1H, $J$=7.3 Hz), 5.01 (d, 1H, $J$=7.3 Hz); IR (KBr), 3064, 2966, 2924, 2235, 1257, 1025, 751, 688 $cm^{-1}$; UV (MeOH), $\lambda_{max}$ 302, 280, 253, 243, 224 nm; Mass (EI), m/e 624 (M), 204, 77.

9. (a) Spectral data of **6a**: $^1H$ NMR ($CDCl_3$), δ 7.88 (d, 1H, $J$=7.3 Hz), 7.87 (d, 1H, $J$=7.3 Hz), 7.79 (dd, 2H, $J$=7.3 Hz, $J$=1.5 Hz), 7.49-7.43 (5H), 7.05 (s, 1H); Mass (EI), m/e 390 (M), 77. (b) Spectral data of **6b**: $^1H$ NMR ($CDCl_3$), δ 7.88 (d, 1H, $J$=7.3 Hz), 7.87 (d, 1H, $J$=7.3 Hz), 7.78 (dd, 2H, $J$=7.3 Hz, $J$=1.5 Hz), 7.49-7.43 (5H), 7.06 (s, 1H); $^{13}C$ NMR ($CDCl_3$), δ 129.6 (CH), 129.3 (CH), 129.1 (2CH's), 128.6 (3CH's), 124.8 (2CH's), 107.7 (CH); IR (KBr), 3064, 1553, 765, 667 $cm^{-1}$; UV (MeOH), $\lambda_{max}$ 395, 389, 272, 212 nm; Mass (EI), m/e 566 (M), 77.

## Rhodium(II)-catalyzed Cycloaddition of Diazodicarbonyl Compounds with Vinyl Sulfides. Synthesis of 3-Acylfurans

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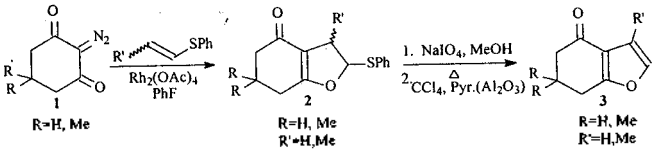
Furans are one of the most important heteroaromatic compounds with widespread occurrence in nature.[1] They are frequently found in many natural products arising from plants and marine organisms.[2] Possessing a variety of biological activities, they are used as pharmaceutical, flavor, insecticidal, and fish antifeedant agents.[3] Their important biological activities and usefulness as synthetic intermediates of natural products have prompted a search for better methods. Although a number of synthetic methods for preparation of 3-acylfurans have been reported, simple and efficient approaches still remain scarce.[4] In particular, the known direct furannulation of a 1,3-diketone by phenylthionitroolefin or an allenic sulfonium salt is limited to a 3-acyl-4-methylfuran substitution pattern.[5]

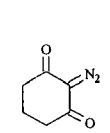
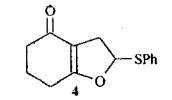
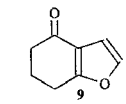
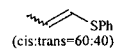
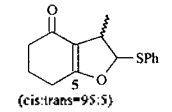
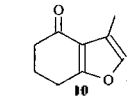
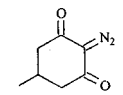
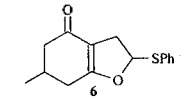
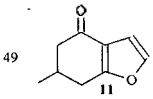
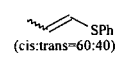
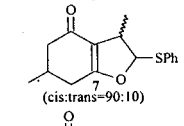
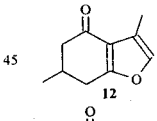
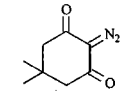
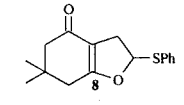
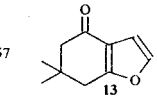
The rhodium-mediated decomposition of diazocarbonyl compounds has become an important method in synthesis of heterocyclic frameworks such as furans.[6] We have been interested in dipolar cycloadditions of 2-diazocyclohexane-1,3-diones with vinyl ethers.[7] We have reported that reactions of these diazoketones with vinyl acetates followed by acid-catalyzed dehydration is a route to benzofuran derivatives.[8] Thus, we have also reported total syntheses of natural products based on the preparation of furo[2,3-b] furan ring catalyzed by rhodium acetate.[9] We describe here the efficient synthesis of 3-acylfurans by rhodium-mediated dipolar cycloaddition of cyclic diazo carbonyl compounds with vinyl sulfides followed by $NaIO_4$ oxidation and syn-elimination under mild conditions.

The sequence that we have developed begins with the




**Scheme 1.**

**Table 1.** Synthesis of Dihydrofurans and Furans

| 2-Diazo-1,3-dicarbonyl compound | Vinyl sulfide | Dihydrofuran | Yield | Furan | Yield |
|---|---|---|---|---|---|
|  |  |  | 50 |  | 80 |
| |  (cis:trans=60:40) |  (cis:trans=95:5) | 56 |  | 54 |
|  |  |  | 49 |  | 87 |
| |  (cis:trans=60:40) |  (cis:trans=90:10) | 45 |  | 61 |
|  |  |  | 57 |  | 89 |

reaction of the cyclic 2-diazo-1,3-dicarbonyl compound **1** with a vinyl sulfide present in 5-fold excess (Scheme 1). The cyclic 2-diazo-1,3-dicarbonyl compound **1** was allowed to react with vinyl sulfides under rhodium acetate catalysis (2 mol %) in fluorobenzene to give dihydrofuran **2** in moderate yields.

The intermediate dihydrofurans were characterized spectroscopically.[10] The intermediate dihydrofurans of **5** and **7** demonstrates an interesting aspect of this process. The dihydrofurans were isolated as a major of *cis* isomer despite the use of a 3 : 2 mixture of stereoisomers of the vinyl sulfide. There is thus kinetic discrimination against the *trans* isomer in the cycloaddition. The stereochemical assignment of *cis*- and *trans*-isomers was defined by observation of coupling constants between vicinal protons. It is also suprising to note that none of the formation of sulfonium ylides and C-H insertion products was observed. The results of synthesized dihydrofurans are summarised in Table 1.

The intermediate dihydrofurans were treated with sodium periodate in aqueous methanol at room temperature for 24 h to form the corresponding sulfoxide, which on directly refluxing for 2 h with pyridine in carbon tetrachloride delivers the 3-acylfurans in high yield. Both stereoisomers of **5** and **7** were also similarly transformed into 3-acyl-4-methylfuran in moderate yield; although, active alumina had to be added in the elimination step to cause epimerization of the *cis*-sulphoxide prior to *syn*-elimination of the sulphenic acid. These transformations had been reported by Yoshikoshi in a 3-me-

thylfuran annulation from 1,3-dicarbonyl compounds by using a phenylthionitroolefin.[11] The data of obtained 3-acylfurans are also collected in Table 1.[10]

The synthesis of evodone **12**, a furanomonoterpene isolated from *Evonia hortensis* Forst,[12] demonstrates an interesting application of this methodology. The spectroscopic properties of our synthetic evodone agreed well with those reported in the literature.[10]

In conclusion, a highly efficient method for constructing fused 3-acylfurans from cyclic diazo carbonyl compounds with vinyl sulfides catalyzed by rhodium acetate is described. The application of this methodology to the synthesis of evodone is also reported. Further application of this furannulation is expected in the synthesis of a variety of furanoterpenoids and now in progress in our laboratory.

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10. Spectral data for **4**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.54-7.33 (5H, m), 6.09 (1H, dd, $J$=9.7, 6.1 Hz), 3.25 (1H, dd, $J$=15.3, 10.1 Hz), 2.83 (1H, dd, $J$=15.7, 5.6 Hz), 2.45 (2H, m), 2.32 (2H, m), 2.02 (2H, m); IR (neat) 2943, 1640, 1481, 1440, 1394, 1222, 1178, 1058, 1021, 900, 870, 839 cm$^{-1}$. **5**: *cis isomer*; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.56-7.32 (5H, m), 6.09 (1H, d, $J$=8.9 Hz), 3.59 (1H, m), 2.47 (2H, m), 2.34 (2H, m), 2.05 (2H, m), 1.37 (3H, d, $J$=6.9 Hz); IR (neat) 3057, 2949, 1640, 1394, 1222, 1179, 1135, 1057, 989, 907, 870 cm$^{-1}$. *trans isomer*; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.56-7.30 (5H, m), 5.54 (1H, d, $J$=5.4 Hz), 3.23 (1H, m), 2.44 (2H, m), 2.30 (2H, m), 2.04 (2H, m), 1.32 (3H, d, $J$=6.8 Hz); IR (neat) 3057, 2947, 1640, 1584, 1481, 1440, 1397, 1222, 1181, 1135, 1057, 1006, 987, 902, 875, 842 cm$^{-1}$. **6**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.53-7.33 (5H, m), 6.09 (1H, dd, $J$=9.6, 6.0 Hz), 3.26 (1H, dd, $J$=15.2, 10.2 Hz), 2.82 (1H, dd, $J$=15.6, 5.3 Hz), 2..54-2.00 (5H, m), 1.10 (3H, d, $J$=6.2 Hz); IR (neat) 2948, 1642, 1480, 1340, 1251, 1204, 1117, 1047, 984, 888 cm$^{-1}$. **7**: *cis-isomer*; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.55-7.30 (5H, m), 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, $J$=7.1 Hz); IR (neat) 2953, 1642, 1439, 1395, 1204, 1138, 1023, 911, 881, 847 cm$^{-1}$. *trans-isomer*; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.53-7.30 (5H, m), 5.55 (1H, d, $J$=5.6 Hz), 3.21 (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 cm$^{-1}$. **8**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.54-7.31 (5H, m), 6.11 (1H, dd, $J$=9.9, 6.1 Hz), 3.27 (1H, dd, $J$=15.3, 10.1 Hz), 2.82 (1H, dd, $J$=15.7, 6.1 Hz), 2.31 (2H, s), 2.20 (2H, m), 1.08 (3H, s), 1.07 (3H, s); IR (neat) 2953, 1644, 1400, 1304, 1273, 1213, 1167, 1043, 912, 877 cm$^{-1}$. **9**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.32 (1H, d, $J$=2.0 Hz), 6.67 (1H, d, $J$=2.0 Hz), 2.89 (2H, t, $J$=6.3 Hz), 2.50 (2H, dd, $J$=6.0, 6.0 Hz), 2.18 (2H, m); IR (neat) 3131, 2948, 1677, 1595, 1516, 1447, 1414, 1294, 1242, 1184, 1119, 1026 cm$^{-1}$. **10**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.07 (1H, s), 2.84 (2H, t, $J$=6.3 Hz), 2.47 (2H, dd, $J$=6.0, 5.7 Hz), 2.20 (3H, s), 2.16 (2H, m); IR (neat) 3065, 2953, 1672, 1560, 1433, 1325, 1146, 1076, 995, 937, 752 cm$^{-1}$. **11**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.32 (1H, d, $J$=1.9 Hz), 6.66 (1H, d, $J$=1.9 Hz), 3.00-2.25 (5H, m), 1.18 (3H, d, $J$=6.3 Hz); IR (neat) 2953, 1678, 1594, 1448, 1413, 1285, 1219, 1119, 1039 cm$^{-1}$. **12**: mp 70 ℃ (lit. mp 70-71 ℃); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.06 (1H, s), 2.92-2.21 (5H, m), 2.18 (3H, s), 1.14 (3H, d, $J$=6.3 Hz); IR (KBr) 3000, 2966, 1662, 1603, 1560, 1456, 1440, 1430, 1410, 1390, 1324, 1242, 1139, 1080, 1045, 1001 cm$^{-1}$. **13**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.33 (1H, d, $J$=1.9 Hz), 6.67 (1H, d, $J$=1.9 Hz), 2.76 (2H, s), 2.39 (2H, s), 1.15 (6H, s); IR (neat) 3132, 2952, 2878, 1678, 1596, 1514, 1445, 1370, 1281, 1228, 1174, 1118, 1042 cm$^{-1}$.
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