

Participation of Charged Species in the Thermocatalytic Addition of Diazo Carbonyl Compounds to Electron-Rich Olefins. Addition-Rearrangement of Dimethyl Diazomalonate to 2-Methoxy-3,4-dihydro-2H-pyrans

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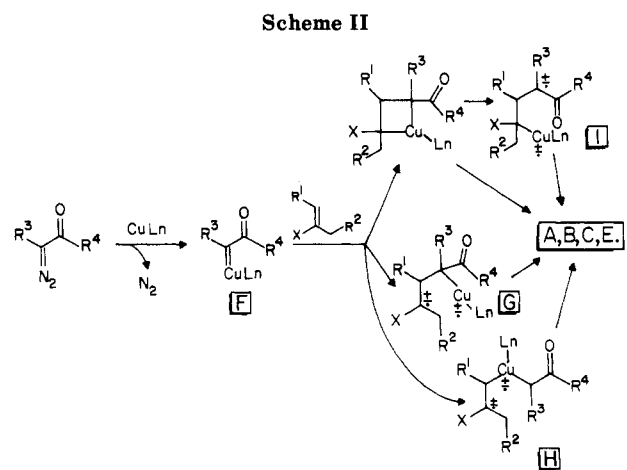
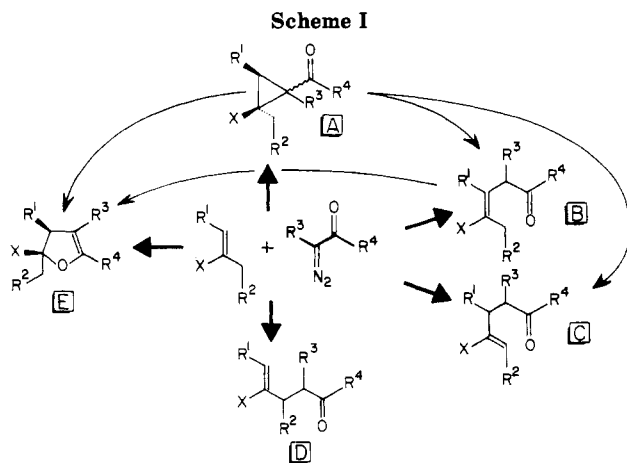
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The addition-rearrangement reaction of dimethyl diazomalonate (MDM) with 2-methoxydihydropyrans **2a,b** under catalysis by copper(II) chelates has been studied. With **2a**, addition-elimination product **3a** was obtained as the sole volatile material. **3b**, obtained as a minor product from **2b** and MDM, was accompanied by *cis*- and *trans*-1-methoxy-2,2-bis(methoxycarbonyl)-3-acylcyclopentanes (**4a,b**). The occurrence of these carbocycles was interpreted as evidence in favor of carbenium ion participation at an intermediary stage. The copper bronze, copper(II) chelate, and dirhodium tetraacetate assisted thermolysis (150 °C) of cyclopropane esters **13a-c** to give cyclopropane ring opened product **14** and open-chained fragmentation compounds **15a,b** was examined. These results were interpreted in terms of the mediation of either a labile β -oxycyclopropane diester, which undergoes quantitative conversion to **3** which parallels that of carbocationic structure **5** leading selectively to cyclopentanes **4**, or a common cationic intermediate that evolves into both 3- and 4-type products.

Typical among the transition metal assisted reactions of diazo esters and ketones with olefins are the cyclopropanation, addition-elimination, and allylic C-H insertion processes,² besides the more recently discovered and synthetically useful [2 + 3] cycloaddition, wherefrom dihydrofurans result.³

Such versatility implies a complex universe of feasible mechanistic routes that has triggered much speculation and a wealth of proposals.⁴ It is unfortunate, however, that insufficient evidence is available at present to support decidedly any one of these proposed mechanistic routes or that accounts for all the observed phenomena. Studies based on product analysis are hardly straightforward if allowance is made for the possible interconversion of the typical products of addition that might well occur under those conditions required by the thermocatalytic decomposition of the diazo compound.^{5,6} Also, unclear reactions



(1) Recipient of Graduate Fellowship from Consejo Nacional de Investigaciones Científicas y Tecnológicas CONICIT, of Venezuela, 1982-1984. Taken in part from the Master's Thesis of M.C.-G.

(2) (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. (g) Patai, S., Ed. "The Chemistry of Diazonium and Diazo Groups"; Wiley-Interscience: New York, 1978; Parts I and II.

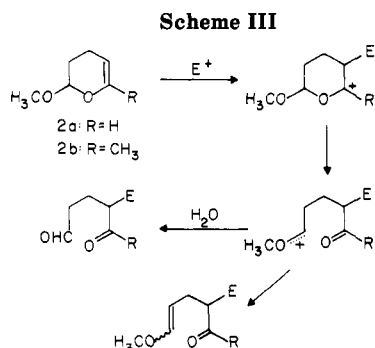
(3) (a) Wenkert, E. *Heterocycles* 1980, 14, 1703 and references cited therein. (b) Alonso, M. E.; Morales, A.; Chitty, A. W. *J. Org. Chem.* 1982, 47, 3747. (c) Alonso, M. E.; Jano, P.; Hernández M. I.; Greenberg, R. S.; Wenkert, E. *J. Org. Chem.* 1983, 48, 3047. (d) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Sánchez, E. L. *J. Am. Chem. Soc.* 1983, 105, 2021.

(4) See inter alia: (a) Moser, W. M. *J. Am. Chem. Soc.* 1969, 91, 1135. (b) Moser, W. M. *Ibid.* 1969, 91, 1141. (c) Nozaki, H.; Moriuti, S.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* 1966, 5239. (d) Shirafuji, T.; Yamamoto, Y.; Nozaki, H. *Tetrahedron* 1971, 27, 5358. (e) Saegusa, T.; Yonezawa, K.; Murase, I.; Konoike, T.; Tomita, S.; Ito, Y. *J. Org. Chem.* 1973, 38, 2319 (f) Wulfman, D. S. *Tetrahedron* 1976, 32, 1231. (g) Wulfman, D. S.; McDaniel, R. S., Jr.; Peace, B. W. *Ibid.* 1976, 32, 1241. (h) Wulfman, D. S.; Peace, B. W.; McDaniel, R. S., Jr. *Ibid.* 1976, 32, 1251. (i) Dötz, K. H. *Pure Appl. Chem.* 1983, 55, 1989.

(5) The thermal and photochemical isomerization of cyclopropyl ketones and imines to dihydrofurans and dihydropyrroles is well documented. See: Cloke, J. B. *J. Am. Chem. Soc.* 1929, 51, 1174. Wilson, C. L. *Ibid.* 1947, 69, 3002. Armitage, D. M.; Wilson, C. L. *Ibid.* 1959, 81, 2437. Dauben, W. G.; Shaffer, G. W. *J. Org. Chem.* 1969, 34, 2301. Zimmerman, H. E.; Boettcher, R. J.; Braig, W. *J. Am. Chem. Soc.* 1973, 95, 2155. Doering, W. V. E.; Birladenau, L. *Tetrahedron* 1973, 29, 499. McGreer, D. E.; McKinley, J. W. *Can. J. Chem.* 1973, 51, 1487. This rearrangement may occur under very mild conditions. See: Alonso, M. E.; Morales, A. *J. Org. Chem.* 1980, 45, 4530.

and extremely reactive intermediates—presumably metal-carbene derivatives—create difficulties in determining reliable and meaningful thermodynamic parameters.⁷

(6) The structural isomerization of cyclopropanecarboxylates has been shown to occur under relatively mild conditions in the presence of a wide variety of transition metal catalysts. See: Doyle, M. P.; van Leusen, D. *J. Am. Chem. Soc.* 1981, 103, 5917. See also ref 22. For the thermal counterpart see: Wenkert, E. *Acc. Chem. Res.* 1980, 13, 27 and references cited. In these instances, addition-elimination products of type B are produced.



Recently, evidence has been advanced from this laboratory indicating that the two new bonds created in the cycloaddition process between an olefin and a diazo carbonyl compound derived metal-carbene that yields *E* type products do not form necessarily in a concerted and simultaneous fashion.^{3b} A conceptually similar, though quantitatively different lack of concert is also conceivable for cyclopropanations of olefins by diazo carbonyl compounds. The extreme case in the spectrum of synchronous to nonsynchronous additions is represented by the addition-elimination reaction where the second C-C bond between the diazo carbon and the olefin is never constructed.

This predicament bespeaks of the appearance of a species either with significant charge separation or diradical character at some point of the reaction coordinate. In fact, intermediates of this sort (see structures G, H, and I) have been postulated by Wulfman for both, synchronous and nonsynchronous cycloadditions of putative copper keto carbenoids F to olefins.^{4c} The translation of this hypothesis in terms of the interaction of a keto carbenoid and a generalized olefin is portrayed in Scheme II.

The occurrence of these intermediates, however, has never been proved in an unambiguous fashion for any of those reactions characteristic of diazo carbonyls and alkenes, in spite of important contributions to the understanding of controversial 1,3-dipolar cycloadditions.⁸

This work purports to investigate the existence of these charged intermediates, in which a cationic center is created at the olefinic carbon that bears an electron-donating substituent X. Also, the role played by the metal catalyst is examined in terms of the possible metal-assisted ring opening of an initially formed cyclopropane ester as a conceivable source of addition-elimination products.

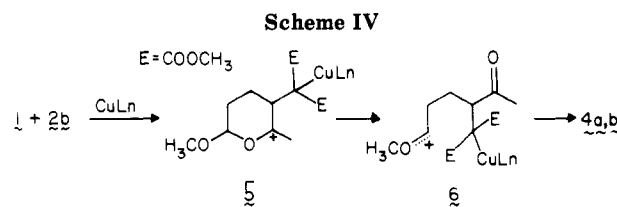
Results and Discussion

Addition-elimination products (AEP) of type B and C are common in some diazo carbonyl-olefin reactions.² These compounds may be interpreted erroneously as the consequence of allylic C-H insertions if unindicating alkenes such as cyclohexene are used as substrates.⁹ In fact, allylic insertion has passed undetected (<2%) in all of those cyclopropanations that we have examined in the past where true AEP's were recognized unequivocally.¹⁰

(7) For the most part, kinetic studies of the fate of diazo alkane derivatives in their reaction with alkenes are based on relative reactivities of pairs of olefins. Absolute values for thermodynamic parameters are not accessible by this method. See: Moss, R. A. "The Application of Relative Reactivity Studies to the Carbene Olefin Addition Reaction", in ref 2f, pp 153-304. For examples of formal kinetic studies of diazo carbonyl decompositions see: Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300. Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petinot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695.

(8) Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171 and references cited.

(9) Wulfman, D. S.; Peace, B. W.; Steffen, E. K. *J. Chem. Soc., Chem. Commun.* **1971**, 1360. For the reaction of diazomalonyl esters with several substituted cyclohexenes see: Wulfman, D. S.; Peace, B. W. *Synthesis* **1971**, 658.



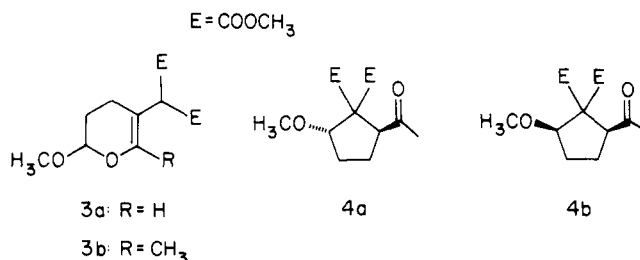
Changes in the electronic structure of both diazo carbonyl and alkene, nevertheless, bring about dramatic modifications of product composition and nature. For instance, the cyclopropanation behavior of ethyl diazopyruvate¹⁰ and alkyl 2-diazo-3-oxobutyrate is complementary to the almost exclusive formation of dihydrofurans when these diazo esters are reacted with electron-rich olefins.³ Similarly, in parallel to well-known cyclopropanations of methyl diazomalonates (MDM) with hydrocarbon alkenes,¹¹ this compound yields AEP's for the most part when exposed to alkyl vinyl ethers under copper catalysis.¹²

Positive charge development on a carbon atom has been evaluated in the past by the degree of fragmentation experienced by a 2-alkoxydihydropyranyl structure **2**.

Thus, fragmentation have been recorded for the addition of **2a** to tetracyanoethylene,¹³ aryl sulfonylazides,¹⁴ dimethyl acetylenedicarboxylate,¹⁵ 4-methylphenyl isocyanate,¹⁶ and *tert*-butylphosphalides¹⁷ and its oxidation with *m*-chloroperbenzoic acid¹⁸ as well as during the silver ion promoted cyclopropane ring cleavage of *gem*-dichlorooxabicycloheptane derivatives.¹⁹

Now, since compound **2** is a vinyl ether, it provided the ideal substrate for the study of positive charge development at carbon C-6 during its metal-catalyzed production of AEP's of type B with MDM.

The copper(II) chelate assisted decomposition of MDM in benzene, in the presence of a 1.5 mol excess of **2a**, was thus examined. From this reaction, however, only the AEP **3a** along with minor amounts of MDM derived carbene dimer was isolated in 28% yield, the remainder being intractable polymeric material.



The absence of fragmentation was interpreted in terms of insufficient charge stabilization at C-6 for the six-membered ring to unravel. In principle, additional stabilization could be provided by placing an alkyl group at

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(19) Duggan, A. J.; Hall, S. S. *J. Org. Chem.* **1975**, *40*, 2234, 2238.

Table I. Product Distribution and Solvent Polarity in the Addition of Diethyl Diazomalonate to 3b under Bis(hexafluoroacetoacetonato)copper(II) Catalysis^a

solvent	3b:4a,b	reactn time, h	total yield, ^b %
cyclohexane	6.1	21	71
benzene	2.5	2	81
DME	0.13	25	26

^a Yields were determined by gas-liquid chromatography, using diethyl phthalate as internal standard, and a 12 ft, 3% SE-30 on Chromosorb column, operating at 150 °C. ^b The remaining product consists of MDM-carbene dimer and intractable resinous material.

this carbon. In fact, such a substitution has led other researchers to observe fragmentation of the oxacyclohexene ring in carbenium ion mediated reactions where 2a had failed to do so.¹⁵⁻¹⁷

The reaction of MDM with 2b in fluorobenzene and bis(hexafluoroacetoacetonato)copper(II) catalysis was thus examined. Surprisingly, along with the predicted AEP 3b, isolated in lesser yield (14%) isomeric cyclopentane diesters 4a,b were also obtained in 22% and 10%, respectively.

That these cyclopentanes were not derived from a subsequent transfiguration of 3b in the reaction medium by way of ring opening and 1,2-hydride transfer was determined by the stability displayed by the latter on refluxing it in benzene containing the copper catalyst for the typical reaction time (2.5 h).

The origin of 4a,b could be traced, in turn, to the anticipated fragmentation of 5 which bear the two active carbons of opposed charges at five atoms distance. Similar couplings that yield six-membered carbocycles have been recorded in the additions of 2a to tetracyanoethylene¹³ and 2b to dimethyl acetylenedicarboxylate.¹⁵

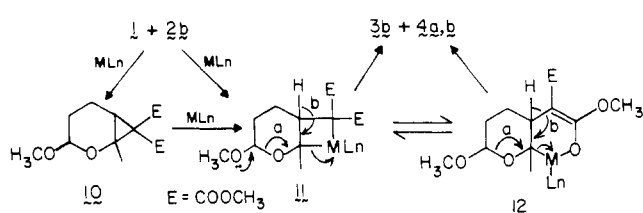
The effect of solvent strength on product ratio was also studied. The reaction of MDM with 2b under bis(hexafluoroacetoacetonato)copper(II) catalysis was run in cyclohexane, benzene, and dimethoxyethane, all solvents showing similar boiling points and a wide range of solvent polarity. The results appear portrayed in Table I. The dramatic change of the 3b:4a,b ratio from 6:1 in cyclohexane to 1:7 in DME speaks clearly in favor of considerable charge separation in the intermediary stage. This conclusion contrasts with persuasive evidence to the contrary in classical cyclopropanation reactions. Indeed, this result would not be compatible with the observed conservation of relative stereochemistry of substituents in olefins leading to cyclopropanes^{2a} and dihydrofurans.^{3b,c} This result, which is classically expressed by the Skell's rule²⁰ has led to the widespread notion of concertedness in the general cycloaddition of diazo carbonyl compounds to olefins.^{8,21} It is clear, therefore, that allowance must be made for the operation of a conceptually different mechanism when AEP's are the result of these additions.

While the postulation of species such as 5 undergoing either fragmentation to cyclopentanes 4a,b or proton elimination to give AEP 3b provides a reasonable explanation of observed facts, it is also conceivable that the metallic center of the catalyst may be involved to some extent with the positively charged carbon. Further, the initial formation of an unstable β -oxycyclopropane diester

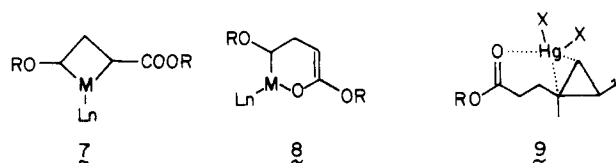
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Scheme V

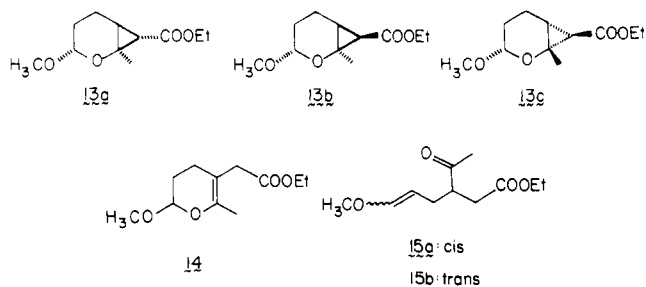


which undergoes fragmentation under the auspices of the catalyst to give the observed addition-elimination products, is a plausible contention. These two ideas find encouragement in the recent work of Doyle et al. They have suggested metal carbocycles such as 7 and 8 to account for copper, rhodium, and palladium catalysis in the *E-Z* isomerization and selective unravelling of β -oxycyclopropane esters, whereby β - γ carbonyl systems analogous to AEP's of type B are produced.²² Also, the mercury-(II)-promoted regioselective rupture of unactivated cyclopropanes has led to the proposition of structure 9 as a feasible intermediate.²³



Translation of this proposal to the present case leads to the working hypothesis indicated in Scheme V. Two assumptions can be advanced; in the first, MDM and the olefin interact to yield cyclopropanediester 10, which undergoes ring opening with the intervention of the metal catalyst to give either 11 or 12. Both metalocycles may be subject to unravelling with concomitant opening of the alkoxytetrahydropyran portion of the molecule (arrow a) to give cyclopentanes or proton exclusion (arrow b) to furnish AEP. In the second assumption 11 and/or 12 may be intermediates en route to cyclopropane 10, which undergoes further ring scission in the mode indicated by Doyle.²²

In order to test this hypothesis, cyclopropane ester 13 was synthesized from ethyl diazoacetate and 2b in its three unseparable stereoisomeric forms 13a-c and its selective cyclopropane breakage examined.²⁴



(22) Doyle, M. P.; van Leusen, D. *J. Org. Chem.* **1982**, *47*, 5326.

(23) Collum, D. B.; Mohamadi, F.; Hallock, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6883. The silver ion promoted fragmentation of cyclopropanes activated by electron donor substituents also has been studied recently. See: Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *Ibid.* **1983**, *105*, 7192.

(24) In principle four stereoisomeric structures are possible, *E*-anti, *E*-syn, *Z*-anti, and *Z*-syn, if the methoxy substituent is fixed in the axial conformation.²⁵ However, structure *Z*-syn requires that the alkoxy and carboxy groups occupy nearly the same position in space. Therefore, this isomer is neither kinetically nor thermodynamically feasible and is assumed to be absent. Further, GLC analysis of the crude reaction mixture reveals the presence of three cyclopropanes (86%) in a *E*-anti:*Z*-anti:*E*-syn ratio 5.1:3.2:1.1. The assignments were made on the basis of assumed relative product stability.

Heating compound **13** at 150 °C in the presence of catalytic amounts of copper bronze, bis(hexafluoroacetoacetonato)copper(II), and dirhodium tetraacetate for several hours, (conditions reported by Doyle), all common catalysts for the decomposition of diazo compounds, afforded AEP **14** and minor amounts of enol ethers **15a,b**, the remainder being unreacted **13**. No cyclopentanes were detected. In consonance with Doyle's results, dirhodium tetraacetate was more effective since it promoted 73% conversion of **13a** and 97% conversion of **13c** within 5 h, while with copper bronze these values were 10% and 38%, respectively, after 7 h. Similarly, 72% AEP **14** was smoothly produced from dirhodium tetraacetate, whereas with copper bronze only 22% of this compound was obtained. Bis(hexafluoroacetoacetonato)copper(II) displayed an intermediate efficiency between those two catalysts because it induced the formation of 49% **14** after 7 h of heating. In all instances, **13b** underwent 100% conversion within the first hour.

The production of **15** was not interpreted as a genuine metal-carbon (C-6) disconnection of either putative intermediate **11** and **12**, on the grounds of the small proportion of **15** present in the reaction mixture. Rather, the metal atom is envisioned as a Lewis acid that is first bound to **13** at the carbonyl oxygen. This condition provides subsidy to the activation energy required to break heterolytically the cyclopropyl C-C bond and would be in competition with the further association of the metallic atom with C-6 that would end up as **11** or **12**.

Conclusion

The failure to reproduce the fragmentation pattern observed during the copper-catalyzed addition-elimination of MDM and **2b** in the catalytic conversion of **13** into **14** may be interpreted in two diverging modes: (1) Assuming a common transition state for the production of AEP and cyclopentanes from **2b** and MDM, the results presented here would rule out the intervention of metalocycles **11** and/or **12** in the reaction pathway from MDM and alkenes to AEP. This transition state would most probably have considerable charge separation in the way indicated in structure **5**. This, in turn, would make untenable the hypothesis of a reaction course wherein a labile β -oxycyclopropane diester **10** is formed initially, followed by its transfiguration to the corresponding AEP under the auspices of the metal catalyst. (2) Assuming different transition states and, therefore, divergent reaction pathways for the construction of AEP and cyclopropanes, the hypothetical participation of a cyclopropane diester followed by its unravelling to AEP via metalocycles **11** and/or **12**, would still be valid. In this case, species **10** would coexist with carbenium ion **5**. The question of multiplicity of transition states in the reaction coordinate that lays between diazo carbonyl compound, alkene, and addition product cannot be solved with presently available data.

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 deuteriochloroform solutions unless otherwise stated. Electron-impact mass spectra were obtained with a DuPont spectrometer, Model 21-492, and exact masses were measured with a AEI-Kratos MS-30 double beam instrument. Dimethyl diazomalonate was prepared

from dimethyl malonate and tosyl azide as described previously.²⁶ 2-Methoxy-3,4-dihydro-2H-pyran (**2b**) was obtained from Aldrich Chemical Co.

2-Alkoxy-6-methyl-3,4-dihydro-2H-pyran (2b).²⁷ Freshly distilled methyl vinyl ketone (20 mL) was placed in a glass-lined pressure reactor.²⁸ Methyl vinyl ether (40 mL) was condensed in a three-necked 100-mL round-bottom flask under a nitrogen atmosphere. The two reagents were mixed in the reactor and heated at 180 °C for 2 h with magnetic stirring. A maximum of 650 psi was recorded. After cooling and evaporation of excess vinyl ether, the crude product containing variable amounts of insoluble clear polymeric material was distilled at reduced pressure. The fraction distilling at 75–76 °C (70 torr) was collected (14.3 g, 46%) and corresponded to the desired product: IR (neat) 1680 (s), 1250 (s), 1045 (s) cm^{-1} ; NMR δ 1.77 (m, 3 H, $=\text{CCH}_3$), 1.53–2.27 (m, 4 H, $(\text{CH}_2)_2$), 3.53 (s, 3 H, CH_3O), 4.57 (t, 1 H, $J = 2.5$ Hz, $\text{HC}=\text{C}$), 4.93 (t, 1 H, $J = 3.0$ Hz, anomeric proton).²⁹

Dimethyl (2-Methoxy-3,4-dihydro-2H-pyran-5-yl)malonate (3a). A solution of dimethyl diazomalonate (1.0 g) in benzene (15 mL) and dihydropyran **2a** (2.0 g) was added dropwise over a 2-h period to a solution of bis(hexafluoroacetoacetonato)copper(II) (10 mg) in benzene (2 mL) at reflux temperature with magnetic stirring and under a nitrogen atmosphere. After the addition was complete heating was continued until the band at 2250 cm^{-1} of the C-N₂ function in the infrared spectrum had disappeared completely (typically 1–2 h). The cold reaction mixture was passed through a pad of neutral alumina to separate the catalyst and solvents were evaporated. Distillation under reduced pressure of this material gave compound **3a** (0.432 g, 28%) as a colorless oil: bp 70 °C (0.025 torr); IR (neat) 1725 (s), 1625 (s) cm^{-1} ; NMR δ 1.70–2.33 (m, 4 H, methylenes), 3.47 (s, 3 H, methoxy), 3.77 (s, 6 H, $(\text{COOCH}_2)_2$), 3.90 (s, 1 H, OOCCHCOO), 4.90 (t, 1 H, $J = 3.0$ Hz, anomeric proton), 6.33 (s (broad), 1 H, $=\text{CH}$); mass spectrum, m/e (%) 244 (M^+ , 4), 213 ($\text{M}^+ - \text{CH}_3\text{O}$, 23), 212 ($\text{M}^+ - \text{MeOH}$, 14), 188 (21), 185 (13), 153 (14), 129 (34), 58 (100); exact mass calcd for $\text{C}_{11}\text{H}_{16}\text{O}_6$ 244.0946, found 244.0954.

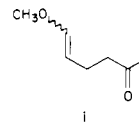
Addition of Dimethyl Diazomalonate to 2b. Dimethyl diazomalonate (1.0 g) and 2-methoxy-6-methyl-3,4-dihydro-2H-pyran (**2b**) (2.1 g) were reacted as described above by using bis(hexafluoroacetoacetonato)copper(II) as catalyst and fluoro-benzene as solvent. After evaporation of solvents, the crude mixture was chromatographed through silica gel (35 g). The column was eluted with mixtures of hexane and diethyl ether. Dimethyl (2-methoxy-6-methyl-3,4-dihydro-2H-pyran-5-yl)malonate (**3b**) was eluted first as a pale yellow oil (0.219 g, 14% yield): IR (neat) 1725 (s), 1675 (s) cm^{-1} ; NMR δ 1.59–2.30 (m, 4 H, methylenes), 1.83 (t, 3 H, $J = 1.5$ Hz, $=\text{CCH}_3$), 3.50 (s, 3 H, methoxy), 3.78 (s, 6 H, $2 \times \text{COOCH}_3$), 4.32 (s, 1 H, OOCCHCOO), 4.90 (t, 1 H, $J = 3.0$ Hz, anomeric proton); mass spectrum, m/e (%) 258 (M^+ , 4), 227 ($\text{M}^+ - \text{CH}_3\text{O}$, 7), 226 ($\text{M}^+ - \text{MeOH}$, 13), 199 ($\text{M}^+ - \text{COOCH}_3$, 9), 167 ($\text{M}^+ - \text{MeOH} - \text{COOMe}$, 13), 58 (100); exact mass calcd for $\text{C}_{12}\text{H}_{18}\text{O}_6$ 258.1103, found 258.1111.

The second compound eluted from the column corresponded to *trans*-1-methoxy-2,2-bis(methoxycarbonyl)-3-acylcyclopentane (**4a**) which appeared as a colorless oil (0.155 g, 10%): IR (neat) 1725 (s), 1700 (s), 1450 (m) cm^{-1} ; NMR δ 1.50–2.23 (m, 4 H, methylenes), 2.25 (s, 3 H, COCH_3), 3.32 (s, 3 H, CH_3O), 3.65 and 3.76 (singlets, 3 H each, COOCH_3), 4.22 (t (broad), 1 H, $J = 6$ Hz, CHOR).

(26) Rosenberger, M.; Yates, P. *Tetrahedron Lett.* 1964, 2285.

(27) Longely, R. I., Jr.; Emerson, W. S. *J. Am. Chem. Soc.* 1950, 72, 3079. Smith, C. W.; Norton, D. G.; Ballard, S. A. *Ibid.* 1951, 73, 5267.

(28) The use of commercial methyl vinyl ketone of technical grade furnished a multitude of products, among which fragmented adduct **i** was the major component.



(29) The method reported by Boeckman for the alkylation of the α -carbon of vinyl ethers (Boeckman, R. K., Jr.; Bruza, J. *J. Tetrahedron* 1981, 37, 5326) failed in our hands when applied to **2a** (LDA, methyl iodide, THF, and various reaction conditions).

(25) The axial conformation of this substituent in 2-alkoxy-2,3-dihydro-2H-pyrans and their cyclopropane derivatives is well established. See ref 19.

Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.79; H, 7.03; O, 37.18. Found: C, 55.86; H, 6.96; O, 37.18.

The third eluted compound was *cis*-1-methoxy-2,2-bis(methoxycarbonyl)-3-acylcyclopentane (**4b**) (colorless oil, 0.357 g, 22%): NMR δ 1.60–2.23 (m, 4 H, methylenes), 2.18 (s, 3 H, COCH₃), 3.38 (s, 3 H, CH₃O), 3.75 and 3.81 (singlets, 3 H each, COOCH₃), 4.23 (t (broad), 1 H, $J = 6$ Hz, CHOR).

Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.79; H, 7.03; O, 37.18. Found: C, 55.84; H, 6.92; O, 37.24.

2-Methyl-3-(ethoxycarbonyl)-3-methoxyoxabicyclo[4.1.0]heptane (13a-c). A solution of ethyl diazoacetate (2.0 g) in benzene (30 mL) containing vinyl ether **2b** (4.0 g) was added dropwise over a 3-h period to a suspension of bis(acetoacetonato)copper(II) (20 mg) in benzene (2 mL) at reflux temperature and magnetic stirring under a nitrogen atmosphere. After the addition was complete, heating was continued for 0.5 h. The cold reaction mixture was passed through a pad of neutral alumina and solvents evaporated. The crude reaction was analyzed by GLC with a 12 ft 3% SE-30 on Chromosorb column at 150 °C. Results are described in the discussion. The mixture was then distilled under reduced pressure and the fraction with bp 88–95 °C (0.15 torr) was collected (2.154 g, 57%) and identified as a mixture of *E* anti, *E* syn, and *Z* anti cyclopropanes **13a-c**. Attempts to separate these isomers by chromatographic methods met with failure and they were characterized as a mixture: IR (neat) 1725 (s), 1255 (s), 1100 (s), 1045 (s) cm^{-1} ; NMR δ 1.27 (t, 3 H, $J = 6.0$ Hz, OCH₂CH₃), 1.53 (s, 3 H, CH₃), 3.50 (s (broad), 3 H, MeO), 4.15 (q, 2 H, $J = 6.0$ Hz, OCH₂CH₃), 4.30–4.60 ((triplets), 1 H, anomeric protons of the three stereoisomers); mass spectrum, m/e (%) 214 (M^+ , 3), 182 ($M^+ - MeOH$, 13), 143 (16), 141 ($M^+ - COOEt$, 12), 127 (20), 109 (16), 58 (100).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.64; H, 8.47; O, 29.88. Found: C, 61.67; H, 8.39; O, 29.90.

Thermolysis of 13. A mixture of oxabicycloheptane **13a-c** (500 mg) and 4% mole of catalyst (dirhodium tetraacetate, bis(hexafluoroacetoacetonato)copper(II), or copper bronze) was heated at 150 °C in a vial stoppered with a rubber septum, under a nitrogen atmosphere.

Aliquots were withdrawn at given times with the aid of a microsyringe and samples analyzed by GLC with a 12 ft, 5% SE-30 on Chromosorb column at 150 °C. After 7 h of heating, a sample of 200 mg was taken from the thermolysis mixture containing the rhodium catalyst. This mixture was then chromatographed on a thick-layer silica gel plate that had been activated previously by heating at 140 °C during 8 h and left at room temperature for 2 h in the open. The plate was developed with petroleum eth-

er-diethyl ether (3:2) and individual compounds were recovered by redissolution in ethyl acetate. After evaporation of solvents two fractions were obtained. The one with the higher R_f value corresponded to a mixture of AEP **14** in admixture with unreacted **13a**. Further purification by thick-layer chromatography with extended activation and the same solvent mixture furnished pure ethyl (2-methoxy-6-methyl-2,3-dihydro-2H-pyran-5-yl)acetate (**14**) (92 mg) as a colorless oil: IR (heat) 1720 (s), 1675 (m) cm^{-1} ; NMR δ 1.28 (t, 3 H, $J = 6.0$ Hz, OCH₂CH₃), 1.82 (t, 3 H, $J = 1.5$ Hz, =CCH₃), 1.50–2.20 (m, 4 H, methylenes), 2.93 (2 × d of AB system, 2 H, $J_{AB} = 15.7$ Hz, CH₂COOEt), 3.47 (s, 3 H, OMe), 4.27 (q, 2 H, $J = 6.0$ Hz, OCH₂CH₃), 4.85 (t, 1 H, $J = 3.0$ Hz, anomeric proton).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.64; H, 8.47; O, 29.88. Found: C, 61.68; H, 8.51; O, 29.81.

The second band of the first thick-layer chromatography corresponded to a 3:2 mixture of *cis/trans*-ethyl 3-acyl-6-methoxy-5-hexenoate (**15a,b**), isolated as a colorless liquid (16 mg): IR (neat) 1725 (s), 1710 (s), 1665 (m), 1650 (m) cm^{-1} ; NMR δ 1.27 (t, 3 H, $J = 6.0$ Hz, OCH₂CH₃), 2.23 (s, 3 H, CH₃C=O), 2.20–2.70 (m, 3 H, CHC=O and CH₂COOR), 3.50 (s, 3 H, MeO of *trans* compound **15a**), 3.60 (s, 3 H, MeO of *cis* stereoisomer **15b**), 4.10–4.30 (m, 1 H, H at C-5 of *cis* isomer), 4.15 (q, 2 H, $J = 6.0$ Hz, OCH₂CH₃), 4.58 (dt, 1 H, $J_1 = 7.5$ Hz, $J_2 = 12$ Hz, H at C-5 of *trans* compound **15a**), 5.97 (dt, 1 H, $J_1 = 1.0$ Hz, $J_2 = 6$ Hz, OCH= of *cis* isomer), 6.30 (d (broad), 1 H, $J = 12$ Hz, OCH= of *trans* isomer).

This compound hydrolyzed to the corresponding aldehyde upon exposure to moist air at room temperature and quickly decomposed thereafter.

Registry No. **2a**, 4454-05-1; **2b**, 28194-35-6; **3a**, 94707-79-6; **3b**, 94707-80-9; **4a**, 94707-81-0; **4b**, 94707-82-1; **13a**, 94707-83-2; **13b**, 94799-05-0; **13c**, 94799-06-1; **14**, 94707-84-3; **15a**, 94707-85-4; **15b**, 94707-86-5; methyl vinyl ketone, 78-94-4; methyl vinyl ether, 107-25-5; dimethyl diazomalonate, 6773-29-1; bis(hexafluoroacetoacetonato)copper(II), 14781-45-4; bis(acetoacetonato)copper(II), 13395-16-9; ethyl diazoacetate, 623-73-4; dirhodium tetraacetate, 15956-28-2; copper bronze, 12597-70-5.

Supplementary Material Available: Figures 1, 2, and 3 consisting of plots of percentage composition vs. time for the thermolysis of **13a-c** to **14** and **15a,b** under the auspices of copper bronze, bis(hexafluoroacetoacetonato)copper(II), and dirhodium tetraacetate (3 pages). Ordering information is given on any current masthead page.