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

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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, Malek[7] has demonstrated the usefulness of Ag(II) oxide for the generation of a carbon radical and Saegusa[8] 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
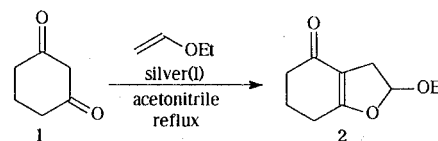
Silver(I)	t, h	Yield, %
AgNO$_3$	5	0
AgOAc	5	0
AgBF$_4$	5	0
Ag$_2$O	4	69
Ag$_2$O/Celite	2	80
Ag$_2$CO$_3$	5	70
Ag$_2$CO$_3$/Celite	3	78
Ag$_2$CO$_3$/silica gel	2	31

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, AgNO$_3$ and AgBF$_4$ 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%).
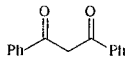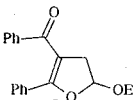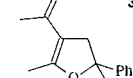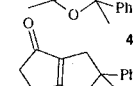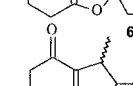
In an effort to optimize reaction conditions, we surveyed several solvents for the production of dihydrofuran **2** with the Ag$_2$O/Celite system (Table 2). Nonpolar solvents such as benzene or heptane gave only low yields (15% or 10%) of dihydrofuran **2** presumably due to the insolubility of silver(I) oxide, while in polar acetonitrile the yield was dramatically improved to 80%.

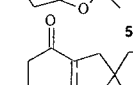Examples of the dihydrofurans synthesized via optimized conditions in acetonitrile are shown in Table 3. The structure of the obtained products is easily established spectroscopically.[10] The *cis* and *trans* products **7** of entry 5 are identified by observation of coupling constants of 9.0 Hz (*cis*) 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

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Table 2. Effect of Solvents in the Reaction of 1,3-Cyclohexane-dione with Vinyl ether under Silver(I) oxide/Celite

Solvent	Temp.	t, h	Yield, %
CH₃CN	reflux	2	80
DMSO	80 °C	1.5	46
DMF	80 °C	1.5	36
PhH	reflux	4	15
heptane	reflux	4	10

Table 3. Synthesis of Dihydrofurans

Entry	1,3-Dicarbonyl compound	Olefin	Silver(I)/Celite	Product	Yield
1			Ag₂O		89
2			Ag₂CO₃		91
3			Ag₂CO₃		41
4			Ag₂CO₃		60
5		(*cis* : *trans*=62 : 38)	Ag₂CO₃	(*cis* : *trans*=49 : 51)	86

as manganese(III) acetate and cerium(IV) ammonium nitrate, it is noteworthy that silver(I)/Celite mediated reactions of 1,3-cyclopentanedione to α-methylstyrene gave the fused dihydrofuran **5** in 41% yield.

In summary, the silver(I)/Celite mediated oxidative addition of 1,3-dicarbonyl compounds to olefins such as vinyl ether and vinyl sulfide offers a facile and simple method for the synthesis of substituted dihydrofurans. Further mechanistic studies and application of this reaction will be investigated, and now in progress in our laboratory.

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10. Spectral data for **2**: ¹H NMR (300 MHz, CDCl₃) δ 5.74 (1H, dd, *J*=7.2, 3.3 Hz), 3.91 (1H, m), 3.64 (1H, m), 2.94 (1H, m), 2.68 (1H, m), 2.49 (2H, m), 2.35 (2H, t, *J*=6.6 Hz), 2.04 (2H, m), 1.26 (3H, t, *J*=7.2 Hz); IR (neat) 2943, 1634, 1406, 1375, 1348, 1242, 1179, 1111, 1059, 1042, 901 cm⁻¹. **3**: ¹H NMR (300 MHz, CDCl₃) δ 7.48-7.07 (10H, m), 5.75 (1H, dd, *J*=7.5, 2.7 Hz), 4.03 (1H, m), 3.74 (1H, m), 3.50 (1H, dd, *J*=14.3, 7.5 Hz), 3.09 (1H, dd, *J*=13.8, 2.7 Hz), 1.33 (3H, t, *J*=6.9 Hz); IR (neat) 3061, 2978, 2932, 1614, 1574, 1491, 1446, 1367, 1248, 1198, 1090, 1069, 984, 883 cm⁻¹. **4**: ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.28 (1H, m), 3.14 (2H, q), 2.33 (3H, s), 2.19 (3H, s), 1.69 (3H, s); IR (neat) 3060, 2978, 1671, 1608, 1495, 1444, 1381, 1246, 1158, 1069, 937, 765 cm⁻¹. **5**: ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.33 (5H, m), 2.91 (2H, q), 2.80 (2H, m), 2.66 (2H, m), 1.81 (3H, s). **6**: ¹H NMR (300 MHz, CDCl₃) δ 2.58 (2H, s), 2.41 (2H, m), 2.34 (2H, t, *J*=6.3 Hz), 2.03 (2H, m), 1.78-1.63 (6H, m), 1.50-1.45 (4H, m); IR (neat) 2934, 2860, 1632, 1449, 1402, 1372, 1271, 1238, 1184, 1138, 1061, 1032, 1003, 910 cm⁻¹. **7**: *cis-isomer* ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.30 (m, 5H), 6.10 (1H, d, *J*=9.0 Hz), 3.57 (1H, m), 2.53-2.11 (5H, m), 1.36 (3H, d, *J*=7.0 Hz), 1.11 (3H, d, *J*=5.9 Hz); IR (neat) 2953, 1642, 1439, 1395, 1204, 1138, 1023, 911, 881, 742 cm⁻¹. *trans-isomer* ¹H NMR (300 MHz, CDCl₃) δ 7.53-7.30 (5H, m), 5.55 (1H, d, *J*=5.6 Hz), 3.20 (1H, m), 2.53-2.04 (5H, m), 1.31 (3H, d, *J*=6.8 Hz), 1.10 (3H, d, *J*=6.2 Hz); IR (neat) 2945, 1641, 1397, 1205, 1022, 890, 742 cm⁻¹.