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DIRECT SYNTHESIS OF FURANS BY 3 + 2 CYCLOADDITIONS BETWEEN RHODIUM(II) ACETATE STABILIZED CARBENOIDS AND ACETYLENES†

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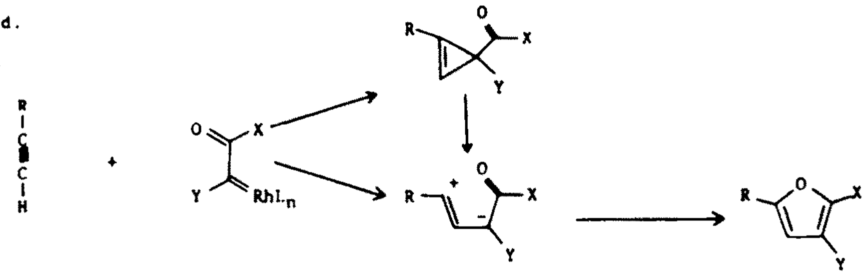
Abstract: When appropriate substituents are used, rhodium(II) acetate catalyzed decomposition of diazocarbonyls in the presence of acetylenes results in the formation of furans, derived from dipolar intermediates.

Generally, metal stabilized carbenoids undergo effective reactions with alkenes to generate cyclopropanes.[1] When the intermediates are appropriately stabilized, however, other reaction pathways involving dipolar intermediates are possible. Many of these processes are synthetically useful and include a series of 2 + 3 cycloadditions between multiple bonds and carbenoids derived from diazocarbonyls. Such reactions result in the formation of dihydrofurans from vinyl ethers,[2] dioxoles from aldeydes[3] and oxazoles from nitriles.[4] Both the ring-opening reaction between furans and carbenoids to generate dienes[5] and the alkylation of pyrroles by carbenoids[6] also appear to involve dipolar intermediates. The actual structure of the dipolar intermediate in many of these reactions is open to debate[7] because subtle questions such as the role of the metal, or the relative rates of bond formation are difficult to answer.

Previous studies have shown that rhodium(II) acetate catalyzed decomposition of ethyl diazoacetate in the presence of acetylenes is a viable method for the synthesis of cyclopropenes.[8] Introduction of suitable functionality to stabilize a dipolar intermediate would be expected to change the reaction pathway and result in the formation of furans (Scheme 1). This could occur either by ring opening of an initially formed cyclopropene or by direct formation of a dipolar intermediate on reaction of a carbenoid with an alkyne. Indeed, there are scattered reports describing the formation of furans in such reactions. For example, copper(II) sulfate catalyzed decomposition of diethyl diazomalonate in the presence of phenylacetylene results in the formation of a mixture of a cyclopropene and a furan,[9a,b] while sensitized photolysis of diethyl diazomalonate in the presence of dialkylacetylenes generates furans as the primary products.[9c] Also, decomposition of 2,2-dibromo-1,3-diones by copper in the presence of acetylenes results in the formation of furans.[10] In this paper our studies into the development of a general synthesis of furans from the reaction of rhodium(II) acetate stabilized carbenoids with acetylenes are described.

Scheme 1



The formation of 2+3 cycloadducts is likely to be favored when the reaction proceeds through a polar transition state. Therefore, in an attempt to shift the major product away from a cyclopropene to a furan, diazo compounds with two electron withdrawing groups (1a-d,2) were substituted for ethyl diazoacetate used by Hubert et al. for the synthesis of cyclopropenes.[8] At first, rhodium(II) acetate catalyzed decompositions of the diazo

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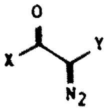
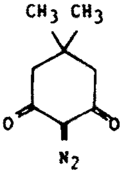
†This paper is dedicated to Professor E.C. Taylor on the occasion of his 65th birthday.

compounds were carried out in the presence of alkylacetylenes, but these reactions did not result in the formation of furans. With terminal acetylenes, cyclopropenes were formed in yields ranging from 46-61% (Table 1, entries 1-3), but no products derived from clean capture of the carbenoid were isolable in the reaction with 3-hexyne (entry 4). Presumably, this suggests that steric effects are important in determining whether or not the carbenoid intermediate can be efficiently trapped. Furthermore, as tert-butylacetylene reacted effectively (entry 3), it would appear that it is necessary for only one end of the acetylene to be readily accessible.



1a X = CH_3, Y = $COCH_3$
1b X = CH_3, Y = COOEt
1c X = OEt, Y = COOEt
1d X = OEt, Y = CH=CHCOOEt



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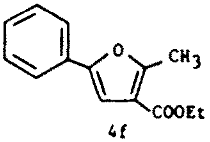
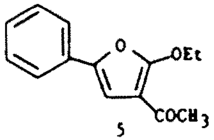
A second approach to enhance a dipolar intermediate would be to introduce electron donating groups onto the acetylene. Based on this expectation, the rhodium(II) acetate catalyzed decompositions of 1a-d were carried out using phenylacetylene as trapping agent. The results of this series of experiments showed a remarkable dependance on the nature of the electron withdrawing groups on the carbenoid (entries 5-8). With diethyl diazomalonate (1c), the cyclopropene 3g was formed, but with 3-diazo-2,4-pentanedione (1a), the furan 4e was the only product. The greater tendency for a ketone carbonyl rather than an ester carbonyl to undergo ring closure to a furan is nicely illustrated in the reaction with ethyl diazoacetoacetate (1b), which resulted in the formation of only 4f and none of 5, the other possible furan isomer. With diethyl 4-diazopentenedioate (1d), the cyclopropene 3h predominated but a trace of the furan 4h was also formed. The structural assignments in these series is based on proton NMR and is straightforward because of a distinctive downfield shift when substituents are directly bound to the furan ring.



4f



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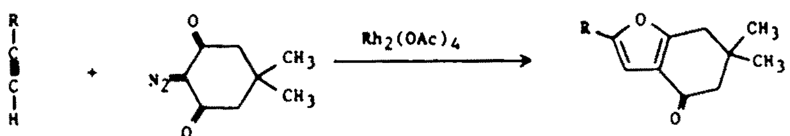
The addition of electron-donating groups to the phenylacetylene further enhanced the formation of furans (entries 9-16). The reaction of diethyl 4-diazopentenedioate (1d) with both 4-methoxy- and 3,4-dimethoxyphenylacetylene resulted in the exclusive formation of furans (entries 12,16). Reaction with diethyl diazomalonate (1c) still resulted in the formation of cyclopropenes, but these compounds were unstable and rearranged to furans during attempted purification by silica gel chromatography. Ethylethynylether did not appear to be stable under these reaction conditions, and no reasonable products were isolated when this compound was used as trapping agent. Diphenylacetylene also failed to effectively trap the carbenoid, but this seemed to be due to problems of steric hindrance, which had been observed earlier with disubstituted acetylenes. The reaction could also be extended to the synthesis of the fused furans 6a-c by the use of the cyclic carbenoid precursor 2.

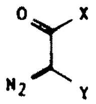
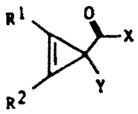
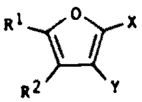
Scheme 2



2

6a R = phenyl
6b R = 4-methoxyphenyl
6c R = 3,4-dimethoxyphenyl

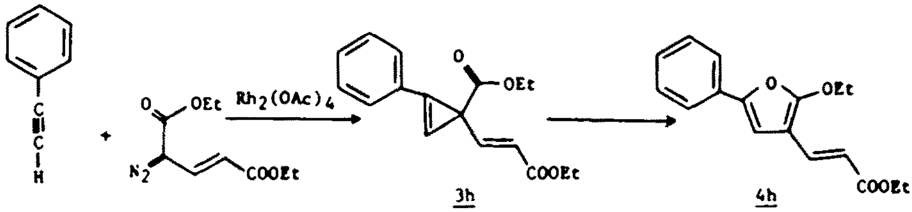
Table I Rhodium(II) Acetate Catalyzed Decomposition of 1a-d in the Presence of Acetylenes

ENTRY	ACETYLENE	DIAZO COMPOUND	PRODUCTS (yield,%)	
				
1	R^1=n-butyl, R^2=H	1c X = OEt, Y = COOEt	3a(54)	-
2	R^1=n-butyl, R^2=H	1d X = OEt, Y = CH=CHCOOEt	3b(61)	-
3	R^1=t-butyl, R^2=H	1d X = OEt, Y = CH=CHCOOEt	3c(46)	-
4	R^1=propyl, R^2=ethyl	1d X = OEt, Y = CH=CHCOOEt	-	-
5	R^1=phenyl, R^2=H	1a X = CH_3, Y = $COCH_3$	-	4e(28)
6	" "	1b X = CH_3, Y = COOEt	-	4f(45)
7	" "	1c X = OEt, Y = COOEt	3g(68)	
8	" "	1d X = OEt, Y = CH=CHCOOEt	3h(85)	4h(6)
9	R^1=4-methoxyphenyl,R^2=H	1a X = CH_3, Y = $COCH_3$	-	4i(52)
10	" "	1b X = CH_3, Y = COOEt	-	4j(41)
11	" "	1c X = OEt, Y = COOEt	-	4k(53)[a]
12	" "	1d X = OEt, Y = CH=CHCOOEt	-	4l(43)
13	R^1=3,4-dimethoxyphenyl,R^2=H	1a X = CH_3, Y = $COCH_3$	-	4m(28)
14	" "	1b X = CH_3, Y = COOEt	-	4n(69)
15	" "	1c X = OEt, Y = COOEt	-	4o(72)[a]
16	" "	1d X = OEt, Y = CH=CHCOOEt	-	4p(54)
17	R^1=ethoxy, R^2=H	1d X = OEt, Y = CH=CHCOOEt	-	-
18	R^1=phenyl, R^2=phenyl	1d X = OEt, Y = CH=CHCOOEt	-	-

a: yield of furan after rearrangement of the initial product, the cyclopropene, during chromatography.

Presumably, furan products arose from dipolar intermediates which were either formed directly or by ring opening of initially generated cyclopropenes. As the reaction between phenylacetylene and 1d was the only one to produce a mixture of cyclopropene and furan products, this system was examined further. When the reaction time was extended from 20 minutes to 5 days, the cyclopropene 3h was totally consumed and the furan 4h was formed in 33% yield. The catalytic role of rhodium(II) acetate in this rearrangement was readily shown by heating 3h in dichloromethane. Under these conditions, only a 30% conversion of 3h was observed after 5 days. Other catalysts such as copper tetrafluoroborate or copper triflate[11] caused rapid conversion of 3h to 4h, but under these conditions, 4h was also quite rapidly destroyed. Some recent studies by Cho and Liebeskind[12] have shown that rearrangement of cyclopropenyl ketones to furans is catalyzed by tetracarbonyldi-μ-chlorodirhodium(I).

Scheme 3



Based on these results, it would appear that at least the 2-ethoxy substituted furans are derived from an initially formed cyclopropene. Whether the 2-alkyl furans are formed directly or by a similar cyclopropene rearrangement remains uncertain. Irrespective of which mechanism is involved, furan formation is enhanced when carbenoids with electron-withdrawing groups and acetylenes with electron-donating groups are used, because these tend to stabilize a dipolar intermediate.

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EXPERIMENTAL

Infrared spectra were determined on a Perkin-Elmer Model 1330 spectrophotometer, and NMR spectra were recorded on a Varian VXR 200 spectrometer. Mass spectral analyses were carried out at Georgia Tech University. Elemental analyses were carried out by Atlantic Microlab, Inc, Atlanta, Georgia.

General Procedure for diazo decomposition in the presence of acetylene. A solution of the diazo compound (3 mmol) in dichloromethane (10 ml) was added dropwise over a certain period (10 min to 7 h) to a stirred solution of the acetylene (15 mmol, 5 equiv) and rhodium(II) acetate (0.015g, 0.03 mmol) in dichloromethane (10 ml), and heated under reflux in an argon atmosphere. After heating for an additional 10 min, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica.

Diethyl 1-Butylcyclopropene-3,3-dicarboxylate (3a). The diazo compound was added over 7 h and the crude product was purified by chromatography with ethyl acetate/hexanes (10:90) as solvent to give 3a (54% yield): Rf 0.3 (ethyl acetate/hexanes (10:90)); IR (neat) 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.34 (t, 1H, J = 1.3 Hz), 4.15 (q, 4H, J = 7.5 Hz), 2.54 (dt, 2 H, J = 7.5, 1.3 Hz), 1.61-1.30 (m, 4 H), 1.26 (t, 6 H, J = 7.5 Hz), 0.90 (t, 3 H, J = 7.3 Hz). Anal. Calcd for $C_{13}H_{20}O_4$:C, 64.98; H, 8.39. Found: C, 64.65; H, 8.35.

Ethyl 3-(2-Butyl-1-ethoxycarbonyl-2-cyclopropen-1-yl)-2-propenoate (3b). The diazo compound was added over 10 min and the crude product was purified by chromatography with ether/petroleum ether (20.80) as solvent to give 3b (61% yield): Rf 0.3 (ether/petroleum ether (20:80)); IR (neat) 1700, 1630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.92 (d, 1 H, J = 15.7 Hz), 6.19 (br s, 1 H), 5.47 (s, 1 H, J = 15.7 Hz), 4.17 (q, 4 H, J = 7.1 Hz), 2.46 (br t, 2 H, J = 6.4 Hz), 1.65-1.21 (m, 4 H), 1.29 and 1.27 (2t, 6 H, J = 7.5 Hz), 0.90 (t, 3 H, J = 7.1 Hz). LRMS, m/z (relative intensity) 266 (M$^+$, 17), 237 (49), 209 (22), 193 (100).

Ethyl 3-(2-(Dimethylethyl)-1-ethoxycarbonyl-2-cyclopropen-1-yl)-2-propenoate (3c). The diazo compound was added over 20 min, followed by further heating for 40 min, and the crude product was purified by chromatography with either/petroleum ether (20:80) as solvent to give 3c (46% yield): Rf 0.5 (ether/petroleum ether (20:80)); IR (neat) 1710, 1630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.95 (d, 1 H, J = 15.5 Hz), 6.10 (s, 1 H), 5.55 (d, 1 H, J = 16.0 Hz), 4.19 and 4.15 (2q, 4 H, J = 7.1 Hz), 1.28 and 1.25 (2t, 6 H, J = 7.1 Hz), 1.16 (s, 9 H). LRMS, m/z (relative intensity) 266 (M$^+$, 3), 251 (11), 237 (5), 221 (11), 193 (59), 177 (60), 163 (17), 147 (100), 119 (89), 105 (56), 91 (52), 77 (44), 57 (43).

1-(2-Methyl-5-phenyl-3-furanyl)ethanone (4e). The diazo compound was added over 10 min and the crude product was purified by chromatography with ether/petroleum ether as solvent to give 4e (28% yield): Rf 0.5 (ether/petroleum ether (20:80)); m.p. 51-5°C; IR (Nujol) 1680, 1610, 1580, 1560 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.67 (m, 5 H), 6.84 (s, 1 H), 2.66 (s, 3 H), 2.45 (s, 3 H). LRMS, m/z (relative intensity) 200 (M$^+$, 100), 185 (100), 157 (49), 115 (42), 105 (18), 77 (30); HRMS calcd for $C_{13}H_{12}O_2$ m/z 200.0837, found m/z 200.0847.

Ethyl 2-Methyl-5-phenyl-3-furancarboxylate (4f). The diazo compound was added over 25 min and the crude product was purified by chromatography with ether/petroleum ether (20:80) as solvent to give 4f (45% yield): Rf 0.8 (ether/petroleum ether (20:80)); IR (neat) 1710, 1610, 1570 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.66-7.26 (m, 5 H), 6.89 (s, 1 H), 4.32 (q, 2 H, J = 7.0 Hz), 2.65 (s, 3 H), 1.38 (t, 3 H, J = 7.0 Hz). Anal. Calcd for $C_{14}H_{14}O_3$: C, 68.34; H, 6.37. Found: C, 68.27; H, 6.40.

Diethyl 1-Phenylcyclopropene-3,3-dicarboxylate (3g). The diazo compound was added over 10 min and the crude product was purified by chromatography with ether/petroleum ether (20:80) as solvent to give 3g (68% yield): Rf 0.3 (ether/petroleum ether (20:80)); m.p. 65-6°C; IR (Nujol) 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.66-7.41 (m, 5 H), 6.89 (s, 1 H), 4.20 (q, 4 H, J = 7.2 Hz), 1.24 1 (t, 6 H, J = 7.2 Hz). Anal. Calcd for $C_{15}H_{16}O_4$: C, 67.23; H, 5.21. Found: C, 67.06; H, 5.26.

Ethyl 3-(1-Ethoxycarbonyl-2-phenyl-2-cyclopropen-1-yl)-2-propenoate (3h) and Ethyl 3-(2-Ethoxy-5-phenyl-3-furanyl)-2-propenoate (4h). The diazo compound was added over 10 min, using two equiv. of phenylacetylene, and the crude product was purified by chromatography with ether/petroleum ether (20:80) as solvent to give two products: 4h (6% yield); Rf 0.4 (ether/petroleum ether (20:80)); m.p. 44°C; IR (neat) 1700, 1620, 1580, 1560 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.60-7.17 (m, 6 H), 6.70 (s, 1 H), 6.01 (d, 1 H, J = 15.9 Hz), 4.44 (q, 2 H, J = 7.1 Hz), 4.22 (q, 2 H, J = 7.1 Hz), 1.47 (t, 3 H, J = 7.1 Hz), 1.32 (t, 3 H, J = 7.1 Hz). LRMS, m/z (relative intensity) 286 (M$^+$, 27), 257 (44), 229 (54), 212 (19), 201 (24), 105 (100), 77 (57); HRMS calcd for $C_{17}H_{18}O_4$ m/z 286.1205, found m/z 286.1230. 3h (85% yield): Rf 0.3 (ether/petroleum ether (20:80)); IR (neat) 1700, 1630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.01 (d, 1 H, J = 15.7 Hz), 7.50-7.37 (m, 5 H), 6.80 (s, 1 H), 5.60 (d, 1 H, J = 15.7 Hz), 4.18 and 4.16 (2q, 4 H, J = 7.1 Hz), 1.25 and 1.25 (2t, 6 H, J = 7.1 Hz). LRMS, m/z (relative intensity) 286 (M$^+$, 14), 257 (33), 241 (6), 229 (10), 212 (20), 201 (9), 183 (19), 105 (100), 77 (38).

1-(2-Methyl-5-(4-methoxyphenyl)-3-furanyl)ethanone (4i) The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether (20:80) as solvent, followed by trituration to give 4i (52% yield): Rf 0.2 (ether/petroleum ether (20:80)); m.p. 88-92°C; IR (Nujol) 1670, 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.57-7.54 (m, 2 H), 6.94-6.90 (m, 2 H), 6.70 (s, 1 H), 3.83 (s, 3 H), 2.64 (s, 3 H), 2.44 (s, 3 H). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.83; H, 6.19.

Ethyl 2-Methyl-5-(4-methoxyphenyl)-3-furancarboxylate (4j). The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether (20:80) as solvent, followed by trituration to give 4j (41% yield); Rf 0.8 (ether/petroleum ether (20:80)); m.p. 54-6°C; IR (Nujol) 1690, 1500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.56 (d, 2 H, J = 9.0 Hz), 6.96 (d, 2 H, J = 9.0 Hz), 6.73 (s, 1 H), 4.30 (q, 2 H, J = 7.5 Hz), 3.83 (s, 3 H), 2.62 (s, 3 H), 1.36 (t, 3 H, J = 7.5 Hz). Anal. Cacld for $C_{15}H_{18}O_4$: C, 69.22; H, 6.20. Found: C, 69.31; H, 6.22.

Ethyl 2-Ethoxy-5-(4-methoxyphenyl)-3-furancarboxylate (4k). The diazo compound was added over 10 min to give the cyclopropene as the crude product. Rearrangement occurred on attempted purification by column chromatography with ether/petroleum ether as solvent to give 4k (53% yield): Rf 0.4 (ether/petroleum ether (20:80)); m.p. 51°C; IR (Nujol) 1700, 1610, 1590, 1510 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.47 (d, 2 H, J = 9.1 Hz), 6.90 (d, 2 H, J = 9.1 Hz), 6.68 (s, 1 H), 4.53 (q, 2 H, J = 7.1 Hz), 4.28 (q, 2 H, J = 7.1 Hz), 3.82 (s, 3 H), 1.51 (t, 3 H, J = 7.1 Hz), 1.35 (t, 3 H, J = 7.1 Hz). Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.20; H, 6.25. Found: C, 66.08; H, 6.28.

Ethyl 3-(2-Ethoxy-5-(4-methoxyphenyl)-3-furanyl)-2-propenoate (4l). The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether (25:75) as solvent to give 4l (43% yield): Rf 0.6 (ether/petroleum ether (25:75)); m.p. 102°C; IR (Nujol) 1690, 1590, 1500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.54 (d, 1 H, J = 15.7 Hz), 7.47 (d, 1 H, J = 9.1 Hz), 6.91 (d, 1 H, J = 9.1 Hz), 6.52 (s, 1 H), 5.99 (d, 1 H, J = 15.7 Hz), 4.43 (q, 2 H, J = 7.1 Hz) 4.23 (q, 2 H, J = 7.1 Hz), 3.83 (s, 3 H), 1.47 (t, 3 H, J = 7.1 Hz), 1.32 (t, 3 H, J = 7.1 Hz). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.27; H, 6.40.

1-(2-Methyl-5-(3,4-dimethoxyphenyl)-3-furanyl)ethanone (4m). The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether (20:80) as solvent, followed by trituration with pentane to give 4m (28% yield); Rf 0.1 (ether/pet ether 20:80); m.p. 79-83°C; IR (Nujol) 1670, 1600, 1550, 1500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.21 (dd, 1 H, J = 8.3, 2.1 Hz), 7.14 (d, 1 H, J = 2.1 Hz), 6.86 (d, 1 H, J = 8.3 Hz), 6.70 (s, 1 H), 3.93 (s, 3 H), 3.88 (s, 3 H), 2.63 (s, 3 H), 2.43 (s, 3 H). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.04; H, 6.28.

Ethyl 2-Methyl-5-(3,4-dimethoxyphenyl)-3-furancarboxylate (4n). The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether (20:80) as solvent, followed by trituration with pentane to give 4n (69% yield): Rf 0.4 (ether/petroleum ether (20:80)); m.p. 64-9°C; IR (Nujol) 1720, 1610, 1570, 1510 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.20 (dd, 1 H, J = 8.5, 2.2 Hz), 7.13 (d, 1 H, J = 2.2 Hz), 6.87 (d, 1 H, J = 8.5 Hz), 6.87 (d, 1 H, J = 7.7 Hz), 6.75 (s, 1 H), 4.31 (q, 2 H, J = 7.0 Hz), 3.94 (s, 3 H), 3.90 (s, 3 H), 2.64 (s, 3 H), 1.36 (t, 3 H, J = 7.0 Hz). Anal. Cacld for $C_{16}H_{18}O_5$: C, 66.20; H, 6.25. Found: C, 66.27; H, 6.26.

Ethyl 2-Ethoxy-5-(3,4-dimethoxyphenyl)-3-furancarboxylate (4o). The diazo compound was added over 10 min to give the cyclopropene as the crude product. Rearrangement occurred on attempted purification by column chromatography with ether/petroleum ether (20:80) to give 4o (72% yield): Rf 0.2 (ether/pet ether 20:80), m.p. 59-65°C; IR (Nujol) 1660, 1580, 1570, 1500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.11 (dd, 1 H, J = 8.3, 2.0 Hz), 7.01 (d, 1 H, J = 2.0 Hz), 6.85 (d, 1 H, J = 8.3 Hz), 6.70 (s, 1 H), 4.52 (q, 2 H, J = 7.1 Hz), 4.28 (q, 2 H, J = 7.1 Hz), 3.91 (s, 3 H), 3.88 (s, 3 H), 1.47 (t, 3 H, J = 7.1 Hz), 1.34 (t, 3 H, J = 7.1 Hz). Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found C, 63.77; H, 6.31.

Ethyl 3-(2-Ethoxy-5-(3,4-dimethoxyphenyl)-3-furanyl)-2-propenoate (4p). The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether (30:70) as solvent to give 4p (54% yield): Rf 0.2 (ether/petroleum ether (30:70)); m.p. 107-12°C; IR (Nujol) 1690, 1620, 1570, 1510 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54 (d, 1 H, J = 16.0 Hz), 7.12 (dd, 1 H, J = 8.4, 2.1 Hz), 7.03 (d, 1 H, J = 2.1 Hz), 6.87 (d, 1 H, J = 8.4 Hz), 6.55 (s, 1 H), 6.01 (d, 1 H, J = 16.0 Hz), 4.44 (q, 2 H, J = 7.1 Hz), 4.23 (q, 2 H, J = 7.1 Hz), 3.93 (s, 3 H), 3.90 (s, 3 H), 1.47 (t, 3 H, J = 7.1 Hz), 1.32 (t, 3 H, J = 7.1 Hz). Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.61; H, 6.44.

2-Phenyl-4-oxo-6,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (6a).[10] The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether as solvent to give 6a (27% yield); Rf 0.3 (ether/petroleum ether (20:80)); m.p. 102-5°C; IR (Nujol) 1680, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.67-7.25 (m, 5 H), 6.89 (s, 1 H), 2.82 (s, 2 H), 2.40 (s, 2 H), 1.17 (s, 6 H).

2-(4-Methoxyphenyl)-4-oxo-6,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (6b). The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether (20:80) as solvent to give 6b (15% yield): Rf 0.2 (ether/petroleum ether (20:80)); m.p. 134-7°C; IR (Nujol) 1670, 1610, 1590, 1580, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.58 (d, 2 H, J = 8.7 Hz), 6.93 (d, 2 H, J = 8.7 Hz), 6.74 (s, 1 H), 3.83 (s, 3 H), 2.80 (s, 2 H), 2.40 (s, 2 H), 1.56 (s, 6 H). Anal. Cacld for $C_{17}H_{18}O_3$: C, 75.53; H, 6.70. Found: C, 75.31; H, 6.73.

2-(3,4-Dimethoxyphenyl)-4-oxo-6,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (6c). The diazo compound was added over 10 min and the crude product was purified by column chromatography with ether/petroleum ether (20:80) as solvent to give 6c (40% yield): Rf 0.1 (ether/petroleum ether (20:80)); m.p. 146-50°C; IR (Nujol) 1660, 1590, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (d, 1 H, J = 2.3 Hz), 7.17 (dd, 2 H, J = 8.1, 2.3 Hz), 6.89 (d, 1 H, J = 8.1 Hz), 6.76 (s, 1 H), 3.94 (s, 3 H), 3.90 (s, 3 H), 2.81 (s, 2 H), 2.39 (s, 2 H), 1.17 (s, 6 H). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.91; H, 6.75.

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