. W. *J. Chem. Educ.* 1965, 42, 502.
- Halon Replacements: Technology and Science*; Mizioek, A.

- W., Tsang, W., Eds.; ACS Symposium Series No. 611; American Chemical Society: Washington, DC, 1995.
12. Hueey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins College Publishers: New York, 1993.
13. (a) Narvor, N. L.; Lapinte, C. *Organometallics* 1995, 14, 634. (b) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 37.
14. (a) Tarr, A. M.; Wiles, D. M. *Can. J. Chem.* 1968, 46, 2725. (b) Borrel, P.; Henderson, E. *Inorg. Chim. Acta.* 1975, 12, 215.
15. Boutevin, B.; Pietrasanta, Y. In *Comprehensive Polymer Science*; Allen, G., Aggarwal, S. L.; Russo, S., Eds.; Pergamon: Oxford, 1991; Vol. 3, p 185.
16. Moad, G.; Rizzardo, E.; Solomon, D. H. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon: London, 1989; Vol. 3, p 141.
17. Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* 1995, 117, 5614.
18. Collins, E. A.; Bares, J.; Billmeyer, F. W., Jr. *Experiments in Polymer Science*; John Wiley & Sons: New York, 1973; p 148.

Silver(I)/Celite Promoted Oxidative Additions of 1,3-Dicarbonyl Compounds to Olefins. A Facile Synthesis of Dihydrofurans

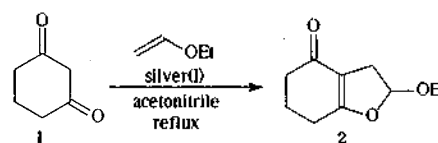
Yong Rok Lee*, Byung So Kim, and Joung Hee Lee

Department of Industrial Chemistry,
College of Engineering, Yeungnam University,
Kyongsan 712-749, Korea

Received April 2, 1996

The oxidative addition reaction of carbon-centered radicals to alkenes mediated by metal salts (Mn^{III} , Ce^{IV} , and Co^{II}) has received considerable attention over the last decade in organic synthesis for construction of carbon-carbon bonds.¹ Utilization of high valent metal salts in oxidative addition reactions has been particularly effective. Among these manganese(III) acetate and cerium(IV) ammonium nitrate (CAN) have been used most efficiently.²⁻³ However, their synthetic exploitations have been limited by the low yield in intermolecular addition reactions, by strong acidic reaction conditions, and by overoxidations due to substitution of acetate or nitroxy groups.⁴⁻⁶ Necessity for overcoming these problems has prompted our search for the possibility of using silver(I) metals. In related work, Malek⁷ has demonstrated the usefulness of Ag(II) oxide for the generation of a carbon radical and Saegusa⁸ has reported the oxidative dimerization of β -diketone by using Ag(I) oxide. It has been reported by Fetizon that silver(I) carbonate/Celite is a valuable reagent

Table 1. Effect of Silver(I) Metals and Celite in the Reaction of 1,3-Cyclohexanedione with Vinyl ether



Silver(I)	t, h	Yield, %
AgNO ₃	5	0
AgOAc	5	0
AgBF ₄	5	0
Ag ₂ O	4	69
Ag ₂ O/Celite	2	80
Ag ₂ CO ₃	5	70
Ag ₂ CO ₃ /Celite	3	78
Ag ₂ CO ₃ /silica gel	2	31

for the oxidation of alcohols to aldehydes and ketones in high yield.⁹ We report here that Ag(I)/Celite is also an efficient and useful reagent for the oxidative addition of 1,3-dicarbonyl compounds to olefins, which allows the synthesis of dihydrofurans in moderate yield. Silver(I) metal promoted oxidative additions are generally heterogeneous reactions which take place under essentially mild neutral conditions. Two equivalents of silver(I)/Celite are used for completion of the reaction and the reactions are typically carried out by refluxing a solution of a 1,3-dicarbonyl compound with an alkene (5 eq) in an anhydrous solvent. The course of the reaction can be readily monitored by TLC. Isolation of products involves a very simple filtration to remove the reduced silver(0) metal followed by evaporation of solvent. Reaction of 1,3-hexanedione 1 with ethyl vinyl ether was attempted utilizing several silver(I) reagents (Table 1). Both silver(I) oxide and silver(I) carbonate provided the desired dihydrofuran 2 in good yields whereas AgOAc, AgNO₃ and AgBF₄ gave no reaction. Most interestingly, we found that the readily available reagent, 50% silver(I) oxide/Celite or 50% silver(I) carbonate/Celite, is more efficient than silver(I) metal for the production of dihydrofuran 2 as shown in Table 1. More importantly, the incorporation of Celite resulted in reduced reaction times and improved yields. However, addition of silica gel resulted in a low yield (31%).

In an effort to optimize reaction conditions, we surveyed several solvents for the production of dihydrofuran 2 with the Ag₂O/Celite system (Table 2). Nonpolar solvents such as benzene or heptane gave only low yields (15% or 10%) of dihydrofuran 2 presumably due to the insolubility of silver(I) oxide, while in polar acetonitrile the yield was dramatically improved to 80%.

Examples of the dihydrofurans synthesized via optimized conditions in acetonitrile are shown in Table 3. The structure of the obtained products is easily established spectroscopically.¹⁰ The *cis* and *trans* products 7 of entry 5 are identified by observation of coupling constants of 9.0 Hz (*cis*) and 5.6 Hz (*trans*) between the two methine protons. While there is no direct precedent for the oxidative addition of 1,3-cyclopentanedione (entry 3) to olefins by using metal salts such