The extent of reaction of the oxiranes to products under several reaction conditions is summarized in Table I.

The allylic alcohols **16b**, **17a**, and **17b** are new compounds; their ^{1}H NMR spectra and other physical properties are summarized below.

16b: δ 7.23–6.91 (4 H, m), 5.32 (1 H, s), 5.05 (1 H, s), 2.93 (2 H, s), 1.37 (3 H, s); λ_{max} 250–251 nm (ϵ 6800) in 95% ethanol. The molecular weight by mass spectroscopy was 160.0878 ± 0.0007 (calcd 160.0888).

17a: δ 7.68–7.09 (4 H, m), 5.61 (1 H, s), 5.27 (1 H, s), 4.52 (1 H, m), 3.09 (1 H, dt), 2.86 (1 H, dt), 2.05 (2 H, m). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.15; H, 7.61.

17b: 7.43–6.86 (4 H, m), 5.36 (1 H, s), 5.25 (1 H, s), 2.84 (2 H, m), 1.87 (2 H, m), 1.35 (3 H, s); λ_{max} 249–250 nm (ϵ 10900) in 95% ethanol. The molecular weight by mass spectroscopy was 174.1044 ± 0.0022 (calcd 174.1045).

A solution of **9** (108 mg) in 10 mL of acetonitrile containing 85 mg of lithium bromide was refluxed for 2 h on a steam bath and worked up as described above. The product was 1,2-benzocyclohepten-4-one. Its NMR spectrum showed absorption at δ 6.95–7.30 (4 H, m), 3.70 (2 H, s), 2.91 (2 H, dd), 2.55 (2 H, t), 2.00 (2 H, m).

Competition Experiments. Indene 2,3-Oxide (1) vs. 3,4-Dihydronaphthalene 1,2-Oxide (5). To a mixture of **1** (49.9 mg, 0.38 mmol) and **5** (52.4 mg, 0.36 mmol) was added 3.12 mL of a solution of LiBr in acetonitrile (1.025 g/50 mL, 0.236 M). The reaction mixture was stirred for 30 min and transferred to a separatory funnel containing water and ether. The organic layer was separated and concentrated. The NMR spectrum of the residue showed that all of the indene oxide had been converted to 2-indanone, while only 50% of **5** had reacted to form β-tetralone. The reactivity of **I** must therefore be at least twice that of **5**.

1-Methyl-3,4-dihydronaphthalene 1,2-Oxide (6) vs. α-Methylstyrene Oxide. To a mixture of **6** (68.0 mg, 0.425 mmol) and **18** (57.6 mg, 0.430 mmol) was added 2.88 mL of 0.238 M LiBr in dry CH_3CN. The reaction was stirred for 10 min and worked up as above. The NMR spectrum showed that **6** had reacted approximately 2.5 times faster than **18** on the basis of the heights of the methyl proton singlets of the epoxides.

Acknowledgment. We express our thanks to Dr. Ulrich Weiss for valuable discussions.

Registry No. **1**, 768-22-9; **2**, 3413-11-4; **3**, 3199-85-7; **4**, 82482-40-4; **5**, 2461-34-9; **6**, 2042-23-1; **7**, 36099-54-4; **8**, 36099-55-5; **9**, 4443-71-4; **16b**, 82482-41-5; **17a**, 82482-42-6; **17b**, 82482-43-7; **18**, 2085-88-3; **19**, 23355-97-7; 3-methylindene, 767-60-2; 2-methylindene, 2177-47-1; 2,3-dimethylindene, 4773-82-4; 1-methyl-3,4-dihydronaphthalene, 4373-13-1; 2-methyl-3,4-dihydronaphthalene, 2717-44-4; 1,2-dimethyl-3,4-dihydronaphthalene, 5195-39-1; 1,2-benzocyclohepta-1,3-diene, 7125-62-4; LiBr, 7550-35-8.

Studies on the Origin of Dihydrofurans from α-Diazocarbonyl Compounds. Concerted 1,3-Dipolar Cycloaddition vs. Nonsynchronous Coupling in the Copper Chelate Catalyzed Reactions of α-Diazodicarbonyl Compounds with Electron-Rich Olefins

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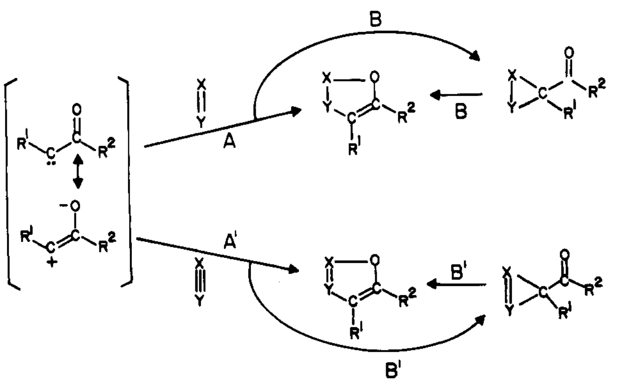
Received September 18, 1981

The copper chelate catalyzed thermolysis of alkyl 2-diazo-3-oxobutyrate (**1**) and of 3-diazo-2,4-pentanedione (**2**) in the presence of several vinyl ethers to give 4-(alkoxycarbonyl)- and 4-acyl-2,3-dihydrofurans is used to probe the mechanism of this transformation in terms of the concerted 1,3-dipolar cycloaddition of the metal–oxocarbene complex vs. the initial formation of the cyclopropane followed by 1,3 sigmatropic rearrangement to the heterocycle. Evidence is presented in favor of a third possibility, namely, that of a nonsynchronous stereospecific addition of the metal–carbene to the olefinic substrate to account for the formation of cyclopropanes, dihydrofurans, and products of apparent allylic C–H insertion and cyclopropane structural isomerization from a common intermediate. This mechanism is supported by a study of the addition of **1b** to benzo[*b*]furan.

The chemistry of photolytically and thermally generated α-ketocarbenes involves the processes of cyclopropane formation, insertion, rearrangement, and dimerization.[1,2] The reactions of alleged metal–carbene complexes derived from reaction of an α-diazocarbonyl system with a transition-metal salt or chelate resemble those of the free carbene, which has given rise to such interpretations as singlet-like and triplet-like "carbenoid species".[1] In addition to the usual cyclopropanes, such heterocyclic compounds as oxazoles,[3-6] dioxoles,[6a] lactones,[6b,c] furans,[7-10] and dihydrofurans[9,11-17] occasionally appear during transformations of these highly reactive compounds, mainly as the

Scheme I



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[1] (a) Kirmse, W. "Carbene Chemistry", 2nd ed; Academic Press: New York, 1971. (b) Moss, R. A. *Sel. Org. Transform.* **1969**, *1*, 35. (c) Cowell, G. W.; Ledwith, A. B. *Q. Rev. Chem. Soc.* **1970**, *24*, 119. (d) Peace, B. W.; Wulfman, D. S. *Synthesis* **1972**, *351*. (e) Marchand, A. P.; Brockway, N. M. *Chem. Rev.* **1974**, *74*, 431. (f) Moss, R. A., Jones, M., Jr., Eds. "Carbenes"; Wiley-Interscience: New York, 1975; Vol. I and II.

[2] Patai, S., Ed. "The Chemistry of Diazonium and Diazo Groups"; Wiley-Interscience: New York,1978; parts I and II.

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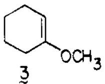
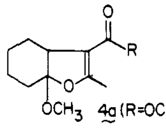
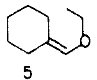
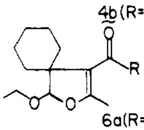
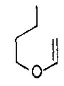
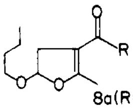
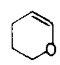
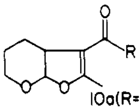
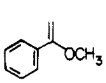
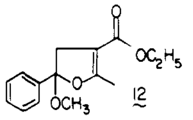
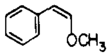
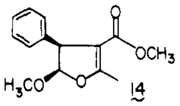
result of formal 1,3- and 1,4-dipolar cycloadditions.[4,17] While the few examples of 1,4-additions suggest that the oxocarbene or metal–carbene complex reacts as in a cyclopropanation,[18] the 1,3-additions have been conceived as the consequence of the α-oxocarbene acting as a 1,3-dipole (routes A and A′ of Scheme I).[4] Alternatively, the five-membered heterocycles may result from the 1,3-sigmatropic rearrangement of initially formed cyclopropanes[19,20] and cyclopropane ketones and esters[21-23] in the reaction medium (routes B and B′ of Scheme I).

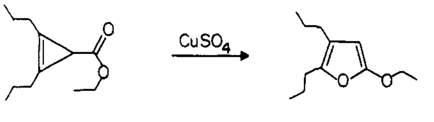
Advocates of the concerted 1,3-dipolar cycloaddition such as Huisgen have accumulated conclusive evidence that such a process occurs in some reactions of α-diazo esters, and α-diazo ketones such as tetrachloroquinone α-diazide, with alkenes, alkynes, nitriles, and ketones.[5a-c] These observations are supported by reports of failure to detect cyclopropane and cyclopropene carbonyl derivatives in reactions from which furans and dihydrofurans are isolated.[9,12] Moreover, the [1 + 2] adducts formed independently of the five-membered heterocycles do not isomerize in reactions in which the carbene is generated either by photolysis or by catalysis with copper or zinc bromide.[12]

Table I. Alkoxydihydrofurans Derived from the Reaction of Compounds 1a,b and 2 with Alkyl Vinyl Ethers under Copper Chelate Catalysis

alkene	diazo compd	adduct	method	yield,[c] %	ref
 3	1a	 4a (R=OCH$_3$)	A	42	a
3	2	4b (R=CH$_3$)	A	6	a
 5	1a	 6a (R=OCH$_3$)	A	25	a
5	2	6b (R=CH$_3$)	A	27	a
 7	1b	 8a (R=OC$_2$H$_5$)	B	75	b
7	2	8b (R=CH$_3$)	B	76	b
 9	1b	 10a (R=OC$_2$H$_5$)	B	67	b
9	2	10b (R=CH$_3$)	B	72	b
 11	1b	 12	B	74	b
 13	1a	 14	B	21	b

[a] Taken from ref 14. [b] This work. [c] Yield of isolated product method A; see ref 14; method B, see Experimental Section.

However, evidence has also been advanced against the hypothesis of 1,3-dipolar cycloaddition. For example, D'Yakonov, who was the first to dectect furan derivatives in reactions of α-diazo esters,[7] initially used this hypothesis to account for the appearance of the heterocycles[7b] but later concluded that furans formed in the copper-catalyzed additions of ethyl diazoacetate to acetylenes resulted from isomerization of initially formed cyclopropene esters.[7a] This view was supported by the facts that furan formation depended on the reaction temperature and the type of copper catalyst used and that the rearrangement of 1,2-di-*n*-propyl-3-(ethoxycarbonyl)cyclopropene to 2,3-di-*n*-propyl-5-ethoxyfuran was catalyzed by copper sulfate. It was found that furans appeared only after cyclopropenyl ketones had accumulated in the reaction mixture and that subsequent heating led to an increase in the amount of furan and a decrease in the amount of cyclopropene.[24] Confirming evidence is found in reports of thermal isomerizations of cyclopropenyl ketones and esters[21] that resemble rearrangements of vinylcyclopropane to cyclopentane[25] and of vinyloxirane to dihydrofuran (eq 1).[19g,26]



(1)

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(18) It has been postulated that dihydrofurans result from the prior formation of a vinyl oxirane at the carbonyl group followed by 1,3-sigmatropic rearrangement in reactions of ethyl diazoacetate with suitable α,β-unsaturated ketones or, alternatively, by the formation of a carbonyl ylide and ring closure at the β carbon. See: Murayama, S. T.; Spencer, T. A. *Tetrahedron Lett.* **1969**, 4479.

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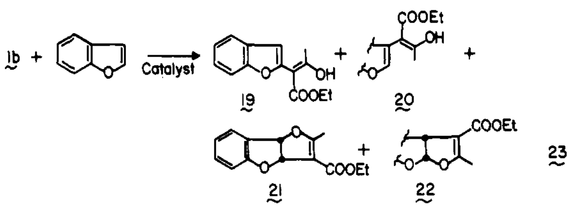
Table II. Selected Proton NMR Signals[a] of the Dihydrofurans Reported

entry	compd	H-C_2	H-C_3	CH_3-C_5	ref
1	**4a**		*d*	2.20 (d, 1.0 Hz)	*b*
2	**4b**		*d*	2.22 (c)	*b*
3	**6a**	5.10 (s)		2.13 (s)	*b*
4	**6b**	5.06 (s)		2.22 (s)	*b*
5	**8a**	5.42 (dd, 8.0, 4.0 Hz)	2.80 (ddq, 15.0, 8.0, 4.0, 1.8 Hz)	2.20 (t, 1.8 Hz)	*c*
6	**8b**	5.42 (dd, 8.0, 4.0 Hz)	2.85 (ddq, 15.0, 8.0, 4.0, 1.8 Hz)	2.18 (t, 1.5 Hz)	*c*
7	**10a**	5.68 (d, 7.5 Hz)	2.90 (m)	2.18 (d, 1.5 Hz)	*c*
8	**10b**	5.62 (d, 7.5 Hz)	2.95 (m)	2.20 (d, 1.5 Hz)	*c*
9	**12**		2.97 (2 dq, 16.5, 2.0 Hz)	2.36 (t, 2.0 Hz)	*c*
10	**14**	5.58 (d, 8.5 Hz)	4.36 (dq, 8.5, 1.8 Hz)	2.35 (d, 1.8 Hz)	*c*
11	**18a**	5.45 (dd, 10.0, 8.0 Hz)	3.05 (ddt, 15.0, 10.0, 7.0, 1.8 Hz)	2.20 (t, 1.8 Hz)	*c*
12	**18b**	4.88 (d, 7.0 Hz)	3.12 (m)	2.22 (d, 1.5 Hz)	*c*
13	**18c**	5.60 (d, 9.5 Hz)	3.12 (m)	2.22 (d, 1.5 Hz)	*c*
14	**21**	6.00 (d, 8.0 Hz)	6.00 (d, 8.0 Hz)	2.24 (d, 1.5 Hz)	*c*
15	**22**	6.56 (d, 8.0 Hz)	4.70 (dq, 8.0, 1.5 Hz)	2.22 (d, 1.5 Hz)	*c*

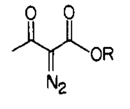
[a] δ, *J* values. [b] Taken from ref 14. [c] This work. [d] Not reported. All spectra were measured in deuteriochloroform solutions.

Scheme II

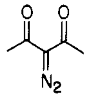


CATALYST	%YIELD OF RECOVERY				
	19	20	21	22	23
$Cu(F_3CCOCH_2COCF_3)_2$	36	6	16	4	3
$Cu(CH_3COCH_2CO_2C_2H_5)_2$	12	–	4	–	6

Previous synthesis of dihydrofurans by the copper-catalyzed reaction of alkyl 2-diazo-3-oxobutyrates (1) or 3-diazo-2,4-pentadione (2) with alkyl vinyl ethers[14] has prompted us to investigate other cycloadditions of 1 and 2 in an attempt to develop evidence pertinent to the controversial cycloaddition mechanism.



1a: R=CH_3
1b: R=C_2H_5

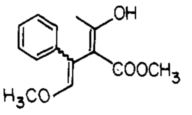


2

Results

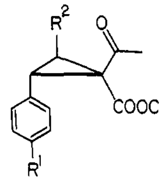
Reactions of 1 and 2 with several vinyl ethers in the presence of bis(hexafluoroacetoacetonato)copper(II) gave dihydrofuran derivatives **8a,b**, **10a,b**, **12**, and **14** only, in generally good yields (Table I). The structures assigned to these substituted dihydrofurans are based on their ^{1}H NMR spectra (Table II) and on their electron impact mass spectra and IR absorptions. All except **12** showed a characteristic NMR peak for the anomeric proton at C_2, and a long-range coupling between the methyl protons at C_5 and the proton at C_3 was evident.[27] Thus the C_5 methyl protons of **8a,b** and **12** showed a triplet at δ 2.18–2.36 (*J* = 1.5–1.8 Hz); this signal became a doublet (*J* = 1.5 Hz) for **10a,b** and **14**, as well as for **18b,c**, **21**, and **22** and a sharp singlet for **6a,b**.

Bis(hexafluoroacetoacetonato)copper(II)[28] catalyst was better than other copper chelates tested as far as yield of heterocycle formed. With this catalyst the formation of dihydrofurans was independent of reaction temperature (70–132 °C), solvents, and molar ratio of catalyst to diazocarbonyl compound (1×10^{-2} to 2×10^{-1}). No cyclopropane or allylic insertion byproducts were formed. Only in the synthesis of **14** from *cis*-methoxystyrene was there a significant byproduct (**15**). The reaction leading to **15** resembles that of dimethyl diazomalonate with enol ethers.[14]

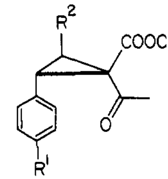


15

In contrast, cyclopropanes **16a** and **17a** were the only products isolated from the copper-catalyzed reaction of **1b** with hydrocarbon alkenes such as styrene.[20] Evidently the alkoxy group plays an important role in directing the addition of the presumed metal–carbene complex regiospecifically to form dihydrofurans.



16a, b, c



17a, b, c

a: $R^1 = R^2 = H$
b: $R^1 = OCH_3$; $R^2 = H$
c: $R^1 = OCH_3$; $R^2 = CH_3$

In an attempt to resolve the question of the independent formation of cyclopropanes and dihydrofurans by [1 + 2] and [1 + 3] cycloadditions, we investigated olefins that might be intermediate between vinyl ethers and alkenes and that might produce both types of adducts in reactions with diazocarbonyl compounds. This objective was not attained by interposing a benzene ring between the alkoxy and olefin functions.[29] Reaction of *p*-methoxystyrene with **1a** gave only cyclopropanes **16b** and **17b** in 1.9:1 ratio (31%). Similar results were obtained with *trans*-anethole, which gave cyclopropanes **16c** and **17c** in 33% yield.[20]

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[26] Vogel, E.; Gunther, D. *Angew. Chem., Int. Ed. Engl.* **1967**, *5*, 385. Pomelet, J. C.; Manisse, N.; Chuche, J. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1970**, *270*, 1894. Paladini, J. C.; Chuche, J. *Tetrahedron Lett.* **1971**, 4383.

[27] Ichikawa, K.; Uemura, S. *J. Org. Chem.* **1967**, *32*, 493. Scribe, M. P.; Delephine, M. M. *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1965**, *261*, 160.

[28] Bertrand, J.; Kaplan, R. *Inorg. Chem.* **1966**, *5*, 489.

[29] For a related operation in the case of α-chlorostyrene see: Alonso, M. E.; Jano, P.; Hernandex, M. I. *J. Org. Chem.* **1980**, *45*, 5229.

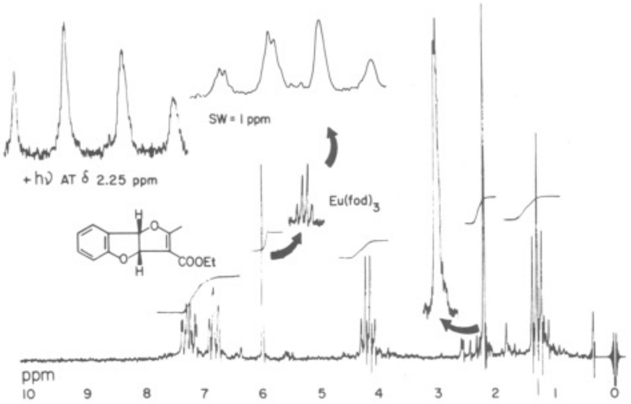
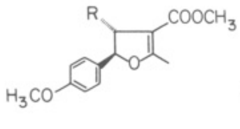
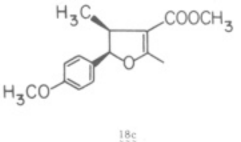


Figure 1. 90-MHz NMR spectrum of compound **21**. Results of double resonance experiments and shift reagent addition.

None of these cyclopropanes could be isomerized to dihydrofurans **18** by refluxing in fluorobenzene with a copper



18a: R= H
18b: R= CH$_3$

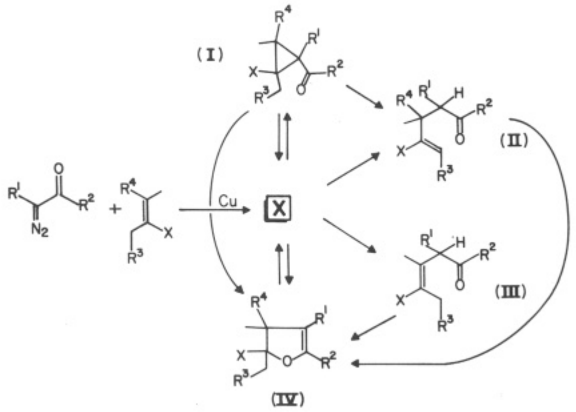


18c

catalyst.[30,31] Only heating mixtures of **16a–c** and of **17a–c** at 200 °C led to the stereoisomeric dihydrofurans **18a** and **18b,c**, respectively, with the anticipated loss of stereochemical identity.[19a,25,32–36]

We then investigated another vinyl ether analogue benzo[*b*]furan, which has been used to trap metal–oxocarbenes, with cyclopropanation at the 2,3 double bond as the dominant process in thermolysis of ethyl diazoacetate.[15,37] Reaction of benzo[*b*]furan with **1b** in refluxing fluorobenzene with bis(hexafluoroacetoacetonato)copper(II) catalyst gave a complex mixture from which four isomeric products with the composition of 1:1 adducts were isolated by thick-layer chromatography in a total yield of 62%. These products were assigned structures **19–22** (Scheme II) on the basis of spectral properties.[38] A small amount of the carbene dimer **23** was also isolated.

Scheme III



The ^{1}H NMR spectrum of the crude product revealed features of all **19–22**, indicating that they had been formed during the reaction and none was the result of the separation procedure. As with **15**, **19** and **20** existed only in their enol forms, probably because of the extended conjugation with the aromatic nucleus. While the structural features of **22** could be established on the basis of the three signals of the angular methines and the vinylmethyl group (Table II, entry 15), interpretation of the ^{1}H NMR spectrum of the isomeric **21** required further elaboration. The vinylic methyl doublet with the characteristic transannular coupling constant (J = 1.5 Hz) strongly suggested a furanoid structure. However, the two angular methines could not be detected as separate signals because of coincidental deshielding effects of the oxivinyl/phenyl and phenoxy/vinyl substituents on each methine. Only a broad singlet integrating for two protons at δ 6.00 was observed. It was reasoned that complexation with europium shift reagents would occur primarily at the carbonyl oxygen rather than at the nuclear oxygens, thus providing a likely differentiation of the two angular methine signals if the assignment of structure **21** was correct. Addition of Eu(fod)$_3$ produced proggressive splitting of the δ 6.00 singlet into clearly defined doublets. The multiplet at lower field showed further coupling as two quartets. This signal callapsed into a simple doublet upon irradiation of the vinylmethyl signal at δ 2.22 (Figure 1), evidence that was deemed to confirm structure **21**.

Bis(ethyl acetoacetonato)copper(II) was less effective as catalyst for the reaction of benzo[*b*]furan with **1b**, yielding only **19** (12%) and **21**(4%) along with 6% of carbene dimer **23**.

Discussion

The interactions in diazocarbonyl–metal–olefin combinations can be considered in terms of at least three successive stages.

(1) Interaction of the Diazocarbonyl Compound and/or the Olefin with the Metal Atom.[39a] Although metal–carbene complexes of chromium, nickel, tungsten, or manganese with diazo compounds have been isolated

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[30] This copper chelate had been treated previously with diazo ester 1 in hot fluorobenzene to promote the formation of the active catalytic species,[1,24] the nature of which remains unknown.

[31] Nevertheless, the smooth transformation of compounds **16** and **17** into dihydrofurans **18a–c** at room temperature upon contact with neutral alumina has been reported from this laboratory.[20]

[32] To be published elsewhere.

[33] Kharasch, M.; Rudy, T. ; Nudenberg, W.; Büchi, G. *J. Org. Chem.* **1953**, *18*, 1030. DePuy, C. H. *Acc. Chem. Res.* **1968**, *1*, 33. Julia, M.; Julia, S.; Guegan, R. *Bull. Soc. Chim. Fr.* **1960**, 1072. Wenkert, E.; Mueller, R. A.; Reardon, E. J., Jr.; Sathe, S. S.; Scharf, D. J. Tosi, G. *J. Am. Chem. Soc.* **1970**, *92*, 7428; Wenkert, E. McPherson, C. A.; Sanchez, E. L.; Webb, R. L. *Synth. Commun.* **1973**, *3*, 255. Wenkert, E.; Buckwalter, B. L.; Sathe, S. S. *Ibid.* **1973**, *3*, 261. Ceccherelli, P.; Pelliciari, R.; Golob, N. F.; Smith, R. A. J.; Wenkert, E. *Gazz. Chim. Ital.* **1973**, *103*, 599. Coates, R. M.; Sandefur, L. O.; Smillie, R. D. *J. Am. Chem. Soc.* **1975**, *97*, 1621. Marshall, J. A.; Ellison, R. H. *J. Org. Chem.* **1975**, *40*, 2070. Rymbrandt, R. H.; Dutton, F. E. *Ibid.* **1975**, *40*, 2282. Corey, E. J.; Ulrich, P. *Tetrahedron Lett.* **1975**, *3685*. Wenkert, E.; Golob, N. F.; Hatch, R. P.; Wenkert, D.; Pelliciari, R. *Helv. Chim. Acta* **1977**, *60*, 1. Wenkert, E.; Chou, K. J.; Hatch, R. P. *Synth. Commun.* **1977**, *7*, 375.

[34] Hanafus, T.; Birladenau, J.; Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 3510. Sims, J. J. *Ibid.* **1965**, *87*, 3511. Sims, J. J.; Selman, L. H. *Tetrahedron Lett.* **1969**, 561. Monti, S. A.; Cowherd, F.; McAninch, T. W. *J. Org. Chem.* **1975**, *40*, 858. Wenkert, E.; de Sousa, J. R. *Synth. Commun.* **1977**, *7*, 457.

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[36] Gajewski, J. J.; Weber, R. J.; Braun, R. Manion, M. L.; Hymen, B. *J. Am. Chem. Soc.* **1977**, *99*, 816.

[37] Wenkert, E.; Alonso, M. E.; Gottlieb, H. E.; Sanchez, E. L.; Pelliciari, R.; Cogolli, P. *J. Org. Chem.* **1977**, *42*, 3945.

[38] The tendency of compounds **19–22** toward uncontrolled decomposition within a few days of storage in the cold and under inert atmospheres precluded their elemental analysis. The exact mass of the corresponding molecular ions is given instead.

[39] (a) Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *43*, C7. (b) See, inter alia: Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857.

and characterized,[39-42] the study of the *presumably analogous* copper complexes is difficult because of their transitory nature.[1] No conclusive evidence is available at the present time.

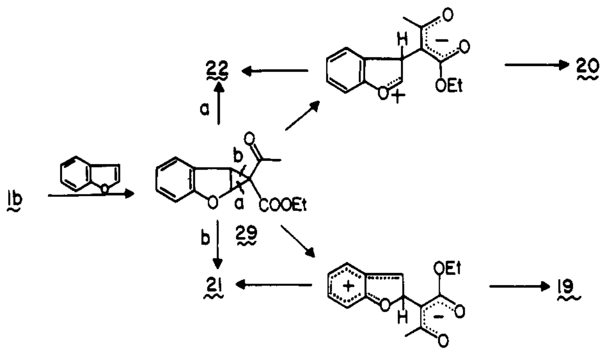
(2) Interaction of the Presumed Complex with the Organic Substrate. Experimental evidence for this step is not yet decisive.[40,42,43]

(3) Coupling of the Two Organic Portions and Further Transformations of the Primary Adducts. This step is complicated by the fact that formation of dihydrofurans IV (Scheme III) may involve (a) isomerization of initially formed cyclopropane keto esters[20] or (b) Lewis acid catalyzed cyclization of olefinic adducts II and III, which have been observed inter alia in additions of diazomalonic esters to olefins and in this work.[4,42]

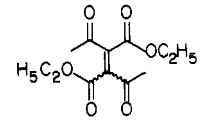
Our data permit some conclusions about the generation of I–IV within the context of step 3. It is risky to claim stereospecificity in a process that furnishes only a 21% yield of an adduct. However, even though the trans isomer of **14** should be stable, the fact that only the cis isomer was detected in the crude reaction product indicates that **1** adds to vinyl ethers stereospecifically to give dihydrofurans, even in the formation of thermodynamically unfavored compounds such as **14**. Moreover, complete retention of the configuration of the starting olefin is seen in the cyclopropanation reactions of **1**, as shown by the synthesis of **16c** and **17c**. This result is similar to other copper-catalyzed cyclopropanations of α-diazocarbonyl compounds with olefins.[29,44,45] Following Skell's postulation[46] this observation has been interpreted in terms of a concerted addition of a singlet carbene to the substrate with a synchronous formation of the two carbon–carbon bonds in cyclopropanations or of the C–C and C–X bonds in the formation of heterocycles. In the latter case, the carbene or metal–carbene complex presumably acts as a 1,3-dipole. An alternative suggestion has been made that the formation of the two bonds is nonsynchronous and that the second bond is formed at a rate greater than that of bond rotation in the intermediate.[47]

In either case, the stereospecific formation of cyclopropanes and dihydrofurans from **1** and **2** rules out the intervention of pyrazoline intermediates, since these compounds are known to rearrange thermally to cyclopropanes in a nonstereospecific fashion,[1a,18,19] even at temperatures as low as 30 °C.[49b] Although thermal isomerization of cyclopropane keto esters to dihydrofurans in the reaction system is conceivable, it is known that such a process would occur with loss of the stereochemical identity of the olefin.[19f,25] In fact, the pyrolysis of **16c** and **17c** gave dihydrofurans of mixed stereochemistry. Thus, the stereospecific formation of the dihydrofurans reported here is evidence against such isomerization during the reaction progress.

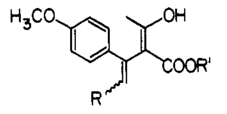
Scheme IV



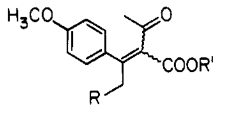
The possibility of a copper-catalyzed stereospecific rearrangement of I into II, III, or IV is negated by our observation that **16b–17b** and **16c–17c** are not isomerized to dihydrofurans **18** or to their structural isomerization products **24** and **25** on prolonged refluxing in fluorobenzene containing the copper catalyst.[30] Moreover, we did not detect any cyclopropanes during early stages of the dihydrofuran-forming reaction. Additional proof comes from the predominance of compound **27** during the acid-catalyzed ring opening of cyclopropane ester **26**, in which the ratio of **27** to **28** was 4:1.[37] If a cyclopropane intermediate such as **29** had preceded adducts **19–22** (Scheme IV), a ratio of **29**/**19** much higher than the 1:6 we found would have been expected. We conclude that the intervention of a cyclopropane adduct in the reaction of **1** with benzo[*b*]furan is unlikely and that this hypothesis probably applies to reactions of **1** with other vinyl ethers.



23

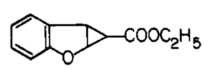


24a,b

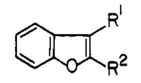


25a,b

a: R= H
b: R= CH_3



26



27: R^1= CH_2COOEt; R^2= H
28: R^1= H; R^2= CH_2COOEt

The copper-assisted or the thermally induced cyclization of adducts II and III can also account for the formation of dihydrofurans. The fact that **19** and **21** are formed in larger amounts than **20** and **22** might suggest that they are interconvertible, although their independent generation from a common intermediate other than cyclopropane **29** is also possible. Only the latter interpretation appears correct in view of our failure to interconvert **19** and **21** by extended refluxing in aromatic solvents containing copper chelates that had been treated first with diazo ester **1**.

These results can be interpreted by assuming that the copper-catalyzed addition of **1** and **2** to olefins proceeds in stepwise fashion (Scheme V). A carbon–carbon bond is formed initially between the carbon atom that carried the diazo function and the negative end of the olefin. The zwitterion VIa (or its copper-stabilized equivalent) thus formed could then undergo five different processes: (1) cyclization to cyclopropane Ia (k_2) by consolidation of the

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(40) Wulfman, D. S. *Tetrahedron* **1976**, *32*, 1231

(41) Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.

(42) Wulfman, D. S.; Peace, B. W. *J. Chem. Soc. C* **1971**, 1360.

(43) Alonso, M. E.; Gomez. M. *Tetrahedron Lett.* **1979**, *2763*.

(44) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F., in ref 2, Chapter 18, p 821.

(45) Dave. V.; Warnoff, E. W. *Org. React.* **1970**, *18*, 217. See also: Takaya, H.; Suzuki, T.; Kumagai, Y.; Hosoya, M.; Kawauchi, H.; Noyori, R. *J. Org. Chem.* **1981**, *46*, 2854.

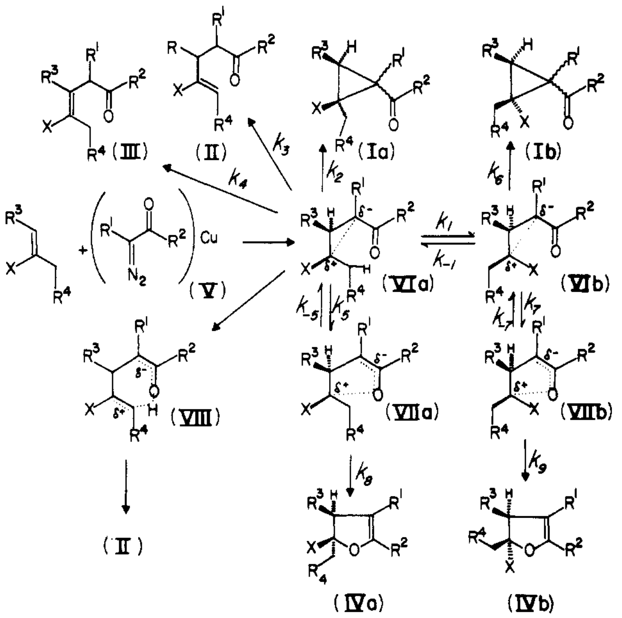
(46) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496, 6427.

(47) Gaspar, P. P.; Hammond, G. S., in ref 1f, Vol. 2, Chapter 6, p 293.

(48) (a) Van Auken, T. V.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 3736. (b) Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *Ibid.* **1977**, *99*, 2108.

(49) The conversion of pyrazolines into cyclopropanes has been known for many years[1], and in some cases their transformation into dihydrofurans and other closely related five-membered heterocycles has been actually observed or postulated.[44]

Scheme V



second C–C bond; (2) cyclization to dihydrofuran IVa (k_6) by trapping the center of low electron density with the carbonyl oxygen in VIIa; (3) 1,4-proton transfer to yield II (k_3); (4) 1,2-proton transfer to yield III (k_4); (5) rotational equilibration with VIb leading to isomerized cyclopropane Ib and dihydrofuran IVb (k_1). The relative values of k_1 and k_6 would depend on the degree of stabilization of the negative center by electron-withdrawing groups in the diazo compound and of the positive center by electron donors in the olefin. Both of these factors would contribute to a nonsynchronous mechanism. The degree of stereospecificity of the reactions leading to cyclopropanes and to dihydrofurans should be a function of the balance among k_1, k_2, and k_6. The achievement of rotational equilibrium between VIa and VIb must be considerably slower than the formation of the second C–C or C–X bond.

Finally, the effect of electron-donor substituents in the olefin should favor the regiospecificity observed in the location of the alkoxy group in the product heterocycle.[50] Efforts to understand more deeply the entire addition process continue in our laboratory.

Experimental Section

Infrared spectra were measured on a Perkin-Elmer 337 spectrophotometer in sodium chloride cells. NMR spectra were obtained with a Varian EM-390 spectrometer operating at 90 MHz, with tetramethylsilane as internal standard and in carbon tetrachloride solutions unless otherwise stated. Electron-impact mass spectra were obtained with a DuPont spectrometer, Model 21-492, and exact masses were measured in a AEI-Kratos MS-30 double-beam instrument. Yields were calculated with respect to the diazo compound. Alkyl 2-diazo-3-oxobutyrates (**1a,b**)[51] and 3-diazo-2,4-pentanedione[52] were prepared from alkyl acetoacetates and 2,4-pentanedione, respectively, by treatment with tosyl azide as described previously.[14]

General Method for the Synthesis of Dihydrofurans from 1a,b and 2. A solution of the diazo compound (20 mmol) and freshly distilled vinyl ether (30 mmol) in dry fluorobenzene (30 mL) was added at a rate of 4 drops/min to a stirred refluxing suspension of bis(hexafluoroacetoacetonato)copper(II) (6 × 10^{-4}mol) in fluorobenzene (2 mL) under a nitrogen atmosphere. After the addition was complete, heating was continued until total disappearance of the C=N$_2$ IR band at 2150 cm^{-1}. The mixture was then cooled to 5 °C and passed through a short column of neutral alumina (activity III) to remove inorganic salts, and solvents were evaporated. The remaining crude material was further purified by vacuum distillation or chromatography.

2-*n*-Butoxy-4-(ethoxycarbonyl)-5-methyl-2,3-dihydrofuran (8a). From ethyl 3-oxo-2-diazobutyrate (**1b**) (3.12 g) and *n*-butyl vinyl ether (3.0 g) 3.42 g of **8a** (75%) was obtained as a colorless oil: bp 100–105 °C (bath, 0.4 torr); IR (neat) 2960 (s), 2870 (s), 1715 (s), 1669 (s), 1390 (m), 1260 (s), 1230 (s) 1180 (s), 1080 (s), 950 (s), 905 (s), 755 (s) cm^{-1}; NMR δ 0.92 (t, 3 H, J = 6.5 Hz, $CH_3(CH_2)_3$), 1.28 (t, 3 H, J = 7.0 hZ, $COOCH_2CH_3$), 1.25–1.75 (m, 4 H, $(CH_2)_2$), 2.20 (t, 3 H, J = 1.8 Hz, $CH_3C{=}$, 2.70 (2 dq, 2 H, J_1 = 15.0, J_2 = 8.0, J_3 = 4.0, J_4 = 1.8 Hz, CH$_2$ of C$_4$), 3.59 (m, 2 H, CH_2OCH_3), 4.10 (q, 2 H, CH_2OCO), 5.42 (dd, 1 H, J_1 = 8.0, J_2 = 4.0 Hz, anomeric proton at C$_2$); mass spectrum, *m/e* (%) 228 (M$^+$, 18), 183 (M$^+$ – OEt, 21), 182 (M$^+$ – HOEt, 35),[53] 155 (M$^+$ – OC_4H_9, 23), 154 (M$^+$ – HOC_4H_9, 16), 126 [$HCOCH_2C(CO)CH_3^+$, 100].

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.12; H, 8.84; O, 28.05. Found: C, 62.95; H, 8.71; O, 27.95.

4-Acyl-5-methyl-2-*n*-butoxy-2,3-dihydrofuran (8b). From 3-diazo-2,4,-pentanedione (**2**) (2.52 g) and *n*-butyl vinyl ether (3.0 g), 3.01 g (76%) of **8b** was obtained by vacuum distillation as a colorless liquid, bp 100–105 °C (bath, 0.2 torr); IR (neat) 2950 (s), 2935 (s), 2850 (m), 1705 (s), 1600 (s), 1490 (s), 1460 (s), 1230 (s), 1190 (s), 1110 (s), 920 (s) cm^{-1}; NMR δ 0.92 (t, 3 H, J = 6.5 Hz, $CH_3(CH_2)_3$), 1.10–1.74 (m, 4 H, $(CH_2)_2$), 2.10 (s, 3 H, CH_3CO), 2,18 (t, 3 H, J = 1.5 Hz, $CH_3C{=}$), 2.85 (2 dq, 2 H, J_1 = 15.0, J_2 = 8.0, J_3 = 4.0, J_4 = 1.5 Hz, CH$_2$ of C$_3$), 3.60 (m, 2 H, CH_2O), 5.42 (dd, 1 H, J_1 = 8.0, J_2 = 4.0 Hz, anomeric proton at C$_2$); mass spectrum, *m/e* (%) 198 (M$^+$, 18), 125 (M$^+$ – OC_4H_9, 13), 124 (M$^+$ – HOC_4H_9, 22), 113 (24), 109 (36), 43 (100).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.62; H, 9.16; O, 24.33. Found: C, 66.49; H, 9.07; O, 24.13.

***cis*-2-Methyl-3-(ethoxycarbonyl)-1,8-dioxabicyclo[4.3.0]non-2-ene (10a).** From **1b** (1.6 g) and freshly distilled dihydropyran (1.3 g) with chlorobenzene as solvent (20 mL), 1.43 g (67%) of pure **10a** was obtained after vacuum distillation; bp 98–100 °C (bath, 0.2 torr); IR (neat) 2930 (s), 1710 (s), 1640 (s), 1390 (s), 1260 (s), 1220 (s), 1140 (s), 1090 (s), 990 (s), 930 (s) cm^{-1}; NMR δ 1.22 (t, 3 H, J = 7.0 Hz, $COOCH_2CH_3$), 1.40–1.90 (m, 4 H, $(CH_2)_2$), 2.18 (d, 3 H, J = 1.5 Hz, $CH_3C{=}$), 2.99 (m, 1 H, CH of C$_4$), 3.70 (m, 2 H, CH_2OCH), 4.10 (q, 2 H, J = 7.0 Hz, $COOCH_2CH_3$), 5.68 (d, 1 H, J = 7.5 Hz, anomeric proton at C$_9$); mass spectrum, *m/e* (%) 212 (M$^+$, 10), 167 (M$^+$ – OEt, 18), 166 (M$^+$ – HOEt, 69)[53] 138 (11), 124 (34), 43 (100).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.23; H, 7.60; 0, 30.16. Found: C, 62.22; H, 7.64; O, 30.00

***cis*-2-Methyl-3-acyl-1,8-dioxabicyclo[4.3.0]non-2-ene (10b).** From diazo ketone **2** (1.3 g) and dihydropyran (1.3 g), 1.3 g (72%) of **10b** was obtained as a thick undistillable oil. Purification was performed by column chromatography through neutral alumina (activity II), with methylene chloride as solvent; IR (neat) 2940

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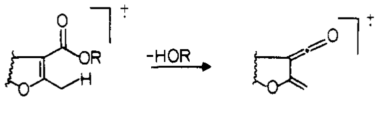
(50) Although the generalization of Scheme V to the transition-metal-assisted addition reactions of α-diazocarbonyl compounds other than **1** and **2** to alkenes is tempting, it will be necessary to collect formal evidence for these other compounds before a universal picture can be drawn. Also, it would be pretentious to assume that our views on a nonsynchronous addition invalidate Huisgen's solid position on the concerted 1,3-dipolar cycloaddition of some oxocarbenes. Our findings only stress the need to limit schemes and mechanistic interpretations to particular cases and to avoid fruitless extrapolations and generalizations when the availabile data is only fragmentary.

(51) Regitz, M.; Hocker, J.; Liedhegener, A. *Org. Prep. Proced.* **1969**, *1*, 99.

(52) Hendrickson, J. B.; Wolf, W. A. *J. Org. Chem.* **1968**, *33*, 3610.

(53) The loss of ethanol from the molecular ion, as indicated by the appearance of the corresponding metastable peak, can be explained on the assumption that 1,5-hydrogen migration from the methyl group at C$_5$ to the ester oxygen to give species **30** takes place under electron impact. Peaks corresponding to this transition were also observed in the mass spectra of compounds **10a**, **12**, and **22**.



30

(s), 1710 (s), 1610 (s), 1400 (s), 1235 (s), 1160 (s), 1140 (s), 1038 (s), 920 (s) cm^{-1}; NMR δ 1.50–1.70 (m, 4 H, $(CH_2)_2$), 2.12 (s, 3 H, CH_3CO), 2.20 (d, 3 H, J = 1.5 Hz, CH_3C=), 2.90 (m, 1 H, CH of C_4), 3.72 (m, 2 H, CH_2O), 5.62 (d, 1 H, J = 7.5 Hz, anomeric proton at C_9); mass spectrum m/e (%) 182 (M^+, 98), 139 (M^+ – CH_3CO, 62), 120 (58), 97 (44), 69 (17), 43 (100).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.90; H, 7.75; O, 26.35 Found: C, 65.71; H, 7.62; O, 26.30.

2-Methoxy-2-phenyl-4-(ethoxycarbonyl)-5-methyl-2,3-dihydrofuran (12). The reaction of **1b** (1.70 g) and 1-methoxy-1-phenylethylene (4.2 g) furnished a brown oily crude material which was fractionally distilled in vacuo to give a first fraction bp 34–5 °C (0.4 torr) (3.08 g) of unreacted enol ether and a second fraction bp 123–5 °C (0.2 torr) of pure **12** (2.212 g, 74% yield) as a slightly yellowish oil: IR (neat) 2990 (s), 2940 (s), 1720 (s), 1665 (s), 1290 (s), 1220 (s), 1100 (s), 1080 (s), 1065 (s), 1045 (s), 1028 (s), 950 (s), 760 (s), 700 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.24 (t, 3 H, J = 7.0 Hz, $COOCH_2CH_3$), 2.36 (t, 3 H, J = 2.0 Hz, CH_3C=), 3.13 (2 dq, 2 H, J_1 = 14.4, J_2 = 2.0 Hz, CH_2 of C_3), 3.20 (s, 3 H, CH_3O), 4.17 (q, J = 7.0 Hz, $COOCH_2CH_3$), 7.30–7.55 (m, 5 H, Ar methines).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.67; H, 6.92; O, 24.41. Found: C, 68.79; C, 6.86; O, 24.38.

***cis*-2-Methoxy-3-phenyl-4-(methoxycarbonyl)-5-methyl-2,3-dihydrofuran (14) and Methyl 2-(1-Hydroxyethylidene)-4-methoxy-3-phenyl-3-butenoate (15).** The *cis*-β-ethoxystyrene used in this experiment (Aldrich) contained as much as 7% (GC, SE-30 5%, 12 ft column) of α-methoxystyrene that could not be separated by repeated fractional distillation. Preparation of β-methoxystyrene by a Wittig process[54] using chloromethyl methyl ether and acetophenone not only gave a cis/trans mixture of the desired enol ether but also provided as much as 11% of α-methoxystyrene. Also, a synthesis based on the reaction of phenol and phenethyl bromide[55] gave a stereoisomeric mixture of olefins. Complications to be described below thus resulted from the presence of this contaminant. The reaction of 4.5 g of this mixture and 2.0 g of **1a** gave a complex crude material that was fractionally distilled under vacuum to yield first unreacted enol ether [bp 62–65 °C (0.01 torr)] and further 1.869 g of a mixture containing adduct **14** (41%), the methyl ester of **12** (41%), and **15** (18%) according to the ^1H NMR spectrum. This material was chromatographed by using a Merck Lobar LiChroprep Si-60 (40 - 63 μm) size B column with a 70:29:1 mixture of hexane/methylene chloride/1-butanol. The first eluted compound corresponded to pure 2-methoxy-2-phenyl-5-methyl-2,3-dihydro-3-furoic acid (0.759 g, 22% yield from **1a**),[54] which displayed spectroscopic characteristics similar to **12** except for a signal at δ 3.72 (s, 3 H) in the NMR spectrum corresponding to the methyl ester. Further elution with the same mixture of solvents gave pure **14** (0.741 g, 21% yield from **1a**), as a yellowish oil: bp 122–3 °C (0.01 torr); IR (neat) 2990 (s), 1725 (s), 1660 (s), 1285 (s), 1110 (s), 1060 (s), 1030 (s), 960 (s), 760 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.35 (d, 3 H, J = 1.8 Hz, CH_3C=), 3.38 (s, 3 H, CH_3OCH), 3.51 (s, 3 H, $COOCH_3$), 4.36 (dq, 1 H, J_1 = 8.5 J_2 = 1.8 Hz, C_6H_5CH), 5.58 (d, 1 H, J = 8.5 Hz, H_3COCHO), 7.10–7.40 (m, 5 H, Ar methines).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.71; H, 6.50; O, 25.79 Found: C, 67.79; H, 6.51; O, 25.60

Further elution with 60:39:1 hexane/methylene chloride/1-butanol gave a crystalline material (mp 198–199 °C (hexane)) which was identified as vinyl ether **15** (0.329 g, 9%): IR (KBr) 2950 (s), 1750 (s) 1660 (m), 1450 (s), 1060 (s), 1020 (s), 760 (s), 695 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.70 (s, 3 H, CH_3CO), 3.32 (s, 3 H, CH_3OCH), 3.72 (s, 3 H, $COOCH_3$), 6.09 (s, 1 H, HC=), 7.40 (m, 5 H, Qr methines), 14.15 (s, 1 H, HO of enol form, exchanges with deuterium oxide).

Anal. Calcd for $C_{1j}H_{16}O_4$: C, 67.71; H. 6.50; O, 25.79. Found: C, 67.88; H, 6.57; O, 25.61.

Reaction of 1b with Benzo[*b*]furan. A solution of diazo ester **1b** (1.6 g, 22 mmol) and freshly distilled benzo[*b*]furan (1.8 g, 30 mmol) in dry fluorobenzene (25 mL) was added dropwise at a rate of 4 drops/min to a stirred refluxing suspension of bis(hexafluoroacetoacetonato)copper(II) (200 mg) and benzo[*b*]furan (0.1 g) in fluorobenzene (3 mL). After the addition was complete (nearly 3 h) heating was continued for 2 h until there was complete disappearance of the diazo function. The cold dark brown reaction mixture was passed through a short column filled with neutral alumina (activity IV), and solvents were removed in a rotary evaporator. Then the complex dark residue was purified by thick-layer chromatography as follows: 1.10 g of crude material was placed on six 20 × 20 Si-60 (2 mm) preparative plates, and these were developed with 1:4 petroleum ether/chloroform. Four fractions were separated. The fraction with the highest R_f value was identified as unreacted benzofuran. The second fraction (412 mg) consisted of **19** in admixture with unidentified impurities. Further purification by thick-layer chromatography using 1:4.5 petroleum ether/methylene chloride yielded pure 2-[1-(ethoxycarbonyl)-2-hydroxy-1-propenyl]benzo[*b*]furan (**19**) (396 mg, 36%) as a colorless thick oil: IR (neat) 1740 (s), 1660 (s), 1290 (s), 1285 (s), 1255 (s), 1175 (m), 1015 (m), 995 (m), 910 (m), 885 (m), 750 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.24 (t, 3 H, J = 7.0 Hz, $COOCH_2CH_3$), 2.04 (s, 3 H, CH_3CO), 4.22 (q, 2 H, J = 7.0 Hz, $COOCH_2CH_3$), 6.50 (s, 1 H, proton at C_3), 7.10–7.60 (m, 4 H, nuclear protons), 13.55 (s, 1 H, HO of enol form); mass spectrum, m/e (%) 246 (M^+, 10), 204 (22), 200 (19), 158 (47), 131 (100).

Exact mass calcd for $C_{14}H_{14}O_4$, 246.0892; found: 246.0899.

The third fraction contained **20** and **22** (242 mg) in admixture with several unidentified impurities. This material was chromatographed again on a 20 × 20 Si-60 (2 mm) plate with 3:1 hexane/ethyl ether from which three fractions were collected: the first one was identified as pure 3-[1-(ethoxycarbonyl)-2-hydroxy-1-propenyl]benzo[*b*]furan (**20**) (65.4 mg, 6%) as a colorless oil: IR (neat) 1730 (s), 1650 (s), 1620 (s), 1570 (s), 1450 (s), 1240 (s), 930 (s), 850 (s), 740 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.13 (t, 3 H, J = 7.0 Hz, $COOCH_2CH_3$), 1.91 (s, 3 H, CH_3CO), 4.12 (q, 2 H, J = 7.0 Hz, $COOCH_2CH_3$), 7.38 (s, 1 H, OCH=), 7.10–7.52 (m, 4 H, Ar H), 13.30 (s, 1 H, HO of enol form); mass spectrum, m/e (%) 246 (M^+, 10), 204 (17), 200 (12), 173 (23), 158 (16), 145 (31), 129 (25), 43 (100).

Exact mass calcd for $C_{14}H_{14}O_4$, 246.0892; found, 246.0898.

The second fraction from this plate was identified as pure *syn*-benzobis(furan) **22** (45.7 mg, 4%), as a slightly yellowish oil: IR (neat) 1710 (s), 1660 (s), 1475 (s), 1460 (s), 1270 (s), 1220 (s), 1205 (s), 1090 (s), 990 (s), 805 (s), 745 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.31 (t, 3 H, J = 7.0 Hz, $COOCH_2CH_3$), 2.22 (s, 3 H, J = 1.5 Hz, CH_3C=), 4.20 (q, 2 H, J = 7.0 Hz, $COOCH_2CH_3$), 4.70 (dq, 1 H, J_1 = 8.0, J_2 = 1.5 Hz, angular benzylic proton), 6.56 (d, 1 H, J = 8.0 Hz, ROCHOR), 6.68–7.50 (m, 4 H, Ar H); mass spectrum, m/e (%) 246 (32), 217 (16) 201 (16), 200 (60[53]), 158 (43), 43 (100).

Exact mass calcd for $C_{14}H_{14}O_4$, 24.0892; found, 246.0888.

The last fraction consisted of intractable impurities (100.2 mg).

The fourth fraction of the first thick-layer chromatography (251 mg) contained impure **21**. It was chromatographed again on a similar preparative plate with 3:3:0.1 petroleum ether/chloroform/acetone yielding in turn two main fractions, in the second of which **21** was located in the pure state (180.7 mg, 16.4%) as a slightly yellowish oil: IR (neat) 1710 (s), 1640 (s), 1480 (s), 1480 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.32 (t, 3 H, J = 7.0 Hz, $COOCH_2CH_3$), 2.22 (d, 3 H, J = 1.5 Hz, CH_C=), 4.20 (q, 2 H, J = 7.0 Hz, $COOCH_2CH_3$), 6.00 (apparent singlet; see discussion above and Figure 1; 2 H, angular methines), 6.72–7.40 (m, 4 H, Ar H); mass spectrum, m/e (%) 246 (M^+, 82), 217 (94), 201 (25, 175 (28), 158 (52), 131 (41), 102 (30), 43 (100).

Exact mass calcd for $C_{14}H_{14}O_4$, 246.0892; found, 246.0894.

***cis*- and *trans*-1,2-Diacetyl-1,2-bis(ethoxycarbonyl)ethylene (23).** The most polar fraction of the above experiment (181 mg) was chromatographed first through silica gel (70–230 mesh) in 1:8 hexane/ethyl ether and then through a Merck Lobar LiChroprep Si-60 (40–63 μm) size A column using 1:6:2 hexane/chloroform/acetonitrile at a constant flow of 1.5 mL/min, from which a soft crystalline material was isolated. Recrystallization from hexane/methylene chloride furnished 53 mg of pure carbene dimer **23** (4%) as a 1:1 cis/trans mixture: mp 89–90 °C; IR (KBr) 1740 (br s) cm^{-6}, NMR ($CDCl_3$) δ 1.24 and 1.27 (2 t, 3 H, J = 7.0 Hz, $COOCH_2CH_3$ of cis and trans stereoisomers), 2.37 and 2.43 (2 s, 3 H, CH_3CO of both isomers), 4.17 and 4.21 (2 q, 2 H, J = 7.0 Hz, $COOCH_2CH_3$ of both isomers), 4.46 and 4.48 (2 s, H_2C=CO of enol form), 13.10 (s, 1 H, HO of enol form).

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Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.79; H, 7.03; O, 37.18. Found: C, 55.61; H, 6.83; O, 37.36

Acknowledgment. This work is dedicated to Zaira Delfino's 20th anniversary of productive and stimulating assistance to chemical research in IVIC. The financial support of the Consejo Nacional de Investigaciones Cientificas y Tecnologicas, CONICIT, of Venezuela is gratefully acknowledged.

Registry No. 1a, 24762-04-7; **1b**, 2009-97-4; **2**, 29397-21-5; **7**, 111-34-2; **8a**, 82469-38-3; **8b**, 82469-39-4; **9**, 110-87-2; **10a**, 82469-40-7; **10b**, 82469-41-8; **11**, 4747-13-1; **12**, 82469-42-9; **13**, 14371-19-8; **14**, 82469-43-0; **15**, 82469-44-1; **19**, 82469-45-2; **20**, 82469-46-3; **21**, 82469-47-4; **22**, 82469-48-5; *cis*-**23**, 69622-59-9; *trans*-**23**, 69622-58-8; $Cu(F_3CCOCH_2COCF_3)_2$, 14781-45-4; $Cu(CH_3COCH_2CO_2C_2H_5)_2$, 14284-06-1; benzofuran, 271-89-6.

Thermolysis of Dioxetanes: 3,3-Diethyl-1,2-dioxetane and 3,3-Dimethyl-4-ethyl-1,2-dioxetane

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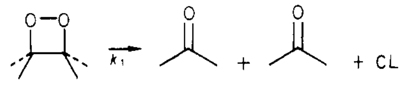
Received November 9, 1981

3,3-Diethyl-1,2-dioxetane (1) and 3,3-dimethyl-4-ethyl-1,2-dioxetane (2) were synthesized in ~10% yield by closure of the corresponding bromo hydroperoxides with base. Thermal decomposition of 1 and **2** produced only the expected cleavage products. Dioxetanes 1 and **2** directly produced high yields of triplet carbonyl products upon thermal decomposition similar to those reported for other alkyl-substituted dioxetanes. The activation parameters of the thermal decomposition of 1 and **2** were determined from Arrhenius plots (for 1, E_a = 24.9 kcal/mol, log A = 13.1, $k_{60\,°C} = 6.5 \times 10^{-4}$ s^{-1}, $\Delta S^* = -0.8$ eu; for **2**, E_a = 24.7 kcal/mol, log A = 12.8, $k_{60\,°C} = 3.4 \times 10^{-4}$ s^{-1}, $\Delta S^* = -2.3$ eu). Also, trimethyl-1,2-dioxetane (**3**) and 3,3-dimethyl-1,2-dioxetane (**4**) were prepared and the activation parameters redetermined (for **3**, E_a = 24.9 kcal/mol, log A = 13.0, $k_{60\,°C} = 4.5 \times 10^{-4}$ s^{-1}, $\Delta S^* = -1.4$ eu; for **4**, E_a = 23.4, log A = 12.5, $k_{60\,°C} = 1.4 \times 10^{-4}$ s^{-1}, $\Delta S^* = -3.6$ eu). The results suggest that a major substituent effect on alkyldioxetane thermolysis is due to 3,3 steric interactions as opposed to 3,4 steric interactions.

Dioxetanes have been studied[1] extensively because of their unique chemiluminescent thermal decomposition to two carbonyl fragments (reaction 1). The thermolysis of



(1)

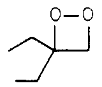
CL = chemiluminescence

simply substituted (alkyl, aryl, alkoxy) dioxetanes has been shown[1,2] directly to produce high yields of excited triplet carbonyl products. Two mechanistic extremes have been proposed[1] to describe the thermal decomposition of alkyl-substituted dioxetanes: (a) diradical and (b) concerted. The electron-transfer mechanism(s)[3] of chemiluminescent decomposition that occurs for certain peroxides does not occur readily with alkyl-substituted dioxetanes. Activation parameters have been rationalized for some dioxetanes by group additivity calculations[4] based on the thermochemistry of the dioxetane and a diradical intermediate. The apparent insensitivity[5] of dioxetane activation parameters to some[6] substituent effects along with the lack of a deuterium isotope effect[7] or ring-strain effect[8] have been interpreted to be consistent with a diradical-like process. Recent results[9] have indicated that structural factors can influence the activation parameters of the thermal decomposition of alkyl-substituted dioxetanes. We report the synthesis and characterization of 3,3-diethyl-1,2-dioxetane (**1**) and 3,3-dimethyl-4-ethyl-1,2-dioxetane (**2**) as well as reinvestigation of the activation parameters for trimethyl-1,2-dioxetane (**3**) and 3,3-dimethyl-1,2-dioxetane (**4**).

Table I. Activation Parameters of the Thermal Decomposition of 1-4 in Xylenes

dioxetane	E_a, kcal	log A	$k_{60\,°C}$, s^{-1}	$\Delta S^{\ddagger}$, eu
1	24.9 ± 0.3	13.1	6.5×10^{-4}	−0.8
2	24.7 ± 0.4	12.8	3.4×10^{-4}	−2.3
3	24.9 ± 0.4[a]	13.0	4.5×10^{-4}	−1.4
4	23.4 ± 0.4[b]	12.5	1.4×10^{-3}	−3.6

[a] Literature value 23.5 (see ref 11). [b] Literature value 23.0 (see ref 10).



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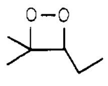

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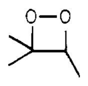

3

4

Results

3,3-Diethyl-1,2-dioxetane (**1**), 3,3-dimethyl-4-ethyl-1,2-dioxetane (**2**), trimethyl-1,2-dioxetane (**3**),[10] and 3,3-dimethyl-1,2-dioxetane (**4**)[11] were prepared in approximately 10% yield by closure of the corresponding bromo hydro-

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