Tetrahedron Vol 43, No. 19, pp. 4265 to 4270, 1987
Printed in Great Britain.

0040-4020/87 $3.00 + .00

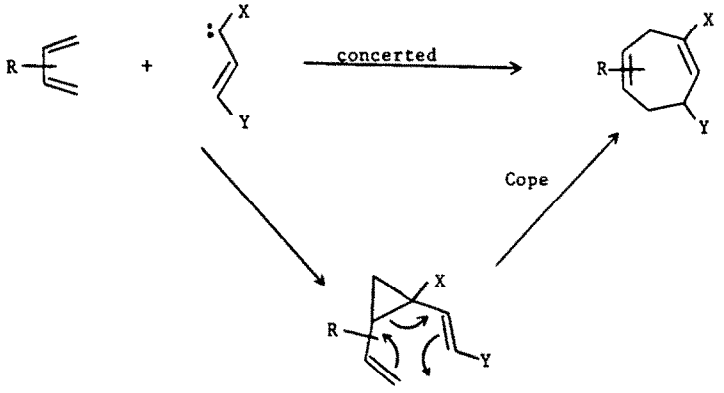
MECHANISTIC ASPECTS OF FORMAL [3 + 4] CYCLOADDITIONS BETWEEN VINYLCARBENOIDS AND FURANS

Huw M.L. Davies*, David M. Clark, David B. Alligood
and Glenn R. Eiband
Department of Chemistry, Wake Forest University,
Winston-Salem, North Carolina 27109

(*Received in USA* 19 *March* 1987)

Abstract: Rhodium(II) acetate catalyzed decomposition of diethyl 4-diazo-2-pentenedioate resulted in the formation of a vinylcarbenoid, which underwent formal [3 + 4] cycloaddition reactions with a series of furans. The most likely mechanism for these reactions involves cyclopropanation followed by a Cope rearrangement of the divinylcyclopropane intermediate.

As five- to seven-membered rings are ubiquitous in natural products, there has been considerable effort to develop flexible synthetic methods to these systems. Even though most five-[1] and six-membered[2-5] rings can now be readily prepared, the synthesis of seven-membered rings is not as straightforward. Ring strain and entropy effects are the main reasons for this, but also, as the ring is more flexible, effective stereocontrol is hard to achieve. The [3 + 4] cycloaddition of allyl cations with dienes has rapidly become a useful method for the synthesis of seven-membered rings.[6,7] Conceptually, the reaction of vinylcarbenoids with dienes could also lead to highly functionalized cycloheptadienes by means of either a concerted process or via divinylcyclopropane intermediates (Scheme 1). We are presently engaged in a program to determine the feasibility of such reactions, and in this paper we describe our completed study on the use of furans to capture vinylcarbenoids.[8]

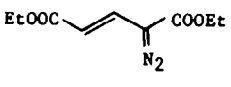


Scheme 1

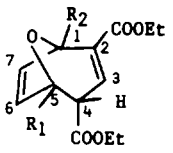
Simple vinylcarbenes undergo a facile rearrangement to cyclopropenes.[9] When appropriately functionalized a variety of other rearrangements are also possible.[9,10] Even though some vinyl carbenes can be efficiently trapped by furans, competing side reactions generally occur.[11] Therefore, more stable vinylcarbenes would be required to ensure effective intermolecular reactions with dienes. One approach, developed by Boger,[12] involves the introduction of electron donating groups into the system. This leads to a nucleophilic vinylcarbene which undergoes efficient reactions with electron deficient alkenes and dienes. Our method[8] to generate stabilized vinylcarbenes uses metal carbenoid complexes. Such complexes are readily formed by metal catalyzed decomposition of diazo compounds[13] and are more stable than the corresponding free carbenes.

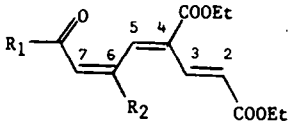
The precursors for our approach, vinyldiazomethanes, are generally considered to be rather elusive, as they tend to spontaneously rearrange to 3H-pyrazoles.[9b,9c,14] However, electron withdrawing substituents next to the diazo group inhibit this rearrangement.[9b] With this in mind, we attempted to prepare vinyldiazomethanes with two or more electron withdrawing groups and found[8] that diethyl 4-diazo-2-pentenedioate 1 is readily formed by diazotization of diethyl glutaconate. Moreover, 1 is indefinately stable at 0° C.

Rhodium(II) acetate catalyzed decomposition of 1 in the presence of a range of furans results in very clean reactions. Two main types of products are formed, namely the desired cycloadducts 2 and the triene side-products 3. As can be seen in Table 1, the ratio of the two products is highly dependent on furan structure. Mono-substituted furans give predominately the triene products, but the [3 + 4] cycloadducts are exclusively formed in the reaction with 2,5-disubstituted furans.



1





2a	R_1 = H, R_2 = H	3a	R_1 = H, R_2 = H
2b	R_1 = CH_3, R_2 = H	3b	R_1 = CH_3, R_2 = H
2c	R_1 = H, R_2 = CH_3	3c	R_1 = OCH_3, R_2 = H
2d	R_1 = CH_3, R_2 = CH_3		
2e	R_1 = $Si(CH_3)_3$, R_2 = CH_3		
2f	R_1 = CH_3, R_2 = $Si(CH_3)_3$		
2g	R_1 = CH_2OCH_3, R_2 = CH_3		
2h	R_1 = CH_3, R_2 = CH_2OCH_3		

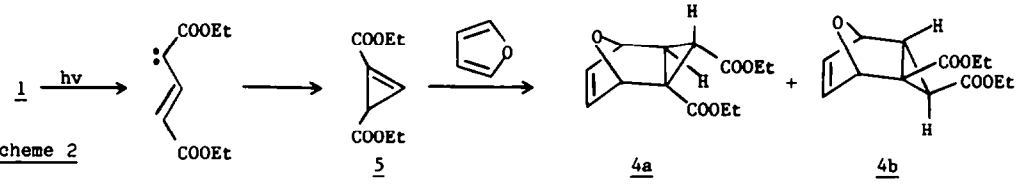
Table 1: Rhodium(II) acetate catalyzed decomposition of 2 in the presence of furans

Substrate	Products (yield,%)	
furan[8]	2a,a' (62)	3a (26)
2-methylfuran[8]	2b (8)	3b (74)
2-methoxyfuran		3c (92)
2,5-dimethylfuran[8]	2d (70)	
2-methyl-5-(trimethylsilyl)furan	2e,f (61)	
2-methoxymethyl-5-methylfuran	2g,h (54)	

The stereospecificity observed in these reactions is quite dramatic. Only the endo cycloadducts are formed, although in the case of 2a some isomerization to the exo isomer 2a' occurs on chromatographic purification. The stereochemical assignment of 2a,a' is based on the coupling constant between H-4 and H-5 (J = 5.8 Hz for the endo isomer, J = 0 Hz for the exo isomer). There is also a characteristic change in the coupling constant between H-3 and H-4 (J = 2.8 Hz for the endo isomer, J = 4.0 Hz for the exo isomer). When the bridgehead position is occupied, as in 2b,d-h, the stereochemical assignment is based on the value of this second coupling constant.[15]

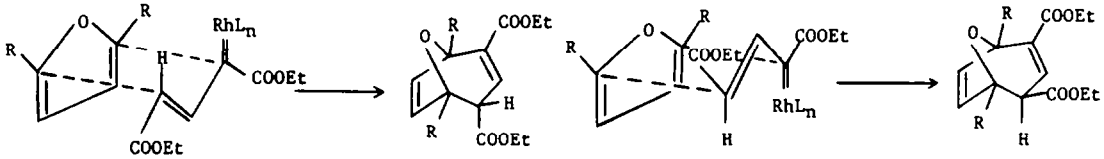
The trienes 3 are also formed as only one isomer. Assignment of the stereochemistry of the disubstituted double bonds in 3 was easily achieved by analysis of the coupling constants, while a NOE difference experiment was required to determine the stereochemistry of the central double bond (strong enhancement of H-6 by irradiation of H-3). The trienes are presumably formed through rearrangement of unstable cyclopropane intermediates,[16] and this raction will be discussed in greater detail later.

As was mentioned earlier, the formation of the desired cycloaddition products 2 was expected to be much more favorable using rhodium-carbenoid complexes, rather than free vinylcarbenes. In order to test this prediction, the photolytic decomposition of 1 was carried out in the presence of furan (Scheme 2). This resulted in the formation of 4a and 4b (2:1 ratio), which are derived from a [4 + 2] cycloaddition of the cyclopropene 5 with furan. This confirms that the free vinylcarbene has a greater propensity to undergo intramolecular cyclization to the cyclopropene 5 than the rhodium carbenoid complex, and in this case occurs prior to capture by furan.



Scheme 2

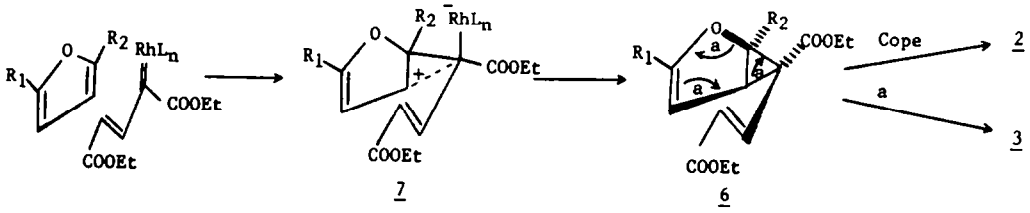
The reaction between 1 and the furans can be envisioned to proceed through two distinct mechanisms. The first of these is a concerted cycloaddition with the vinylcarbenoid acting as a delocalized 2π system[17] (Scheme 3). The observed stereospecificity can be explained by assuming a transition state similar to the one described by Hoffmann[18] for the reaction of allyl cations with dienes. The reaction could proceed through either a boat or a chair transition state. The boat form should be the favored transition state due to secondary orbital interactions, and this would result in the formation of the observed endo products. However, the remarkable changes in product distribution with the different substrates and the total stereospecificity in these reactions is difficult to rationalize by this mechanism.



Scheme 3

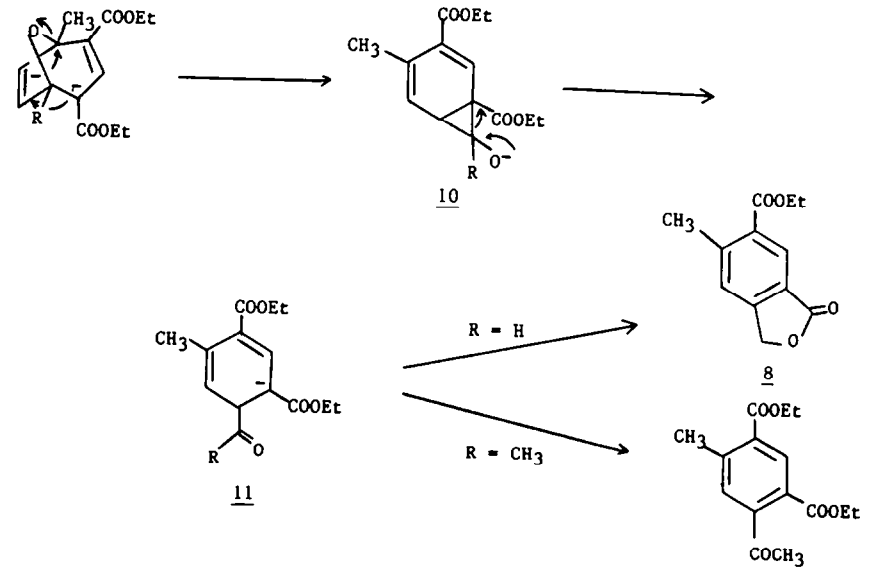
A more plausible mechanism involves initial cyclopropanation to form 6 followed by a Cope rearrangement to give the observed cycloadducts (Scheme 4). Only cis divinylcyclopropanes can undergo a Cope rearrangement in a concerted manner,[19] and such a rearrangement of 6 would give exclusively the endo cycloadducts 2. The formation of the trienes 3 with the observed stereochemistry also requires the intermediacy of the same endo furanocyclopropanes 6. Therefore, we propose that the formation of 2 and 3 proceeds through common intermediates. This remarkable selectivity for the endo product in cyclopropanation reactions involving vinylcarbenes has been reported previously.[11a,11d,12] The formation of only 2b (and none of the regioisomer 2c), and also of only one isomer of the triene products 3b and 3c in these reactions is then easily explained by assuming that cyclopropanation occurs at the least hindered double bond. Also, Wenkert[20] has reported that, in contrast to furan, the reaction of ethyl diazoacetate with 2,5-dimethylfuran forms a stable furanocyclopropane, which rearranges to a diene only on exposure to acid. Therefore, the furanocyclopropane intermediates from 2,5-disubstituted furans may be incapable of effective rearrangement to trienes, and thus give high yields of the cycloaddition products by a

Cope rearrangement. A variation of this mechanism which cannot be ruled out at this stage is that the products 2 and 3 arise from the dipolar intermediates 7 prior to the actual formation of the furanocyclopropanes 6.[21]



Scheme 4

We have briefly examined the ring opening reactions of the cycloadducts 2 as this could be a useful method for the synthesis of highly functionalized tropones and tropolones. We have found, however, that cycloheptatrienes are not formed in these reactions. For example, treatment of 2b and 2d with DBU as base forms 8 (84% yield) and 9 (50% yield), respectively, while a similar reaction with 2a,a' gives a mixture of products. A reasonable mechanism for the formation of 8 an 9 is given in Scheme 5. On treatment with base, rearrangement occurs to give 10, which then undergoes ring opening to give 11. The probable transition state for the formation of 9 is potentially homoaromatic, and is related to the widely studied carbocyclic system.[22] The further reaction of 11 is dependent on its structure. With 11 (R = CH_3) oxidation occurs to give 9, while with 11 (R = H) an intramolecular oxidation-reduction followed by lactonization occurs, which results in the formation of 8.



Scheme 5

Based on these studies we can conclude that formal [3 + 4] cycloadditions with vinyl carbenoids are indeed feasible. The more reasonable mechanism for these transformations appears be cyclopropanation followed by a Cope rearrangement of the resulting divinylcyclopropanes. Further studies are in progress to determine the full scope of this reaction with other vinyl carbenoids and dienes.

Acknowledgement: Financial support of this work by a William and Flora Hewlett Grant of Research Corporation, the Petroleum Research Fund and the National Science Foundation (CHE 8517881) is gratefully acknowledged. Mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, a National Science Foundation regional instrumentation facility (grant number CHE 8211164). The Bruker AM 300WB was purchased in part with funds from the National Science Foundation (grant number PCM-8313203).

EXPERIMENTAL SECTION

Infrared spectra were determined on a Perkin-Elmer Model 1330 spectrophotometer, and NMR spectra were recorded on a Perkin-Elmer R-32 (90 MHz), a Varian VXR 200 or a Bruker AM 300WB spectrometer. Mass spectral analyses were carried out by the Mid-West Center for Mass Spectrometry at the University of Nebraska-Lincoln. Elemental analyses were carried out by Atlantic Microlab, Inc, Atlanta, Georgia.

Diethyl 4-Diazo-2-pentenedioate (1). Triethylamine (7.9 g, 78 mmol) was added to a stirred solution of diethyl glutaconate (11.2 g, 60 mmol) and p-acetamidobenzenesulfonyl azide[23] (22.2 g, 63 mmol) in acetonitrile (150 ml) at 0°C. After the mixture was warmed to room temperature and stirred for 12 h, the solvent was evaporated under reduced pressure. The residue was triturated with ether/petroleum ether (1:1), filtered, and the solvent was evaporated under reduced pressure. Further purification was carried out on a short silica column with ether/petroleum ether (1:4) as solvent to give 10.7 g (84%) of 1 as an orange gum: IR (neat) 2105, 1720, 1710, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (d, 1 H, J = 16 Hz), 5.72 (d, 1 H, J = 16 Hz), 4.29 (q, 2 H, J = 7 Hz), 4.17 (q, 2 H, J = 7 Hz), 1.30 (t, 3 H, J = 7 Hz), 1.27 (t, 3 H, J = 7 Hz); mass spectrum, m/e (relative intensity) calcd for $C_9H_{12}N_2O_4$ M^+ 212.0814, found M^+ 212.0802 (17), 184 (18), 167 (100), 156 (15), 140 (64), 121 (75), 67 (46).

General Procedure for the Rhodium(II) Acetate Catalyzed Decomposition of 1 in the Presence of Furans. A solution of 1 (1.06 g, 5 mmol) in dichloromethane (10 ml) was added dropwise over 10 min to a stirred mixture of rhodium(II) acetate (0.021 g, 0.05 mmol) and the furan (10-50 mmol) in dichloromethane (5 ml), heated under reflux in an argon atmosphere. After heating for a further 10 min, the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica.

Diethyl 8-Oxabicyclo[3,2,1]octa-2,6-diene-2,4-dicarboxylate (2a,a') and (2E,4E,6Z) Ethyl 4-Ethoxycarbonyl-8-oxooctа-2,4,6-trienoate (3a). Ten equivalents of furan were used and the residue was chromatographed on silica with ether/petroleum ether (10:90 to 30:70) as solvent gradient to give two principal products:

2a,a' (1:1 mixture): 62% yield, pale yellow gum; Rf 0.3 (ether/petroleum ether, 10:90); IR (neat) 1725, 1705, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2 6.71-6.68 (m, 2 H), 5.94 (dd, 1 H, J = 6.0, 1.7 Hz), 5.31 (br d, 1 H, J = 5.8 Hz), 5.15 (br s, 1 H), 4.26-4.12 (m, 4 H), 3.79 (ddd, 1 H, J = 5.8, 2.8, 0.9 Hz), 1.33-1.26 (m 6 H), **2a'** 6.68 (1H, superimposed), 6.60 (dd, 1 H, J = 5.9, 1.6 Hz), 6.09 (dd, 1 H, J = 5.9, 1.9 Hz), 5.30 (br s, 1 H), 5.25 (br s, 1 H), 2.82 (d, 1 H, J = 4.0 Hz), 1.33-1.26 (m, 6 H). Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.83; H, 6.40

3a: 26% yield; Rf 0.15 (ether/petroleum ether, 10:90); IR (neat) 1715, 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.31 (d, 1 H, J = 7 Hz), 8.20 (d, 1 H, J = 12 Hz), 7.58 (d, 1 H, J = 16 Hz), 7.43 (t, 1 H, J = 12 Hz), 6.63 (d, 1 H, J = 16 Hz), 6.20 (dd, 1 H, J = 12, 7 Hz), 4.40-4.10 (m, 4 H), 1.30 (m, 6 H); **3a** was insufficently stable under chromatographic conditions to be isolated in an analytically pure form.

Purification of the crude product by Kugelrohr distillation gave a 40% yield of **2a**: bp 110 °C (0.5 mm Hg).

Endo Diethyl 5-Methyl-8-oxabicyclo[3,2,1]octa-2,6-diene-2,4-dicarboxylate (2b) and (2E,4E,6Z) Ethyl 4-Ethoxycarbonyl-8-oxonona-2,4,6-trieneoate (3b). Five equivalents of 2-methylfuran were used and the residue was chromatographed on silica with ether/petroleum ether (10:90 to 25:75) as solvent gradient to give two principal products:

2b: 0.11 g (8% yield); IR (neat) 1735, 1715, 1636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.69 (d, 1 H, J = 2.9 Hz), 6.59 (dd, 1 H, J = 5.8, 1.8 Hz), 5.85 (d, 1 H, J = 5.8 Hz), 5.15 (s, 1 H), 4.26-4.14 (m, 4 H), 3.49 (br d, 1 H, J = 2.9 Hz), 1.68 (s, 3 H), 1.30 (t, 3 H, J = 7 Hz), 1.29 (t, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 168.8, 164.5, 139.4, 137.2, 134.7, 132.0, 84.8, 76.7, 61.2, 60.7, 49.9, 23.5, 14.1, 14.1. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.20; H, 6.83.

3b: 0.98 g (74% yield), yellow gum; IR (neat) 1715, 1705, 1620, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.31 (d, 1 H, J = 11 Hz), 7.66 (d, 1 H, J = 16 Hz), 6.94 (t, 1 H, J = 11 Hz), 6.50 (d, 1 H, J = 16 Hz), 6.39 (d, 1 H, J = 11 Hz), 4.28 (m, 4 H), 2.32 (s, 3 H), 1.36 (t, 3 H, J = 7 Hz), 1.32 (t, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 198.3, 166.4, 165.6, 137.1, 134.4, 133.5, 133.3, 131.6, 125.8, 61.3, 60.6, 31.5, 14.0, 14.0. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 62.88; H, 6.90.

When 2-methylfuran was used as solvent, **2b** and **3b** were formed in 28% and 44% yield, respectively.

(2E,4E,6Z) 1-Ethyl 8-Methyl 4-Ethoxycarbonylocta-2,4,6-trienedioate (3c). Two equivalents of 2-methoxyfuran were used and the residue was chromatographed on neutral alumina with ether/petroleum ether (1:1) as solvent to give 1.30 g (92% yield) of **3c**, gum; IR (neat) 1730, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.49 (d, 1 H, J = 11.8 Hz), 7.66 (d, 1 H, J = 15.8 Hz), 7.15 (t, 1 H, J = 11.7 Hz), 6.53 (d, 1 H, J = 15.8 Hz), 6.09 (dd, 1 H, J = 11.5, 1.2 Hz), 4.32 (q, 2 H, J = 7.1 Hz), 4.25 (q, 2 H, J = 7.1 Hz), 3.79 (s, 3 H), 1.37 (t, 3 H, J = 7.1 Hz), 1.32 (t, 3 H, J = 7.1 Hz). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.65; H, 6.48.

Endo Diethyl 1,5-Dimethyl-8-oxabicyclo[3,2,1]octa-2,6-diene-2,4-dicarboxylate (2d). Five equivalents of 2,5-dimethylfuran were used and the residue was chromatographed on silica with ether/petroleum ether (15:85 to 20:80) as solvent gradient to give 0.98 g (70% yield) of **2d**, gum; IR (neat) 1720, 1705, 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.53 (d, 1 H, J = 2.7 Hz), 6.47 (d, 1 H, J = 5.7 Hz), 5.72 (d, 1 H, J = 5.7 Hz), 4.23-4.13 (m, 4 H), 3.48 (d, 1 H, J = 2.7 Hz), 1.67 (s, 3 H), 1.60 (s, 3 H), 1.30 (t, 3 H, J = 7.1 Hz), 1.27 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 168.7, 165.4, 143.3, 140.7, 133.9, 131.2, 84.9, 83.8, 60.8, 60.3, 49.4, 23.9, 19.7, 13.9. Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.41; H, 7.20.

Endo Diethyl 1-Methyl-5-(trimethylsilyl)-8-oxabicyclo[3,2,1]-octa-2,6-diene-2,4-dicarboxylate (2e) and Endo Diethyl 5-Methyl-1-(trimethylsilyl)-8-oxabicyclo[3,2,1]octa-2,6-diene-2,4-dicarboxylate (2f). Five equivalents of 1-methyl-5-(trimethylsilyl)furan were used and the residue was chromatographed on silica with ether/pentane (3:97 to 10:90) as solvent gradient to give 1.03 g (61% yield) of a mixture of **2e** and **2f**; IR (neat) 1725, 1705, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ major isomer 6.64 (d, 1 H, J = 2.8 Hz), 6.49 (d, 1 H, J = 5.7 Hz), 5.69 (d, 1 H, J = 5.7 Hz), 4.25-4.10 (m, 4H), 3.44 (d, 1 H, J = 2.8 Hz), 1.64 (s, 3 H), 1.32-1.24 (m, 6 H), 0.13 (s, 9 H) minor isomer 6.49 (d, 1 H, J = 5.7 Hz), 6.39 (d, 1 H, J = 2.5 Hz) 5.76 (d, 1 H, J = 5.8 Hz), 4.25-4.10 (m, 4 H), 3.74 (d, 1 H, J = 2.6 Hz), 1.56 (s, 3 H), 1.32-1.24 (m, 6 H) 0.13 (s, 9 H); mass spectrum m/e (relative intensity) 338 (5), 323 (3), 291 (3), 277 (2), 265 (10), 191 (29), 73 (100). Anal. Calcd for $C_{17}H_{26}O_5Si$: C, 60.33; H, 7.74. Found: C, 60.33; H, 7.77.

Endo Diethyl 5-Methoxymethyl-1-methyl-8-oxabicyclo[3,2,1]octa-2,6-diene-2,4-dicarboxylate (2g) and Endo Diethyl 1-Methoxymethyl-5-methyl-8-oxabicyclo[3,2,1]octa-2,6-diene-2,4-dicarboxylate (2h). Five equivalents of 1-methoxymethyl-5- methylfuran were used and the residue was chromatographed on silica with ether/petroleum ether (10:90) as solvent to give 0.83 g (54%

yield) of a mixture of **2g** and **2h**, IR (neat) 1720, 1705, 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ major isomer 6.58 (d, 1 H, J = 2.8 Hz), 6.40 (d, 1 H, J = 5.7 Hz), 5.83 (d, 1 H, J = 5.7 Hz), 4.24-4.09 (m, 4 H), 3.99 (d, 1 H, J = 10.6 Hz), 3.74 (d, 1 H, J = 10.6 Hz), 3.55 (d, 1 H, J = 2.8 Hz), 3.35 (s, 3 H), 1.70 (s, 3 H), 1.32-1.25 (m, 6 H) minor isomer 6.56 (d, superimposed, 1 H), 6.56 (d, 1 H, J = 5.7 Hz), 5.70 (d, 1 H, J = 5.7 Hz), 4.24-4.09 (m, 4 H), 3.96 (d, 1 H, J = 2.8 Hz), 3.64 (m, 2 H), 3.46 (s, 3 H), 1.63 (s, 3 H), 1.32-1.25 (m, 6 H); mass spectrum m/e (relative intensity) calcd for $C_{16}H_{21}O_6$ M + H 309.1368, found M + H 309.1339 (20), 277 (34), 263 (10), 95 (100).

Photolysis of 1 in the Presence of Furan. Formation of 4a and 4b. A solution of **1** (0.53 g, 2.5 mmol) in furan (20 ml) in a pyrex tube was photolyzed for 12 h by means of a Rayonet photochemical reactor. The furan was evaporated under reduced pressure and the residue was chromatographed with ether/petroleum ether (10:90 to 25:75) as solvent gradient to give three principal products:

recovered **1**: 0.11 g (21% yield).

4a: 0.19 g (36% yield); IR (neat) 1735, 1715 cm^{-1}; ^1H NMR ($CDCL_3$) δ 6.69 (dd, 1 H, J = 5.7, 1.5 Hz), 6.57 (dd, 1 H, J = 5.7, 1.6 Hz), 4.98 (d, 1 H, J = 1.5 Hz), 4.84 (d, 1 H, J = 1.6 Hz), 4.19-4.04 (m, 4 H), 3.07 (d, 1 H, J = 4.6 Hz), 2.45 (d, 1 H, J = 4.6 Hz), 1.27 (t, 3 H, J = 7.2 Hz), 1.22 (t, 3 H, J = 7.4 Hz); mass spectrum m/e (relative intensity) calcd for $C_{11}H_{10}O_6$ M^+ - C_2H_5 223.0602, found M^+ - C_2H_5 223.0604 (10), 207 (44), 178 (19), 151 (26), 123 (64), 105 (100), 79 (64).

4b: 0.11 g (21% yield); IR (neat) 1735, 1718 cm^{-1}; ^1H NMR ($CDCL_3$) δ 6.32 (dd, 1 H, J = 5.7, 1.85 Hz), 6.21 (dd, 1 H, J = 5.7, 1.7 Hz), 5.47 (t, 1 H, J = 1.75 Hz), 5.09 (dt, 1 H, J = 4.3, 1.7 Hz), 4.25-4.10 (m, 4 H), 3.09 (t, 1 H, J = 4.4 Hz), 2.31 (d, 1 H, J = 4.5 Hz), 1.27 (t, 3 H, J = 7.2 Hz), 1.26 (t, 3 H, J = 7.7 Hz); mass spectrum m/e (relative intensity) calcd for $C_{11}H_{10}O_6$ M^+ - C_2H_5 223.0602, found M^+ - C_2H_5 223.0604 (3), 207 (40), 178 (59), 151 (30), 123 (84), 105 (100), 79 (24).

Ring opening of 2b by DBU. DBU (0.108 g, 0.71 mmol) was added to a stirred solution of **2b** (0.19 g, 0.71 mmol) in dichloromethane (20 ml) at room temperature, and the mixture was stirred for 15 min. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica with ether/petroleum ether (30:70 to 50:50) as solvent gradient to give 0.13 g (83% yield) of **8** as a white solid, mp 115-119°C; IR (mineral oil) 1760, 1728, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.47 (s, 1 H), 7.37 (s, 1 H), 5.31 (s, 2 H), 4.38 (q, 2 H, J = 7.0 Hz), 2.73 (s, 3 H), 1.40 (t, 3 H, J = 7.0 Hz). Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.38; H, 5.55.

Ring opening of 2d by DBU. DBU (0.152 g, 1 mmol) was added to a stirred solution of **2d** (0.28 g, 1 mmol) in dichloromethane (20 ml) at room temperature, and the mixture was stirred for 18 h. The solvent was then evaporated under reduced pressure and the residue was chromatographed on silica with ether/petroleum ether (20:80 to 40:60) as solvent gradient to give 0.14 g (50% yield) of **9** as a white solid, mp 58-59°C; IR (mineral oil) 1735, 1715, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.43 (s, 1 H), 7.17 (s, 1 H), 4.39 and 4.35 (2q, 4 H, J = 7.1 Hz), 2.65 (s, 3 H), 2.52 (s, 3 H), 1.41 and 1.37 (2t, 6 H, J = 7.1 Hz. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.63; H, 6.53.

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